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# Synthesis and Characterization of Conjugated Polymers and Their Blends for Optoelectronic Applications

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**Summary:** Various polymeric blends of hole transporting materials, (such as MEH-PPV and P3HT) and electron transporting materials (such as poly(phenyl-vinyl-quinoline) and poly[2-(4-methacryloxyphenyl)-5-phenyl)-1,3,4-oxadiazole]) have been prepared and investigated. Moreover a soluble, main chain oxadiazole bearing polyether has been synthesized, aiming towards an efficient electron transporting polymeric material which was also used for blend preparation together with P3HT. A deeper investigation into their spectroscopic characteristics using, primarily, FT-IR spectroscopy, but also UV-Vis spectroscopy has been conducted. The surface morphology of these blends was investigated using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) in an attempt to gather information for their solid state properties and morphologies. Finally, DSC measurements provided additional insight into the thermal behaviour of these materials.

**Keywords:** blends; conjugated polymers; polyoxadiazoles; polyquinolines; spectroscopic characterization

## Introduction

Since the discovery of electrical conductivity in doped conjugated polyacetylene in 1977, [1] the field of polymer semiconductors has received intense scientific attention over the past decades. Conjugated polymers are suitable candidates as active materials in a number of electronic applications, such as light emitting diodes (LEDs), [2,3] photovoltaic cells, [4,5] and field effect transistors (FETs). [6] More specifically conjugated polymers present excellent possibilities towards the fabrication of low cost and efficient large area flat-panel displays due to their unique

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processability, band gap tunability and mechanical flexibility. Derivatives of polythiophene (PT), poly(*p*-phenylene) (PPP), poly(*p*-phenylene-vinylene) (PPV) and polyfluorene (PF) have already been employed in such aforementioned electronic devices.

Highly efficient polymer LED devices have mainly been prepared from multilayered thin films owing to improved injection of both electrons and holes, whereas multicolor electroluminescence (EL) have been reported in layered and phase-separated blends. [7] Improved performance has been obtained from photovoltaic devices comprised of layered heterojunction or bulk heterojunction blends due to efficient charge photogeneration and separation. [8,9] However bulk heterojunction blend-based devices are advantageous to multiple layered devices because of the large interfacial area owed to the three-dimensional heterojunction.

PPV and its soluble derivates such as MEH-PPV and MDMO-PPV are rather chemically and thermally stable materials which are good candidates for both light emitting diodes [10,11] and bulk heterojunction plastic solar cells. [12,13] Photovoltaic effect has been observed in diode structures comprised of thin films of PPV sandwiched between electrodes of ITO and various metals as cathodes. [14] These polymers act as hole transport layers and have exhibited photoinduced charge transport properties onto electron accepting molecules such as $C_{60}$. [9] On the other hand, PPV derivatives such as CN-PPV have been studied regarding their electron accepting properties. These bulk heterojunction polymer blends of MEH-PPV and CN-PPV have already shown promising results regarding their use in photovoltaic cells. [15]

The development of substituted regioregular poly(3-alkylthiophenes) (P3AT's) [16,17] has created a new class of conjugated polymers presenting high optical absorptions, high environmental and thermal stabilities, increased solubilities and processability. Thus they have found a number of practical applications in LEDs. [18,19] Recently bulk heterojunction blends of poly(3-hexylthiophene-2,5-diyl) (P3HT) with a soluble derivative of $C_{60}$ (PCBM) yielded highly efficient photovoltaic cells. [20]

In addition polyquinolines are characterized by high thermal and oxidative stability, outstanding mechanical properties and an ability to form optically clear films. [21-25] Polyquinolines have shown optical and electronic properties such as electroluminescence [26-28] and photoconductivity. [29] Polyquinoline-derivatives and copolymers have been incorporated as the electron transporting layer in two layer heterojunction LEDs, [30] photovoltaic devices [31,32] and selective chemosensors. [33]

