Regioregular Phenyl and Phenoxy Substituted Polythiophenes for Bulk Heterojunction Solar Cells

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Summary: Poly[3-(4-octylphenyl) thiophene] (POPT) and poly[3-(4-octylphenoxy) thiophene] (POPOT) with high head-to-tail regioregularities have been synthesised and photovoltaic properties have been investigated. POPT-*blend*-PCBM exhibits an interesting behaviour in bulk heterojunction whereas POPOT presents poor photovoltaic performances. UV-visible absorption and AFM images of the blends are presented to explain these results.

Keywords: AFM; optical characterisation; photovoltaic; poly[3-(4-octylphenoxy) thiophene]; poly[3-(4-octyphenyl) thiophene]; synthesis

Introduction

Recently, polythiophenes have mainly been developed for their application in organic photovoltaic cells. Poly(3-hexylthiophene) (P3HT) in blend with the acceptor [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) currently gives the best performances with a power conversion efficiency around 5%.[1,2] The attractive features of this system are the high tendency of the P3HT to crystallise while allowing the PCBM to form aggregates. One possible limitation to a further increase in power conversion efficiency could be the absorption that it is insufficient in the range 600-800 nm. Therefore, we have undertaken the study of phenyl and phenoxy substituted polythiophenes in order to get polymers with improved absorption towards the infra-red. It has been reported that poly[3-(4-octylphenyl) thiophene] (POPT) exhibits an extended conjugation due to connection of the phenyl ring to the polythiophene backbone.[3] Poly[3-(4-octylphenoxy) thiophene] (POPOT) has been prepared to study the effect of the introduction of electron-donating groups on optical properties.

We report here on the synthesis of highly regioregular POPT and POPOT and on their results obtained from UV-visible absorption and from photovoltaic measurements. We compare the effect of introducing phenyl and phenoxy groups onto polythiophenes, also based on the morphology of the blend with PCBM studied by AFM.

Experimental Part

Materials

2,5-dibromo-3-tolylthiophene (**1**) and 2,5-dibromo-3-(4-octylphenyl)thiophene (**2**) were prepared according to the literature.[4] 3-(4-octylphenoxy)thiophene was prepared by using a CuBr catalyzed reaction of 3-bromothiophene with sodium 4-octylphenolate.[5] All other chemicals were obtained from Aldrich (France), and used as received. Solvents (Baker, France) were distilled over standard drying agents under dry nitrogen. Diphenyl ether (DPE) was dried over CaH_2 under nitrogen and filtered

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via a syringe equipped with a Whatman® type 'B' glass filter prior to use. All reactions were performed under dry nitrogen.

Grignard Metathesis Chain-Growth Polymerization (GRIM) Procedure (PToT, POPT, POPOT)

In a three-necked round bottomed flask, monomer was dissolved in dry DPE. Isopropylmagnesium chloride (iPrMgCl) in THF (2 M) was added and the mixture was stirred at 40 °C for 2 h. Ni(dppp)Cl_2 was added in one portion and the reaction mixture was stirred at 60 °C for an additional 60 h. The polymerization was terminated by the addition of CH_3MgBr in THF (3 M, 0.03 mmol) and stirring for 1 h. Precipitation in methanol yielded crude polymer. This was washed in a Soxhlet apparatus with diethyl ether and recovered with chloroform.

