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## n-TYPE POLYIMIDES INCORPORATING OXADIAZOLE AND PERYLENE FLUOROPHORES

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### Abstract

The main topic of this study is the photo-optical and electrochemical behavior of a series of fluorinated copolyimides containing both oxadiazole and perylene moieties in the main chain. The polymers prove a strong photo-optical stability on a large temperature domain and display different types of photoluminescent behavior in solution and in solid state, with emission maxima in the bluish and green–yellow domains. Cyclic voltammetry investigations suggest that the polymers can be easily n-doped and show very good electron injection and transport characteristics. The polymers are suitable for application as thermally stable, light-emitting and electron transporting materials for opto-electronic devices.

**Keywords:** electrochemistry, films, optical properties, optoelectronic applications, polyimides

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### 1. Introduction

Perylene tetracarboxylic diimides (PDIs) benefit from significant consideration from both academic and industrial research due to a favorable combination of interesting characteristics such as excellent thermal and photostability, chemical inertness, high fluorescence quantum yields, electron accepting properties and singlet energy transfer over unusually long distances (Dimitrakopoulos and Malenfant, 2002; Gregg et al., 1997; Huang et al., 2011; Jones et al., 2004).

Furthermore, the optical and electric features of these materials are comparable with those of inorganic broad-band semiconductors. On these basis, PDIs have been employed in a handful of applications in the developing area of organic electronics such as organic light-emitting diodes, field effect transistors, optical switches, biosensors, organic photovoltaics, and molecular wires (Elemans et al., 2006; Nogaret, 2014; Schmidt-Mende et al., 2001; Wang and Yu, 2010).

Since processability and particularly film formation is a prerequisite for the majority of the above-mentioned applications, most of PDI-based thin films were prepared by blending several perylene dyes with a polymer matrix. The major drawback of this procedure is dye migration upon aging and subsequent phase separation, which could be avoided by covalently attaching the perylene dye to a macromolecular backbone. Moreover, the polymeric structure brings the additional benefit of three-dimensional stability. As a result, much research is being carried in order to develop novel modified, soluble and easy to process polyperyleneimides, without significant impairment of their excellent properties (Mikroyannidis et al., 2010; Niu et al., 2012; Xu et al., 2010; Wang et al., 2009). Copolymerization is an effective approach in this regard, which could enhance the properties of the resulting polymers and produce various materials with new structures. Small and macromolecular architectures incorporating oxadiazole units represent

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another attractive topic to both academic and industrial research due to the special features of this heterocycle. Most of all, the oxadiazole moiety was successfully used as a building block in the outline of active organic materials in light-emitting systems with the purpose of upgrading their efficiency (Konk et al., 2012; Kulkarni et al., 2004). The employment of highly thermostable polymers containing this moiety, as long as they fit the requirement of providing good quality thin films represents a feasible solution to the issue of short lifetime of low molecular weight materials containing oxadiazole (Damaceanu et al., 2014; More et al., 2012; Pei and Yang, 1995). The downside of fully aromatic polyimides and polyoxadiazoles is their rigid nature which severely decreases their application potential by rendering them infusible and insoluble and therefore of limited processability (Lisa et al., 2018; Peng and Zhang, 1999). One frequently used approach to this issue is the introduction of flexible aryl-ether linkages in the macromolecular backbone, which conveys better solubility, melt-processing possibilities, and improved toughness as compared with their counterparts without an aryl-ether linkage (Akcelrud, 2003; Jin et al., 2000). Likewise, the usage of flexible hexafluoroisopropylidene groups brings great benefits for solubility as well as electrical and dielectric performances (Bruma et al., 1996).

Bringing together such molecular design features, namely the integration of rigid oxadiazole and perylene fluorophores together with ether and hexafluoroisopropylidene flexible bridges in a macromolecular architecture, it is assumed to generate highly thermally stable polymeric materials with efficient luminescent and electron-transporting features for future use as new, proficient active materials in opto-electronic devices. This article focuses on an in-depth study of the photo-optical and electrochemical characteristics of such copoly(oxadiazole-perylenimine)s.

## 2. Experimental

### 2.1. Synthesis of the polymers

The monomer structure, detailed synthesis and basic characterization of the present copolymers were

reported previously (Damaceanu et al., 2012; Rusu et al., 2010).

In short, copolyimides **P1**, **P2** and **P3** have been prepared by one-step polycondensation reaction in solution, at high temperatures (200-210°C), of three different aromatic diamines containing preformed oxadiazole rings with a mixture of 3,4,9,10-perylenetetracarboxylic dianhydride and 4,4'-(hexafluoroisopropylidene)-diphthalic dianhydride taken in equimolar ratios, using N-methylpyrrolidinone (NMP) with 3.5% LiCl as a solvent. The structures of these three copoly(oxadiazole-perylenimine)s are displayed in Fig. 1.

### 2.2. Basic properties of the copolymers

The investigated copolymers **P1**, **P2** and **P3** are soluble in NMP, a more environmental friendly solvent as compared to the frequently used m-cresol. However, their solubility in other organic solvents is limited and therefore, we were not able to determine their corresponding molecular weights. Their initial decomposition temperature values are higher than 465°C; the temperatures of 10% gravimetric loss are between 480 and 510°C, while the temperature corresponding to the maximum rate of decomposition is higher than 525°C, indicating the envisaged high thermal stability. The copolymers display glass transition temperatures ( $T_g$ ) between 227° and 266°C, as it was evaluated by differential scanning calorimetry (DSC).