Furthermore several oxadiazole-containing polymers have been employed as electron transporting/injecting materials [34,35] in organic LED devices. This ability to carry electrons is believed to arise from the high electron affinity of the oxadiazole ring in the molecule. Various oxadiazole bearing polymers have already been reported in the literature as light-emitting materials. [36-38] Poly(aromatic oxadiazole)s are well known for their thermal, hydrolytic and photo stability and moreover for their high glass transition temperatures. [39-44] However at the same time insolubility problems usually rising due to the rigid structure of these polymers may be overcome two main routes. The first is to incorporate the oxadiazole units as side chain on a main polymeric backbone and the other is to produce copolymers bearing main chain oxadiazole and other solubilizing groups such as fluorenes or alkoxy-substituted phenylene rings.

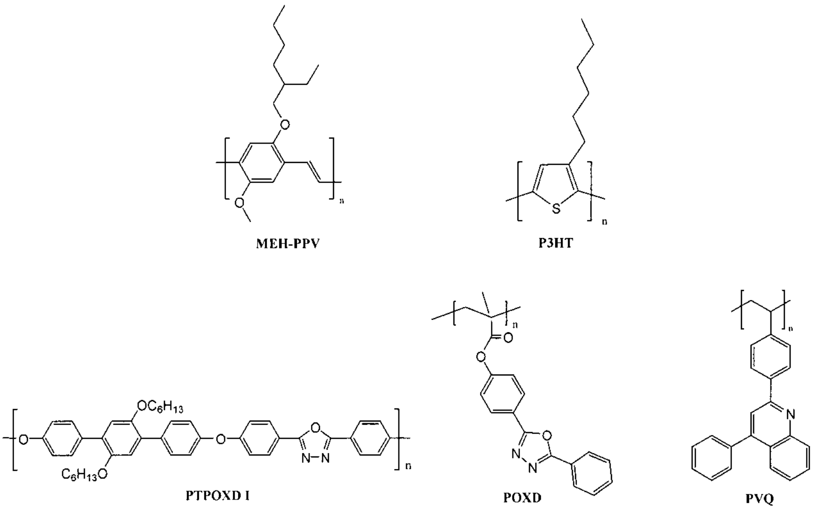
The main objective of this work is to examine the morphology and properties of conjugated polymers and their blends. Main chain conjugated polymers such as, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (**MEH-PPV**) and regioregular poly(3-hexylthiophene-2,5-diyl) (**P3HT**) have been characterized in order to be used in optoelectronic devices. In addition, blends of these polymers with poly[2-(4-methacryloxyphenyl)-5-phenyl)-1,3,4-oxadiazole (**POXD**), an alkoxy-substituted terphenyl polyether containing oxadiazole units (**PTPOXD**) and poly(vinyl-diphenylquinoline) (**PVQ**) have been also prepared and studied. The chemical structures of polymers are presented in Scheme 1.

## Experimental

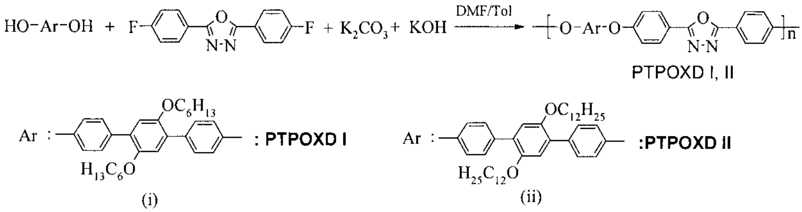
### Materials and measurements

P3HT and MEH-PPV were purchased from Aldrich and used without further purification. All solvents were purchased from Aldrich or Merck. Poly[2-(4-methacryloxyphenyl)-5-phenyl)-1,3,4-oxadiazole] was provided from KONARKA technologies Lowell MA, USA. PVQ, [45] 2′,5′-Bis(dodecyloxy)-p-terphenyl-4,4′′-diol [46] and 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole [47] were synthesized according to literature procedures. For the PVQ synthesis, commercial polystyrene (BDH laboratory chemicals) was used with Mn=100.000.