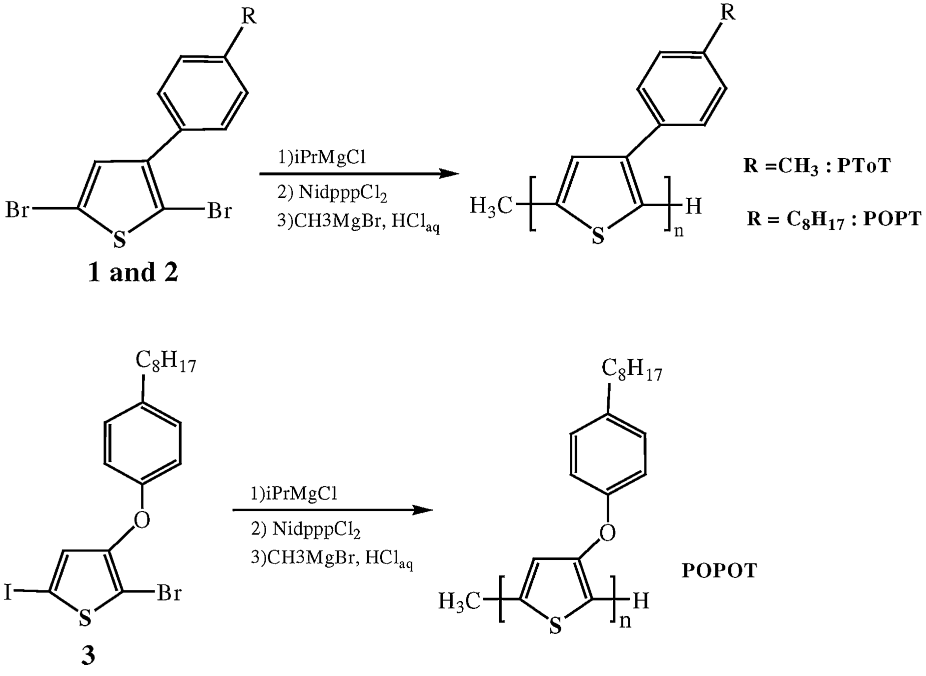
Apparatus

Conditions and apparatus used for gel permeation chromatographic measurements and fabrication of photovoltaic cells have been previously reported.[6] UV-Visible absorption spectra were recorded on a Shimadzu UV-21021PC spectrometer from solutions and spin-coated thin films. Surface morphology of the deposited layers from chlorobenzene on devices without cathode was studied with Atomic Force Microscopy (AFM) using a MultiMode Probe Microscope VEECO operating in the tapping mode.

Results and Discussion

The synthesis of three different polythiophenes substituted by aromatic groups is outlined in Scheme 1.

Poly(3-tolylthiophene) (**PToT**) was synthesized from monomer **1** (2,5-dibromo-3-tolylthiophene) using the GRIM chain-growth method initially reported by Yokoyama *et al.*[7] and McCullough *et al.*[8] The GRIM method was used to produce highly regioregular, head-to-tail (HT)



Scheme 1.
synthesis of homopolymers PToT, POPT and POPOT.

poly(3-alkylthiophene) and with predetermined molecular weights, simply by varying the ratio of metallated monomer to Ni(dppp)Cl_2 in the starting mixture. The synthesis of PToT was carried out in DPE, which has been shown to be an excellent solvent for Grignard based polymerization of phenyl substituted thiophenes.[6] The obtained polymer PToT was, however, insoluble in any common organic solvent. In order to obtain a soluble polythiophene substituted with phenyl groups, poly[3-(4-octylphenylthiophene)](POPT) was prepared using the similar conditions from monomer **2** [2,5-dibromo-3-(4-octylphenyl)thiophene]. The introduction of the octyl chain was efficient in improving the solubility of this polymer compared to PToT. Indeed, the obtained POPT exhibited good solubility in common solvents. The ^1H NMR analysis of POPT (Figure 1) confirms the high degree of regioregularity (94%) and characterization by GPC indicated $M_w = 39\ 000\ g \cdot mol^{-1}$ and Mw/Mn = 1.8 (Table 1).

Table 1.
Molecular weights of polymers (determined by GPC against polystyrene standards) and optical band gaps (determined from the edge of the absorption spectrum).

Polymer	M_w ($g \cdot mol^{-1}$)	M_w/M_n	Eg (eV)
POPT	39000	1.8	1.75
POPOT	9000	1.3	1.70

As presented in Scheme 1, the polythiophene derivative with octylphenoxy side chains poly[3-(4-octylphenoxylthiophene)](POPOT) was synthesized from the monomer **3** (2-bromo-5-iodo-3-(4-octylphenoxy)thiophene) *via* the GRIM method and with the same conditions reported for PToT. The obtained polymer presented a low molecular weight ($Mw = 9\,000\ g \cdot mol^{-1}$, $M_w/M_n = 1.3$). The ^1H NMR spectrum of POPOT (Figure 1) confirmed the high degree of regioregularity of