### 2.3. Polymer films

Diluted polymer solutions in NMP (1% concentration) were used to prepare thin films from copolymers **P1**, **P2** and **P3** by spin-coating (1000 rpm) or drop-casting technique on quartz or ITO-covered glass substrates. The residual solvent was cleared by heating the films at 200°C under vacuum for more than 6 h. UV-Vis-NIR technique was used to evaluate the films' thickness, by means of optical transmission (T) and reflectivity (R) spectra. Kramer-Kronig relations were used to determine the refractive indexes (n) of the films from the reflectivity spectra.

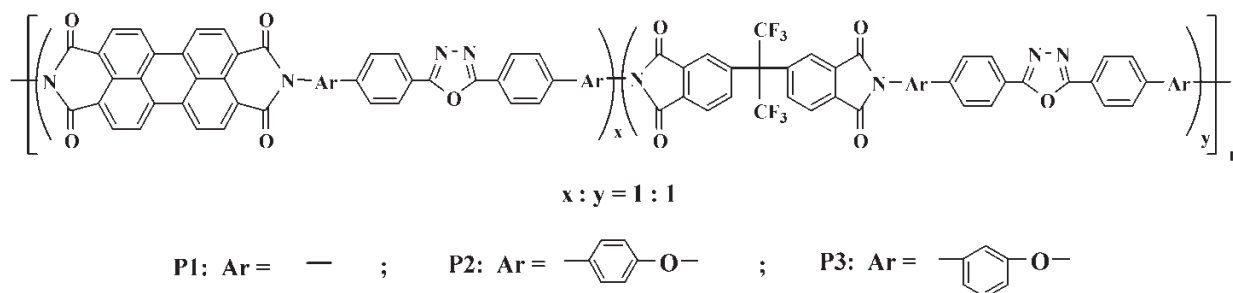


Fig. 1. Structures of poly(oxadiazole-perylenimine)s **P1** – **P3**

## 2.4. Measurements

Transmission and reflectivity spectra were determined with a two beam JASCO V 570 spectrophotometer working at room temperature in the 200–2500 nm domain. The photoluminescent behavior of the investigated copolymers in solution ( $\sim 10^{-5}$  M) or thin films (quartz substrates) was evaluated with a Perkin Elmer LS 55 device. Fluorescence quantum yields ( $\Phi_f$ ) and chromaticity coordinates were established by using a FluoroMax-4 spectrofluorometer (with a Quanta-phi integrating sphere). The absolute values of these two parameters were obtained at room temperature by exciting the sample solutions (at optimized concentrations as to attain absorbance values below 0.1) at the wavelengths corresponding to absorption maxima. A good optical luminescence signal-to-noise ratio was achieved by optimizing the experimental setup (slit widths, detector parameters) and therefore maximizing (not saturating) the excitation Rayleigh peak.

Cyclic voltammetry (CV) measurements were carried out on a Bioanalytical System, Potentiostat-Galvanostat (BAS 100B/W) working at room temperature under a nitrogen atmosphere and by using the following electrodes: polymer film on ITO-coated substrate ( $2.5 \times 2.5$  cm<sup>2</sup>, working electrode); platinum wire (auxiliary electrode); AgCl-coated silver wire (reference electrode) and tetrabutylammonium perchlorate (TBAP)/acetonitrile (CH<sub>3</sub>CN) as electrolyte. Calibration was performed with ferrocene as external reference (+0.425 vs. Ag/AgCl).

## 3. Results and discussion

Since 1,3,4-oxadiazole rings and perylenediimide units were used as monomeric building blocks mainly due to their ability to act as fluorophore moieties, (Xu et al., 2006; Yao et al., 2005) the light-emitting behavior of these oxadiazole-containing copolyperyleneimides was one of the main targets of this work. The photo-optical features of **P1**–**P3** were investigated by means of UV-Vis absorption and photoluminescence spectra which were measured for polymer solutions in NMP and for thin films made from these kinds of solutions, after excitation with UV or visible light. The chromaticity diagrams were also recorded in order to survey the color of the emitted light.

One of the prevailing characteristics of these materials is their extended conjugated  $\pi$ -system, a feature mirrored by their electronic absorption spectra. A preliminary study regarding the main optical properties of these copolymers in solution and in solid state (wavelengths of the maximum absorption peaks and of the absorption edges, optical energy band gap values) was previously reported (Damaceanu et al., 2010; Rusu et al., 2010). Briefly, all investigated polymers display quite identical spectra in solution, showing one strong UV absorption maximum in the range of 304–313 nm, and three weak peaks around

463, 492 and 529 nm. The presence of diphenyl-1,3,4-oxadiazole unit in the macromolecular structure of these copolymers is responsible for the absorption maxima at 304–313 nm (Iosip et al., 2001), while the less intense absorption peaks are generated by chain fragments involving perylenediimide units.

The spectra recorded for polymer films casted from NMP solutions displayed one strong UV absorption maximum around 300 nm, roughly blue-shifted as compared to the absorption of isolated molecules and attributed to  $\pi$ - $\pi^*$  transitions involving oxadiazole chromophore. Additional weaker absorption peaks coming from the perylenediimide units were recognized for copolyimide films **P2** and **P3**, in the range of 467–469 nm, 500 nm and 534–539 nm. These absorption peaks were missing in the case of polymer **P1**, which does not employ ether bridges in the macromolecular structure, thus facilitating the solid-state aggregation of the perylenediimide units.

The copolymers display band gap values around 2.25 eV in solution and between 1.97 and 2.16 eV in the solid state. The later values are influenced by the ether bridges from the polymer backbone and are smaller as compared to solution due to a more aggregated polymer chain conformation in the solid state.