The FT-IR spectra were collected on a Nicolet Magna System 850 with a liquid nitrogen cooled MCT/A detector using a resolution of 4 $cm^{-1}$. For a better signal to noise ratio, 128 repetitions of each spectra were collected. NMR spectra were recorded on a Bruker Avance 400 MHz in $CDCl_3$ with TMS as internal standard. Atomic force microscopy (AFM) images were obtained using a Topometrix Explorer SPM Microscope. Scanning Electron Microscopy (SEM) was performed using a Jeol Scanning Microscope J.S.M. 6300. DSC measurements were taken on a TA instruments Q100 using the following program: 1st heating run, 0-200 °C, rate 20 °C/min, cooling run, 200-0 °C, rate 20 °C/min, 2nd heating run, 0-200 °C, rate 10 °C/min. Only data from the 2nd heating run were taken into account in order to avoid the effect of thermal history. Optical absorption spectra were obtained using a Hewlett Packard 8452A spectrophotometer. Polymer blends of MEH-PPV/PVQ and MEH-PPV/POXD were prepared by dissolving a total of 10mg of both polymers in 1ml of chloroform ($CHCl_3$). The P3HT/PTPOXD blend was prepared by dissolving 10 mg of both polymers in 1ml of o-dichlorobenzene (o-DCB). For these blends only results from PTPOXD I are presented. All the blends were prepared with the following ratio of 25% in the hole transport material and 75% in the electron transport material. The blends' solutions were drop casted or spin coated with the following spin program: 1500rpm for 1min and 3000rpm for 1min yielding uniform films of around 100nm thickness.



Scheme 1. Molecular structures of the polymers used in this study.



Scheme 2. Synthetic route for the polymerization of PTPOXD series of polyethers.

Synthesis of main chain oxadiazole co-polymers PTPOXD I and II.

A round bottomed flask fitted with a Dean-Stark trap, was degassed and filled with argon three times. 2,5-bis(4-fluorophenyl) 1,3,4 oxadiazole (0.6024 mmol), 2,5 dialkoxy terphenylene diols (i-ii) (0.6024 mmol), potassium carbonate (0.6928 mmol) and potassium hydroxide (1.2048 mmol) were placed together and the flask was purged with argon three times. A mixture of dimethylformamide (1.31 mL) and toluene (0.79 mL) were then added and the obtained mixture was heated at 140 $^0$C under stirring for 12 hr. Afterwards the temperature was increased at 180 $^0$C for another 6 h. After cooling to RT, the reaction mixture was poured in methanol and the precipitate thus formed was filtered, washed with excess of water and methanol and dried in vacuum.

**PTPOXD I:** $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.110 (d, 4H), 7.648 (d, 4H), 7.185 (m, 8H), 7.020 (s, 2H), 3.991 (t, 4H), 1.732 (m, 4H), 1.397 (m, 4H), 1.282 (m, 8H), 0.878 (t, 6H).

**PTPOXD II:** $^1$H-NMR (400 MHz, $CDCl_3$) δ: 8.111 (d, 4H), 7.645 (d, 4H), 7.180 (m, 8H), 7.014 (s, 2H), 3.996 (t, 4H), 1.725 (m, 4H), 1.393 (m, 4H), 1.288 (m, 32H), 0.879 (t, 6H).

## Results and discussion

### Preparation and solubility of copolyethers

The polymers PTPOXD I-II were synthesized by nucleophilic substitution of the 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole from bisphenols (i-ii) as shown in Scheme 2. The molecular characteristics and the solubilities of the obtained copolymers are presented in Table I.