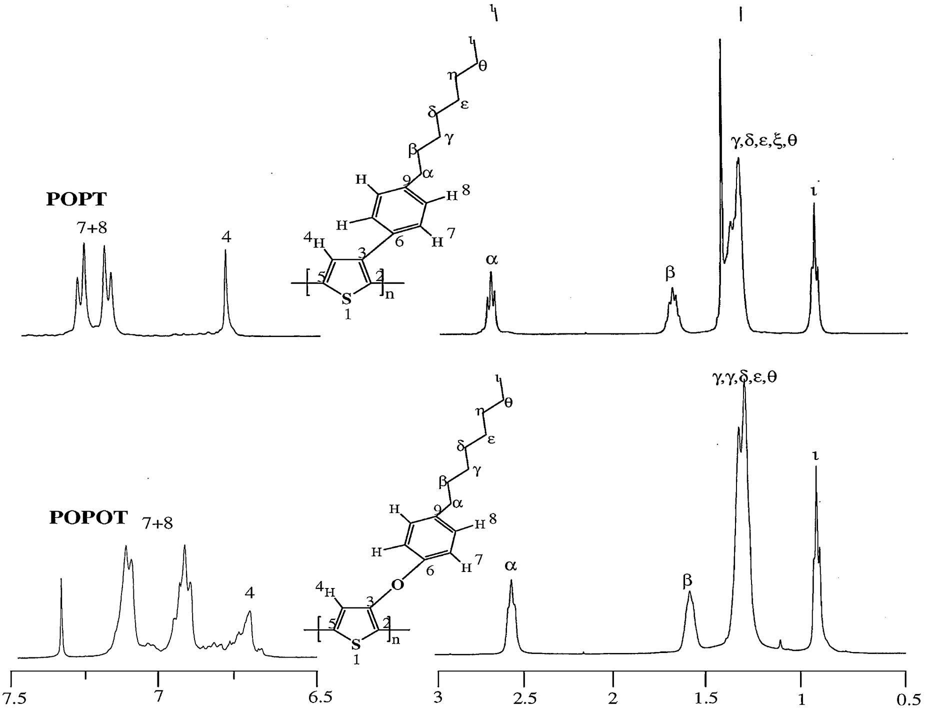


Figure 1.
^1H NMR spectra of POPT (in CD_2Cl_4) and POPOT (in $CDCl_3$:CS_2).

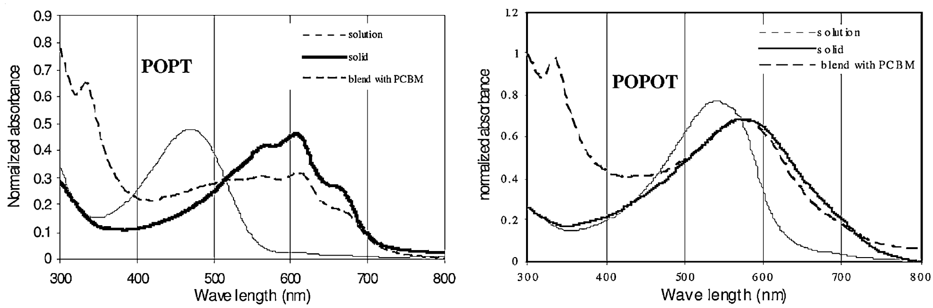


Figure 2.
UV-visible absorption spectra of the samples in chloroform solution, in thin solid films and blended with PCBM (spin coated films).

POPOT (95%). POPOT exhibited poor solubility in solvents such as chloroform and chlorobenzene.

The UV-visible absorption spectra of polymers in chloroform solution, in the solid state (spin-coated films) and blends with PCBM as spin-coated films are presented in Figure 2. The maximum absorption obtained with POPT in solution at 470 nm is red-shifted to 606 nm in the solid state with a vibronic fine-structure. This can indicate that the confinement of the polymer chains in the condensed phase is anticipated to support a coplanar arrangement of the adjacent thiophene rings and to enhance the delocalisation of π-electrons between phenyl groups and polythiophene backbone, which results in a red-shift in the absorption maximum with respect to POPT in solution.

The obtained spectrum of POPT-*blend*-PCBM showed a slight increase in the λ_{max} (approximately 6 nm) compared to that of POPT alone. In solution, POPOT showed a maximum band absorption at 540 nm red shifted by about 70 nm with respect to that of POPT in solution. This red shift may be due to the strong electron-donating of octylphenoxy side chains on thiophene rings. In the solid state, the λ_{max} of POPOT is red shifted to 580 nm corresponding to a shift of 40 nm. The maximum band absorption of the thin solid film of POPOT-*blend*-PCBM is slightly blue-shifted by 5 nm comparatively to the λ_{max} of the POPOT without PCBM. The optical band gap (E_g) of polymers was determined from the formula $Eg = 1240/\lambda_{edge}$ (λ_{edge} is the onset value of absorption spectrum in long wave direction) (Table 1). The POPOT and POPT present a lower band gap, at around 1.7 eV, which is slightly lower than that obtained with P3HT (1.9 eV).[9]

Bulk heterojunction solar cells based on POPT or POPOT blended with PCBM were fabricated with a structure ITO/ PEDOT:PSS/ Polymer:PCBM (1:1)/LiF/ Al. Table 2 reports the photovoltaic characteristics obtained before and after heat treatment.