Among others, this work intends to reach new areas and perform a deeper characterization of these materials in terms of optical properties and their stability with temperature. By employing the formula given by Jarzabek et al. (1996), we determined the absorption coefficient  $\alpha$  (in cm<sup>-1</sup>) from the transmission ( $T$ ) and reflectivity ( $R$ ) spectra (displayed in Fig. 3 for the **P3** film) and the refractive index ( $n$ ) and film thickness ( $d$ ) values of the corresponding polymer film. A refractive index value,  $n$ , of 1.86, together with an extinction coefficient,  $k$ , of 0.02, which are common values for polymer films (Jarzabek et al., 2008) were obtained by applying the Kramers-Kronig analysis (Fellman and Westerlund, 1992) to the reflectance spectra of **P3** polymer film. Thickness interferences (seen in the insert of Fig. 2) for the optical transmission and reflectivity spectra of **P3** were used to evaluate a thickness of about 1.16  $\mu$ m.

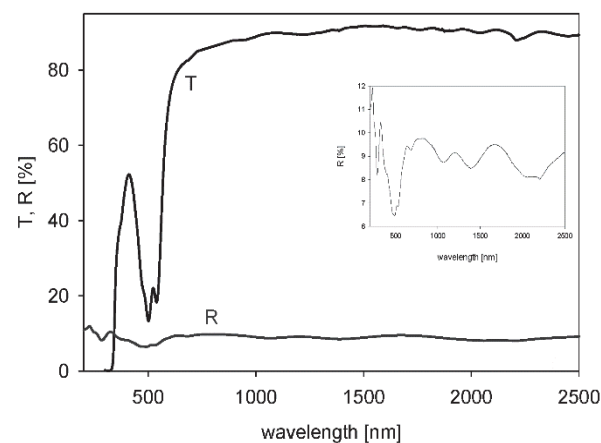


Fig. 2. Transmission (T) and reflectivity (R) spectra of polymer **P3** thin film

Fig. 3(a) presents the absorption coefficient ( $\alpha$ ) and Tauc dependence 3(b) of copoly(oxadiazole-teryleneimide) film **P3**. The absorption edges obtained as described by Rohlffing and Bradley (1998), have been found to comply with the relationship  $(\alpha E)^{1/2} = f(E)$ , which is characteristic for amorphous semiconductors (Mott, 1968). It is generally accepted that this amorphous feature of the absorption edge is coming from various structural deficiencies determined by macromolecular chains with distinct length and orientations. The same method was previously applied to establish the energy gap values for amorphous polymer foils (Jarzabek et al., 2002), and thin films (Jarzabek et al., 2008). The so-called Tauc relation (Tauc and Menth, 1972) was used to calculate the energy gap ( $E_g$ ) of **P3**. The linear estimation of the  $(\alpha E)^{1/2} = f(E)$  dependence, at an energy range  $E > E_g$  gave an energy gap value of 2.04eV.

The spectroscopic features of copoly(oxadiazole-teryleneimide)s **P1** – **P3** were surveyed by employing UV-vis absorption spectroscopy during thermal treatment from room

temperature up to 350°C, in order to determine the temperature dependence of the optical stability of these polymers. Fig. 4 displays representative temperature dependence for one of the investigated films. It is reasonable to reckon that the copolymers display a robust optical stability in a wide temperature domain, well below and even above Tg. Small changes (less than 15%) of absorption intensity and moderate switching (~10 nm) of absorption position towards shorter wavelengths come into sight when increasing temperature, mostly around or above Tg. This conduct suggests slight changes in the chain conformation of the envisaged polymer.

The attraction forces between the conjugated segments of the macromolecular chain decrease with increasing temperature, followed by a growth of thermal energy and subsequent conformational disorder. The good optical stability at elevated temperatures of these copolymers, as evidenced by this preliminary annealing study confirms their potential as feasible materials for opto-electronic devices, since time- and thermal-durability are prerequisites for this type of applications.