Table I: Molecular characteristics of PTPOXD polyethers and their solubilities in various organic solvents

| **POLYMERS** | $\bar{M}_n$ | $\bar{M}_w$ | Tol | THF | $CHCl_3$ | DMSO | DMF | DMA | TCE |
|---|---|---|---|---|---|---|---|---|---|
| (I) | 18600 | 33500 | ++ | ++ | ++ | + | + | + | ++ |
| (II) | 25993 | 57200 | ++ | ++ | ++ | + | + | + | ++ |

++ soluble
\+ partially soluble
\- not soluble

## UV-Vis

Absorption maxima of all examined polymers in either thin film form or dilute solutions are presented in Table II. For their solid state characterization the polymers were spin coated from $CHCl_3$ solutions onto a glass substrate in order to obtain thin uniform films.

Table II: Contains the absorption maxima of the polymers used for the blend preparation

| Polymers | Film (nm) | Solution (nm) |
|---|---|---|
| MEH-PPV | 502 | 498 |
| P3HT | 524, 554, 604 | 450 |
| POXD | 298 | 285 |
| PTPOXD | 322 | 316 |
| PVQ | 334 | 334 |

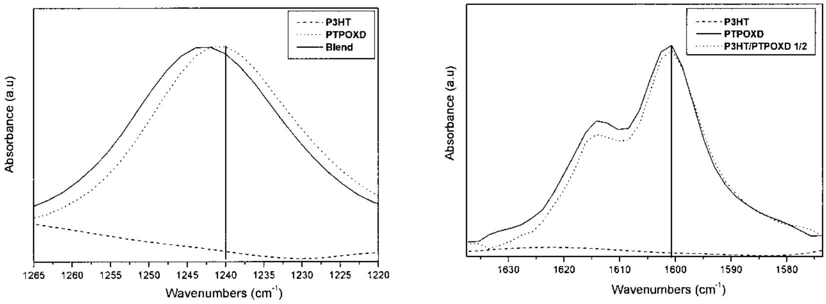
## FT-IR spectroscopic study of blends

Characteristic FT-IR bands of the polymers in use, before and after blending were recorded in order to determine possible changes in the spectra due to specific chain interactions between polymers. In particular bands attributed to C-N, C=N, C-O-C, C=O, C-S bonds are most sensitive to changes induced by interaction phenomena such as hydrogen bonding, thus increased attention was paid to these specific bands.

One of the more interesting blends in this work is the P3HT/PTPOXD system.

## P3HT / PTPOXD

The band at 1240 $cm^{-1}$ is associated with the main chain C-O-C stretching of PTPOXD. As it is shown in Fig. 1a), the spectrum of the blend shifts to lower frequencies for about 2 $cm^{-1}$.
However this shift is below the resolution used for this experiment and cannot indicate any interaction taking place in the blend. The same observations can be made for the 1600 $cm^{-1}$ region. This band at 1602$cm^{-1}$ is associated with the -C=N- vibration of oxadiazole unit of PTPOXD polymer (Fig 1b).



a) b)

Figure 1. a) 1240 $cm^{-1}$: C-O-C stretching vibration of main chain PTPOXD polymer and b) 1600 $cm^{-1}$: -C=N- stretching of the oxadiazole group in PTPOXD.

DSC measurements conducted in the pristine polymers as well as their blend (Figure 2) suggest that the two polymers exhibit some degree of miscibility. From the DSC the pristine PTPOXD polymer exhibits a glass transition temperature of 103 °C while the P3HT presented a glass transition temperature 45,5 °C (P3HT has been reported in the literature [48] to exhibit a Tg = 12 °C). On the other hand the DSC curve of the blend shows a broad glass transition temperature intermediate of the Tg of the two pristine polymers, demonstrating a partial miscibility for these two polymers.

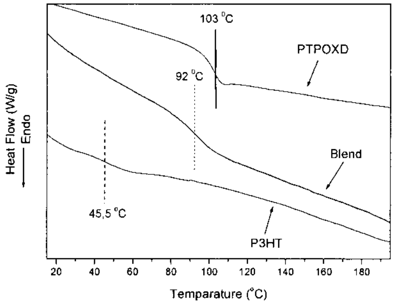


Figure 2. DSC thermograms of the P3HT/PTPOXD blend. Tgs of the blend as well as the pristine polymers are depicted.