The device based on POPT without heat treatment exhibited a promising photovoltaic performance with $V_{oc} = 0.61$ V, $J_{sc} = 4.71$ mA · cm^{-2}, FF = 44% and $\eta = 1.29\%$. After thermal annealing at 100 °C for 5 min, a slight increase of J_{sc} and FF was obtained yielding to an increase of power conversion efficiency to 1.43%, in spite of a voltage decrease to 0.56 V. This enhancement of

Table 2.
Photovoltaic properties of the polymers blended with PCBM (1:1 by weight).

Polymer	POPT		POPOT	
Temperature (°C)	25	100	25	100
Voc (V)	0.61	0.63	0.35	0.19
Jsc (mA · cm^{-2})	4.71	5.7	0.34	0.59
FF (%)	44	43	26	27
η (%)	1.29	1.56	0.03	0.025

Voc: open circuit voltage; Jsc: short circuit current density; FF: fill factor; η: power conversion efficiency.

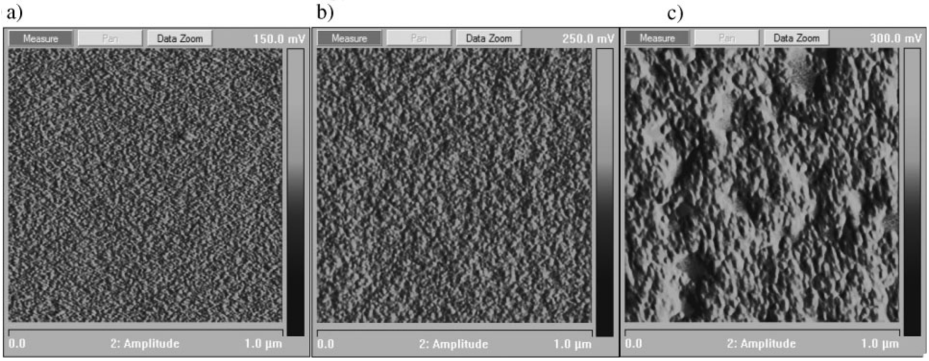


Figure 3.
Amplitude AFM images of blends of POPT with PCBM (1:1 weight) (a) before and (b) after annealing at 90 °C for 5 min; (c) blend of POPOT with PCBM without annealing.

the photovoltaic performance with annealing is not as high as that usually observed with devices based on P3HT.[6] In spite of the large red-shift of the absorption band of the POPT, the low value of the current density limits its overall performance compared to the those of P3HT. This low value of Jsc even after heating can be explained by the poor phase separation between the POPT and PCBM as shown in AFM images (Figure 3 (a) and (b)).

The device built around POPOT-*blend*-PCBM exhibited a $V_{oc} = 0.35$ V, $J_{sc} = 0.34$ $mA \cdot cm^{-2}$, FF = 26% and a power conversion efficiency of 0.03%. This poor photovoltaic performance can be explained by the inhomogeneous film forming during spin coating of the blend solubilised in chlorobenzene as observed in the AFM image (Figure 3 (c)). This could due to a limited solubility of the POPOT in chlorobenzene. Moreover, the thermal annealing at 100 °C had a little effect on the power conversion efficiency of this latter device.

Summary

Both phenyl and phenoxy substituted polythiophenes with high degrees of regioregularity have been synthesised and their optical and photovoltaic properties have been investigated. It was found that the introduction of phenyl or phenoxy groups on polythiophene yielded to a red-shift in absorption and thus optical band gaps around 1.7 eV were obtained. Promising power conversion efficiencies were obtained with cells based on POPT whereas poor photovoltaic performances were observed with POPOT. For POPT, in spite of improvement in absorption, the photovoltaic results are probably limited by a too high dispersion of the two components within the photoactive layer, as shown by the morphology obtained. For phenoxy substituted polythiophene, POPOT, no vibronic fine-structure was observed in absorption spectra, indicating the poor organisation of the polymer in the solid state. Moreover, the morphology study of the blend showed a very bad film-forming during spin-coating explaining the very low power conversion efficiency. Based on these results, conditions of deposition must be optimised to increase photovoltaic performances.

Acknowledgements: The authors thank the French National Agency of Research (ANR) through the project NANORGYSOL and the Conseil Régional d'Aquitaine for the funding of this work.

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