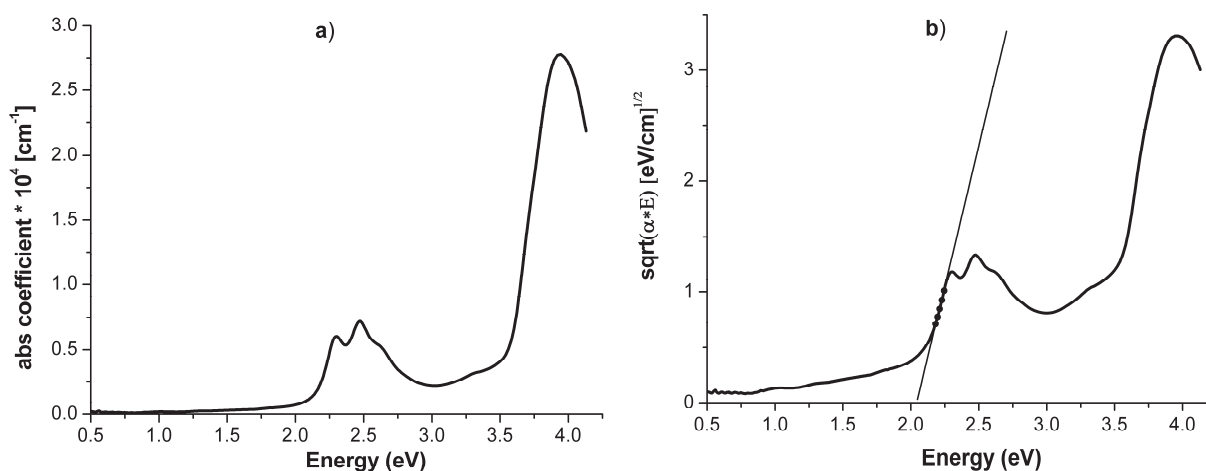


Fig. 3. Absorption coefficient (a) and Tauc dependence (b) of thin film **P3**

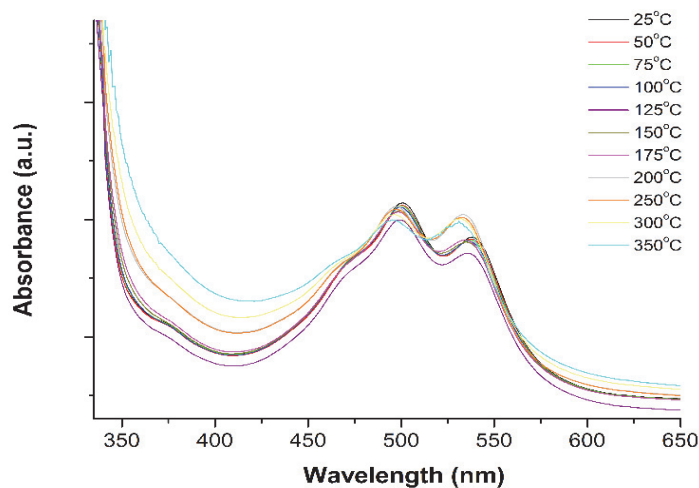


Fig. 4. UV absorption spectra of **P3** thin film at different temperatures

Since the main envisaged application of the present polymers is as light-emitting materials we evaluated this feature by investigating the photoluminescent behavior in solution and solid state. The photoluminescent behavior of these copolymers in solution (Rusu et al., 2010) and in solid state was investigated by irradiation with light of different wavelengths in order to cover all characteristic absorptions of each individual chromophore (Table 1).

Copolymer **P1** displays similar spectra in solution when excited at approx. 300 and at 360 nm, which present a strong, broad emission in the blue spectral range (around 403 nm) coming from the oxadiazole units and two weaker emissions in the green and yellow domain (at 534-537 nm and 577-586 nm, respectively) given by the emission of perylenediimide moieties.

The perylenediimide emission in solution of the other two products, **P2** and **P3**, at the same excitation wavelength, 304 nm, remains in the same spectral range, while the oxadiazole emission seems to be completely quenched, due to an excitation energy transfer through the oxygen bridge from the oxadiazole moieties to the perylenediimide ones (Rusu et al., 2010).

A similar conclusion was previously mentioned by other authors (Xu et al., 2006). An additional broad, weak emission in the UV domain, revolving around 370 nm, appears for these two copolymers at the same excitation wavelength. When irradiated with 360 nm, the above mentioned UV domain band is divided and red-shifted to 407 nm and roughly 440 nm (blue domain), due to the emission of imide rings involving segments of different conjugation length. All copolymers show a similar behavior when excited by a 492-494 nm light, with two peaks around 538 nm and 578 nm coming from the emission of perylenediimide units (Table 1).

By irradiation at the maxima absorption wavelengths corresponding to diphenyl-1,3,4-oxadiazole chromophore (approx. 300 nm) the copolymers display fairly good values of the fluorescence quantum yield ( $\Phi_f$ ) - 9.7 % for **P1**, 10.95% for **P2** and 5.80% for **P3**, respectively - comparable with those of other oxadiazole-containing polymers (Damaceanu et al., 2012, 2013).

The lack of oxadiazole emission for the **P2** and **P3** solutions when excited with 360 nm is also clearly reflected in the fluorescence quantum yield values obtained at this wavelength (3.14% for **P2** and 3.07% for **P3**), much lower as compared to the ones generated at 304 nm. The absolute values of fluorescence quantum yield of the copolymers **P1-P3** in solution, by excitation at 492-494 nm, reach for 20.84% **P1**, 2.26% for **P2** and 74.65% for **P3** and seem to be influenced by the diamine segment of each macromolecular compound. The color of the PL emission was surveyed on the basis of chromaticity coordinates, according to the available CIE 1931 (Commission Internationale de l'Éclairage) standard (Smith and Pokorny, 2003). Maximum emission wavelength values and the CIE coordinates of copoly(eryleneimide)s **P1-P3** in solution and as films are collected in Table 1. In the study of color perception, one of the first mathematically defined color spaces is the CIE-1931 XYZ color space (Smith and Pokorny, 2003). The chromatic sensation of human eyes to a specific optical spectrum is usually characterized by a chromaticity diagram. According to the available CIE standard, the chromaticity coordinates of the investigated polymers depend on the excitation wavelength (Fig. 5). All chromaticity coordinates of these copolymers in solution are located in the blue and green region of the diagram, except for the ones of **P2** irradiated with 360 nm which are out of the diagram.