## AFM

The FT-IR and DSC data prompted us to further investigate the morphology of this particular blend. Figure 3 shows an AFM image of P3HT/PTPOXD blend spin coated from o-DCB solution where phase separated regions are clearly visible. More specifically the peak-to-valley roughness of the AFM images is ~30nm. From the data collected it can be assumed that this polymeric system consisting of partially miscible P3HT/PTPOXD regions and PTPOXD-rich regions. A deeper investigation of this system taking into account possible solvent and concentration effects, progress. This system has shown photovoltaic response and optimization of this bulk heterojunction blend is intended.

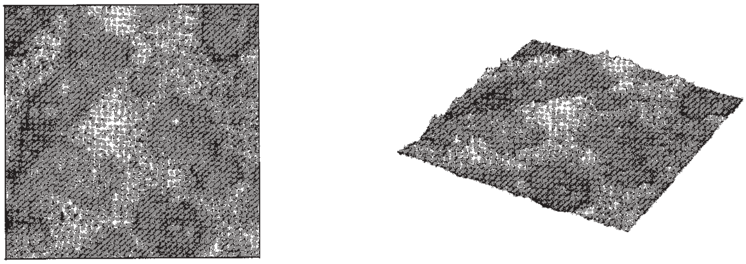


Figure 3. The 10x10μm AFM images of the P3HT/PTPOXD blend (left) and 3D view of the same area (right).

## MEH-PPV / PVQ and MEH-PPV/POXD blends

MEH-PPV is a conjugated polymer that is extensively studied. Blends of MEH-PPV with two different electron transporting materials are examined here.

MEH-PPV presents two strong bands at 1203 and 1040 cm$^{-1}$ due to the phenyl-oxygen and alkyl-oxygen stretching vibrations, respectively. Figure 4 reveals that no specific interaction takes place in the blend concerning these particular bands.

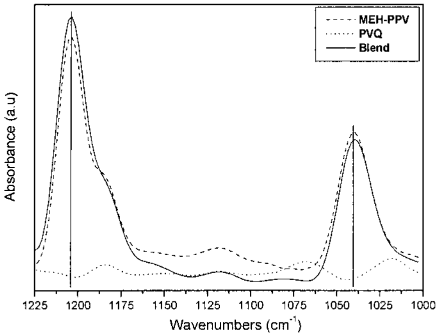


Figure 4. 1203 and 1040 cm$^{-1}$ bands attributed to the phenyl-oxygen and alkyl-oxygen stretching vibrations of MEH-PPV.

The FT-IR spectra indicate that phase separation must be taking place in the MEH-PPV/PVQ blends. Moreover microscopy studies employing TEM and SEM techniques conducted on the blend cannot lead to the assumption that this blend exhibits some degree of miscibility. On the other hand these microscopy techniques clarified whether this phase separation takes place in a micrometer or nanometer scale.

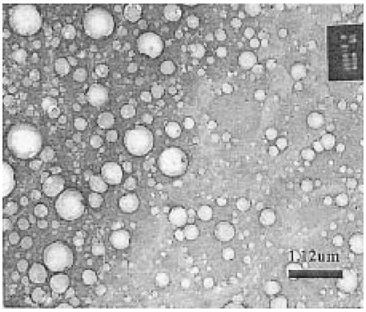


Figure 5. TEM picture of the MEH-PPV/PVQ blend.