**Table 1.** Photoluminescence (PL) and chromaticity coordinates of polymers **P1-P3**

<i>Solution (N-methylpyrrolidinone as a solvent)</i>							
<i>Polymer</i>	<i>PL (at 304 nm)</i>		<i>PL (at 360 nm)</i>		<i>PL (at 492-494 nm)</i>		$\Phi_f^{b)}$
	$\lambda_{em}^{a)}$ , nm	CIE (X, Y)	$\lambda_{em}^{a)}$ , nm	CIE (X, Y)	$\lambda_{em}^{a)}$ , nm	CIE (X, Y)	
<b>P1</b>	403, 537, 577 <sup>s</sup>	0.1556, 0.0248	404, 534, 586 <sup>s</sup>	0.1510, 0.0426	536, 578	0.3793, 0.6008	9.70
<b>P2</b>	370, 538, 581	0.1422, 0.0853	407, 442, 538, 578	0.0357, -0.1735	538, 578	0.3521, 0.6252	10.95
<b>P3</b>	370, 536, 580	0.2014, 0.4098	407, 438, 536, 577	0.3644, 0.5753	538, 579	0.3798, 0.6043	5.80
<i>Solid state</i>							
<i>Polymer</i>	<i>PL (at 300 nm)</i>						$\Phi_f^{b)}$
	$\lambda_{em}^{a)}$ , nm			CIE (X, Y)			
<b>P1</b>	385, 416 <sup>s</sup> , 445 <sup>s</sup> , 481 <sup>s</sup> , 515, 542			0.1831, 0.2251			5.21
<b>P2</b>	360, 382, 412 <sup>s</sup> , 444 <sup>s</sup> , 481 <sup>s</sup> , 518, 542			0.1831, 0.2262			5.41
<b>P3</b>	362, 380, 414 <sup>s</sup> , 450 <sup>s</sup> , 486 <sup>s</sup> , 519, 544			0.1824, 0.2237			5.12

<sup>a)</sup>  $\lambda_{em}$  - wavelength of the maximum PL emission peak; <sup>b)</sup>  $\Phi_f$  - the absolute values of fluorescence quantum yield determined by irradiation with approx. 300 nm; <sup>s</sup> - shoulder

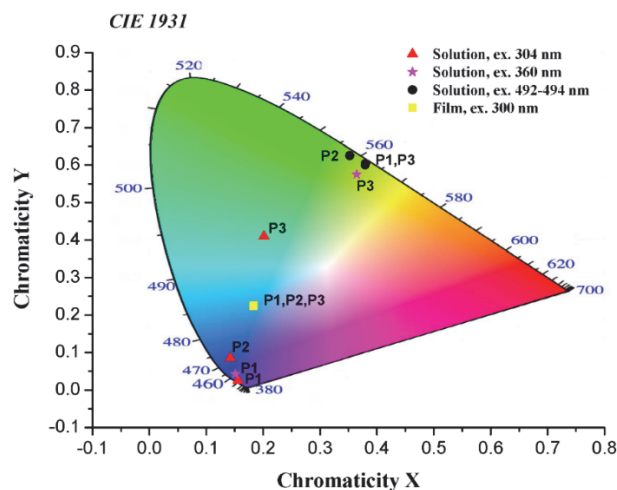


Fig. 5. Chromaticity diagrams of polyperyleneimides **P1-P4**

The chromaticity coordinates of **P1**, obtained by excitation at both 304 and 360 nm are placed quite close to the spectral locus and correspond to pure hue blue light of a single wavelength. The CIE coordinates corresponding to **P2** and **P3**, by exciting at 304 or 360 nm are shifted inside the diagram, displaying a less saturated light – a mixture of blue and green, with a blue shade for **P2** and a green shade for **P3**. The chromaticity coordinates of these copolymers, obtained by excitation at the main maximum absorption wavelength characteristic to perylenediimide (492 nm) are located on the spectral locus and correspond to pure saturated green monochromatic light.

The photoluminescent characteristics of the investigated copolymers changed significantly from solution to solid state. The light-emitting ability in the film state was observed only by exciting at the maxima absorption wavelength (300 nm) corresponding to the diphenyl-1,3,4-oxadiazole chromophore. The PL spectra of these polymers present only one absorption maxima in the UV domain, between 360 and 385 nm, and several shoulders in the blue spectral range, between 412-414 nm, 444-450 nm and 481-486 nm, determined by the emission of diphenyl-oxadiazole, imide and phenylene fragments, and very weak emission peaks coming from the perylenediimide moieties at 518 and 544 nm (Fig. 6). Unlike most conjugated polymers, the main emission peak suffers hypsochromic shifts in thin films as compared to solutions, suggesting a certain degree of solid-state arrangement which interrupts the conjugation length. When exciting at 360 nm, the PL spectra of polymer films display only very weak, insignificant emission peaks characteristic to the perylenediimide moiety. When the excitation was done at even higher wavelengths, no emission attributed to this chromophore was observed. The high content of perylenediimide chromophore is responsible for this behavior, leading to fluorescence quenching through aggregation. The CIE coordinates corresponding to **P1-P3** films irradiated with 300 nm are almost

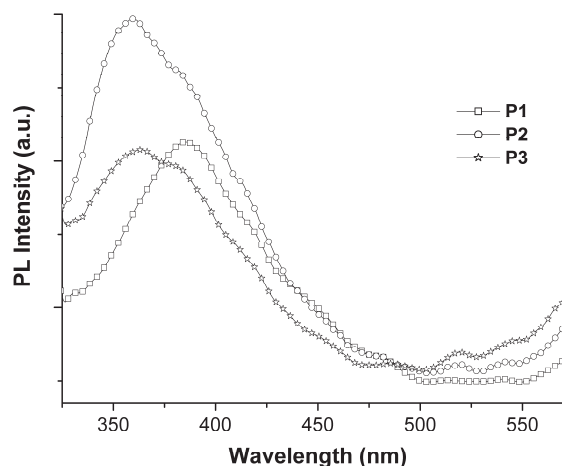


Fig. 6. Photoluminescence spectra of thin films of copolyimides **P1 – P3** (irradiated at 300 nm)

superposed in the blue spectral domain, clearly validating the ability of these polymers to emit blue light of similar shades (Fig. 5). Low fluorescence quantum yields, between 5.12 and 5.41% were obtained for thin films proving that the aggregation plays an important role in the fluorescence behavior of these polyperyleneimides in the solid state.

As suggested by the high Stokes shift values (the difference between the main fluorescence and UV-vis peaks) between 63 and 90 nm, no reabsorption takes place in these polymers. It is known that low Stokes shift values translate into a strong overlap of emission and absorption spectra which is followed by a drop in the overall luminescence efficiency of a device due to a self-absorption phenomenon. (Sun and Wang, 2001). The high Stokes shift values of the investigated copoly(oxadiazole-imide)s are more than adequate to ensure fine luminescence efficiency.

Further work is necessary to study the appropriate perylene content in the macromolecular architecture so as to overcome the fluorescence quenching through aggregation and to analyze their use and performance in opto-electronic devices.

Copolymers **P1 – P3** are all electroactive. Cyclic voltammetry was employed to evaluate the electrochemical features of film samples casted on ITO-coated glass substrates, which also served as working electrodes. The experiments were performed under nitrogen, in dry acetonitrile (MeCN) solutions (by using a 0.1 M of tetrabutylammonium perchlorate (TBAP) electrolyte salt).

Fig. 7 (a: anodic scan; b: cathodic scan) depicts the cyclic voltammograms of polymer **P1** recorded at a scan rate of 100 mV/s, while the results of the electrochemical measurements of all the polymers are summarized in Table 2.

From the cyclic voltammetry measurements it can be observed that these copolymers can be easily reduced (*n*-doping), meaning that they have the capability of electron injection.

Copolyimide **P1** displays two pairs of stable and reversible redox reduction peaks in the negative

potential range at  $E_{pc}^{red}$  of -1.20 V ( $E_{onset}^{red} = -0.78$  V),  $E_{pc}^{ox}$  of -0.47 V and  $E_{pc}^{red}$  of -1.72 V,  $E_{pc}^{ox}$  of -1.38 V, respectively. This redox couples are associated with the diphenyl-oxadiazole unit and conjugated perylenediimide moiety, which is more easily reduced electrochemically than other non-perylene imides such as phthalimide, also present in the macromolecular structure. In correlation to a proposed mechanism for low molecular weight perylene products (Turkmen et al., 2009), the first redox couple corresponds to the reduction of the neutral form to the radical anion, while the second redox couple relates to the reduction of oxadiazole rings (Damaceanu et al., 2012). The expected second reduction/oxidation peak belonging to the perylenediimide unit seems to be overlapped by that of oxadiazole moiety. We consider these reversible redox processes to be stable since almost no change in the position and current intensity of the cathodic peaks was observed (Fig. 8) after four cyclic scans in the negative potential range, at the scan rate of 100 mV/s. The CV diagram of copolyimide P1 in the positive potential range displays three distinct irreversible oxidation processes at anodic peak potentials ( $E_{pa}$ ) of 0.92 V ( $E_{onset}^{ox} = 0.55$  V), 1.42 V and 1.73 V, respectively, and three irreversible reduction processes at anodic peak potentials of 0.92 V, 0.75 V and 0.42 V, respectively.

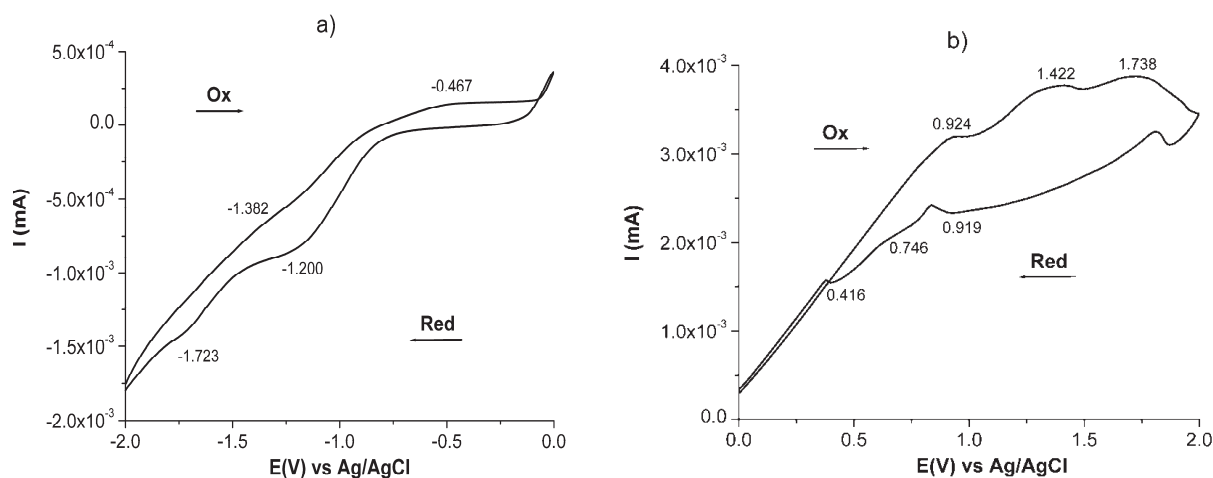
The oxidation processes occur at the two distinct types of N atoms present in the macromolecular unit: N belonging to the 1,3,4-oxadiazole rings and N coming from the of imide cycles. The first oxidation peak is attributed to the irreversible oxidation of oxadiazole rings, while the other two peaks are connected with the irreversible oxidation of perylene,  $Per \rightarrow Per^+$ , and phthalimide present in the macromolecular structure, also. Removal of electrons in the oxidation processes leads to the formation of radical cations and perhaps dications coming from radical recombination. After the oxadiazole and perylene oxidation, the reversible reduction peaks in the negative potential region do not change their position or intensity, even after several cycles, indicating that the formation of oxadiazole or perylene cations does not hinder the insertion of cationic species from solution to polymer film during the reduction of imide groups.