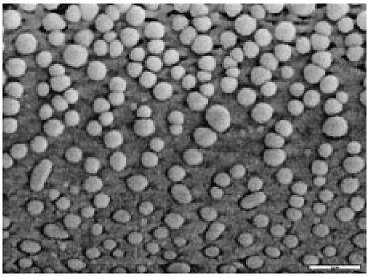
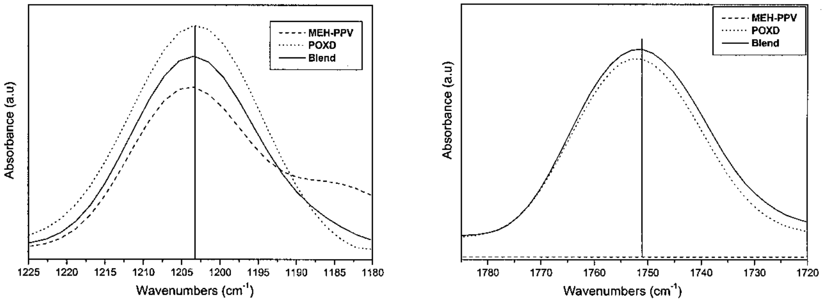


Figure 6. SEM picture of the MEH-PPV/PVQ blend.

The surface SEM and TEM pictures for MEH-PPV/PVQ for a 25/75 blend composition are depicted in Figures 5 and 6. Spherical particles were observed from both techniques. These particles have been identified through formic acid extraction of the blend as PVQ rich regions. Thus the two polymers exhibit, indeed, phase separation, an observation in agreement with FT-IR spectroscopy results. It is worth noting that although the blend is PVQ rich and a continuous PVQ phase is expected, the images show discrete fairly uniform PVQ spheres with sizes ranging from 100-500nm.

This nanophase separation observed in the above blend makes these materials promising candidates for optoelectronic applications, since nanophase separation is desirable for bulk heterojunction blends. Experimental studies of a novel side chain quinoline derivative have revealed that the morphology of these blends can be altered by various methods such as annealing and concentration of the solution from which the films are spun. Quinoline polymer's particle size can be altered proportionally to the concentration of the quinoline derivative in the blend. We have also examined the blend of MEH-PPV with POXD using FT-IR spectroscopy, AFM and TEM techniques. The informations obtained also revealed that the blend is phase separated.



a) b)

Figure 7. a) 1203 cm$^{-1}$ attributed to the phenyl-oxygen stretch b) 1750 cm$^{-1}$ owed to the C=O stretch vibration of the oxadiazole ring.

This blend appears to be phase separated since no interactions were observed from the FT-IR spectra (Figure 7). The same conclusion can be drawn by examining the TEM images obtained for the blend (Figure 8).

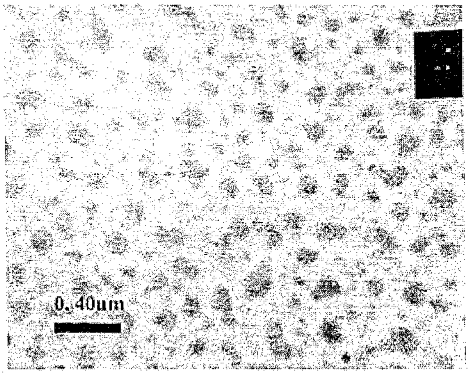


Figure 8. TEM image of the MEH-PPV / POXD blend.

More specifically, nanophase separation was observed (in agreement with FT-IR spectroscopy). Identification of the darker regions is to be conducted. However this blend could be a good candidate for bulk heterojunction optoelectronic devices that ideally require, 10-20nm in particle diameter, since the strong point of bulk heterojunction blends is the large interfacial area. In this particular blend, the particle size of the darker regions ranges from 60-150 nm. Altering the casting conditions (e.g. solvent) may provide the desirable smaller particle size.

## Conclusion

FT-IR measurements provided information for the phase separated behaviour of various blends consisting of various hole transporting/electron accepting pairs. In addition, microscopy measurements employing AFM, SEM and TEM techniques support the idea of nanophase separation in these systems. From the systems examined, blends comprising of P3HT/PTPOXD revealed partial miscibility. Blends of MEH-PPV with PVQ and POXD clearly presented a phase separation tendency, as demonstrated from FT-IR spectroscopy and microscopy studies. These particular blends could be ideal candidates for optoelectronic applications as they are phase separated in the nanometer scale.

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