Additionally, polymer P1 presents three irreversible distinct reduction peaks which are caused by the reduction of other non-perylene imide groups in the copolyimide and could be correlated with the lack of any ether bridges in the macromolecular unit of this copolymer, since the other two presented only one (as in the case of copolyimide P2) or no reduction peaks (as in case of P3) in the positive potential range.

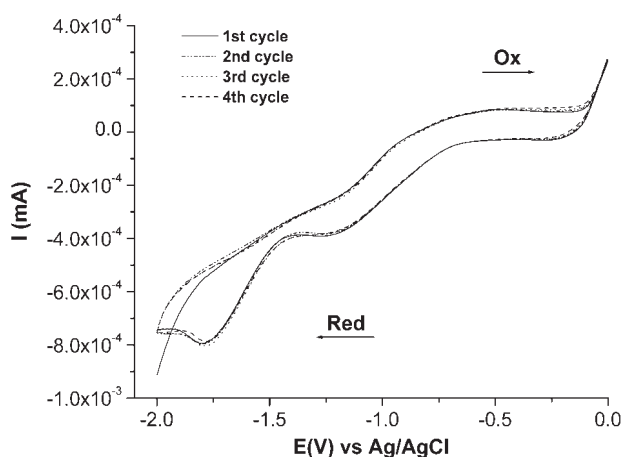
**Table 2.** Electrochemical properties of copoly(oxadiazole-eryleneimide)s P1 – P3

Polymer	<sup>a)</sup> $E_{onset}^{ox}$ (V)	<sup>c)</sup> $E_{pa}^{ox}$ (V)	<sup>c)</sup> $E_{pa}^{red}$ (V)	<sup>b)</sup> $E_{onset}^{red}$ (V)	<sup>d)</sup> $E_{pc}^{red}$ (V)	<sup>d)</sup> $E_{pc}^{ox}$ (V)	<sup>e)</sup> $E_{HOMO}$ (eV)	<sup>f)</sup> $E_{LUMO}$ (eV)	<sup>g)</sup> $E_g$ (eV)
P1	0.555	0.924 1.422 1.738	0.919 0.746 0.416	-0.779	-1.200 -1.723	-1.382 -0.467	4.92	3.59	1.33
P2	0.435	0.656 0.943 1.336	1.657	-0.711	-1.239 -1.794	-1.387 -0.937	4.89	3.66	1.14
P3	0.311	0.742 0.981 1.609	–	-0.722	-0.923 -0.685	–	4.68	3.65	1.03

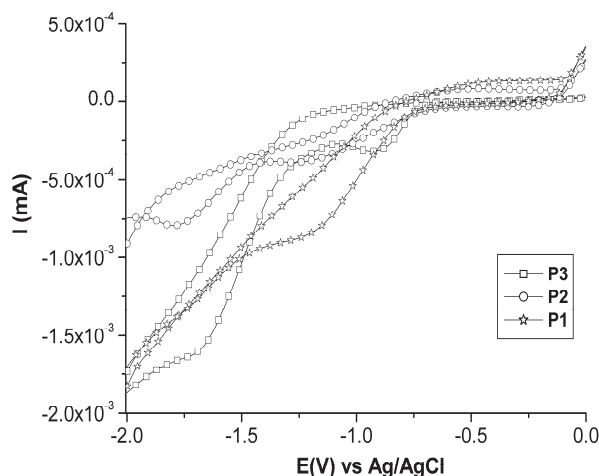
Note: <sup>a)</sup>  $E_{onset}^{ox}$  - oxidation onset potential; <sup>b)</sup>  $E_{onset}^{red}$  - reduction onset potential; <sup>c)</sup>  $E_{pa}$  - anodic peak potential; <sup>d)</sup>  $E_{pc}$  - cathodic peak potential; <sup>e)</sup>  $E_{HOMO}$  - the HOMO energy levels; <sup>f)</sup>  $E_{LUMO}$  - the LUMO energy levels; <sup>g)</sup>  $E_g$  - energy gap measured from electrochemical data according to the  $E_{onset}$ .



**Fig. 7.** The first CV scan of the cast film of copolyimide P1 on ITO coated glass substrate (a - cathodic scan, b - anodic scan)



**Fig. 8.** Repetitive CV scans of copolyimide **P2** film on ITO electrode in 0.1 M TBAP/MeCN solution (4 cycles, cathodic scan)



**Fig. 9.** Cyclic voltammograms of cast films of copolyimides **P1 – P3** on ITO-coated glass substrate in 0.1 M TBAP/MeCN solution at a scan rate of 100 mV/s

However, these oxidation and reduction processes taking place in the anodic region are not very stable.

A comparison between the CV curves of structurally similar copolymers **P1**, **P2** and **P3** in the negative potential range is depicted in Fig. 9. The significant difference between the electrochemical reduction responses in the negative potential range of the investigated polymers is coming from the different nature of the diamine units which can affect the reduction potentials, especially the first reduction step, as it was observed by other authors, as well (Lu et al., 1999).

Copolyimides **P1** and **P2** present the same behavior in the positive potential range, while polymer **P3** did not exhibit any oxidation or reduction responses in the negative or positive potential domain, respectively. This feature is determined by the presence in the macromolecular backbone of copolyimide **P3** of *meta*-catenated phenylene units, which leads to a modification of electronic conjugation along the macromolecular structure. Both first and second reduction waves of copolyimide **P3** in the cathodic region were observed at slightly higher potentials as compared with the other two polymers, suggesting that this polymer is somewhat easier to reduce than the similar copoly(oxadiazole-*peryleneimide*s) containing ether bridges.

The reduction process was accompanied by evident color changes for all three copolymers and therefore they might display electrochromic properties, an expected feature for perylene-containing polyimides.

The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels are considered key features in the configuration of a light-emitting device. We determined these parameters based on the oxidation ( $E_{onset}^{ox}$ ) and reduction ( $E_{onset}^{red}$ ) onset potentials versus Ag/AgCl, as described by Li et al. (1999) (Eq. 1 and Eq. 2):

$$E_{LUMO} = E_{onset}^{red} + 4.37 \quad (1)$$

$$E_{HOMO} = E_{onset}^{ox} + 4.37 \quad (2)$$

and the energy gap by using (Eq. 3):

$$E_g = E_{HOMO} - E_{LUMO} \quad (3)$$

All obtained values are summarized in Table 2.

A disparity was observed between the band gap energy values measured by spectroscopic and electrochemical methods. Even if the differences go as high as 1 eV, there is no conflict between these values, since they are strongly dependent on the films preparation method and thicknesses and describe distinct processes. The spectroscopic measurements provide an estimation of the energy difference of the frontier orbitals and the obtained optical band gap corresponds to the energy required to form a tightly-bound exciton, whereas the redox potentials give the absolute energetic positions of the HOMO and LUMO levels and the electrochemical or transport band gap corresponds to the energy required to form free charge carriers (Takeda et al., 2012). A broad range of reasons for this disparity are provided in the literature, from the influence of the film thickness upon the optical band gap (Sanchez-Vergara et al., 2012) to the effect of the energy barrier at the interface between a polymer thin film and the electrode surface (Djurovich et al., 2009).

The investigated copolymers display LUMO energy values between 3.59 and 3.65 eV. These values suggest a more than reasonable electron-injection ability when compared to polymers generally considered very good in this regard, like cyano-polyphenylenevinylene (CN-PPV) (3.02 eV) or other aromatic polyoxadiazoles (2.8-3.2 eV) (Akcelrud, 2003). The HOMO energy values between 4.68 and 4.92 eV indicate a very good hole injection ability if compared to the standard methoxy-ethyl-hexyloxy-polyphenylenevinylene (MEH-PPV) (4.87 eV) (Cervini et al., 1997). The hole ( $\Delta E_h$ ) and electron ( $\Delta E_e$ ) injection barriers were determined by the following equations (Eq. 4 and Eq. 5):

$$\Delta E_h = E_{HOMO} - 4.8(eV) \quad (4)$$



where: 4.8 eV represents the work function corresponding to the ITO anode.

$$\Delta E_e = 4.3 - E_{LUMO} \text{ (eV)} \quad (5)$$

where: 4.3 eV represents the work function corresponding to the aluminum cathode. The balance of hole and electron injection is usually characterized by the difference ( $\Delta E_e - \Delta E_h$ ) between the above-mentioned injection barriers, lower values indicating a very good injection balance of charges from the cathode to the anode. Their values are displayed in Table 3.

Low values of the energy barrier corresponding to the electron injection from the Al electrode to the polymer are determined by the perylenediimide units and 1,3,4-oxadiazole moieties from the polymer backbone. It is clear from the CV investigation that the envisaged copolymers readily support a reduction process (*n*-doping) and therefore display an electron injection function. Moreover, these copolymers show very low values of barrier energy differences ( $\Delta E_e - \Delta E_h$ ) if compared to poly(p-phenylene-vinylene (PPV) (Bradley, 1993), a very popular polymer in the field of light-emitting devices. Therefore it can be concluded that the investigated copolymers represent feasible materials for opto-electronic devices, due to the favorable electron injection function and low values of barrier energy.

**Table 3.** The barrier energies of polyimides **P1 – P3**

Polymer	<sup>a)</sup> $\Delta E_h$	<sup>b)</sup> $\Delta E_e$	<sup>c)</sup> $\Delta E_e - \Delta E_h$
<b>P1</b>	0.12	0.71	0.59
<b>P2</b>	0.09	0.64	0.55
<b>P3</b>	0.12	0.65	0.53

<sup>a)</sup>  $\Delta E_h$  - barrier energy for hole injection from ITO to polymer; <sup>b)</sup>  $\Delta E_e$  - barrier energy for electron injection from Al to polymer; <sup>c)</sup>  $\Delta E_e - \Delta E_h$  - the difference of barrier energy between electron injection and hole injection to polymer.

#### 4. Conclusions

An in-depth study of the photo-optical and electrochemical behavior of some fluorinated copolyimides incorporating oxadiazole and perylene moieties was the main objective of this work.

The polymer solutions displayed light emission in the blue and green spectral ranges, with fairly high quantum yield values and pure saturated emitted light. Moreover, the high Stokes shift values lead to the conclusion that no reabsorption takes place in these polymers. The photoluminescent behavior of the investigated copolyimides changed significantly from solution to solid state. The high content of perylenediimide moieties generates fluorescence quenching through aggregation, and therefore the solid state polymers are able to emit light of a lower quantum yield only when irradiated at the maxima absorption wavelength characteristic to the oxadiazole chromophore. The polymeric films also proved a robust optical stability in a wide temperature domain, well below and even above glass transition.

Cyclic voltammetry measurements substantiated the electron injection capability of the investigated compounds by showing that they can be easily reduced (*n*-doping). The polymers exhibited very good electron and hole injection properties and very low barrier energy between electron injection and hole injection from electrodes to polymer, thus being promising for application in electroluminescent devices.

Further research is necessary to study the suitable perylene content in order to overcome the fluorescence quenching through aggregation and to analyze their use and performance in blue-light-emitting devices. These polymers provide an important guideline for the design of new materials for organic electronic devices with high stability.

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