E-MRS Spring Meeting 2011, Symposium S: Organic Photovoltaics: Science and Technology

Alkoxy side chains in low band-gap co-polymers: impact on conjugation and frontier energy levels.

P. Lévêque[a*], L. Biniek[b], S. Fall[a], C.L. Chocos[b], N. Leclerc[b] and T. Heiser[a]

[a]Institut d'Electronique du Solide et des Systèmes, Laboratoire Commun UdS-CNRS, UMR 7163, 23 rue du Loess, 67037 Strasbourg, France
[b]Laboratoire d'Ingénierie des Polymères pour les Hautes Technologies, Université de Strasbourg, Ecole Européenne de Chimie, Polymères et Matériaux, 25 rue Becquerel, 67087 Strasbourg, France

Abstract

The molecular design of electron donor conjugated polymers with accurate optoelectronic properties for efficient bulk heterojunction photovoltaic devices has attracted a lot of attention worldwide. Ideally, the polymer should have i) appropriate photon harvesting properties, ii) frontier orbitals that allow both, efficient exciton dissociation and a high open circuit voltage, iii) high charge carrier mobilities, iv) high solubility and v) high molecular weights. Charge transfer D/A copolymers are promising materials that have allowed significant progress in this field. However, although a lot of attention has been given to the design of their molecular conjugated backbone, only few investigations have considered the influence of their solubilizing side chains. The aim of the present work is to show how the nature and the position of side chains may influence above mentioned polymer properties. For that purpose, our team has designed and characterized a series of donor-acceptor alternating conjugated polymers using 2,1,3-benzothiadiazole as electron-deficient unit, and thieno[3,2-b]thiophene as well as thiophenes moieties as electron-rich units. Various side-chains were introduced onto different positions along the same conjugated backbone and the molecular structure/polymer properties relationships have been investigated systematically.

Keywords: Electron donor low band-gap co-polymers; photovoltaic devices; side chains

---

* Corresponding author. *E-mail address*: patrick.leveque@iness.c-strasbourg.fr

1. Introduction

Bulk heterojunction (BHJ) solar cells appear like a very promising alternative to conventional inorganic photovoltaic devices. Indeed, continuously increasing efficiencies have been reported for BHJ solar cells [1] and the 10 % efficiency estimated as a reasonable boundary for this type of cell seems more than ever reachable [2]. The efficient active layers for BHJ solar cells are a blend of an electron donor polymer and an electron acceptor small molecule like [6,6]-C61-butyric acid methyl ester ($PC_{60}BM$). The general rules to obtain a good candidate for the electron donor polymer are well established. The polymer should have a low energy band-gap to present good photon harvesting properties (typically 1.5 eV [3]), an energy difference between the HOMO and the LUMO of the electron donor and acceptor higher than the exciton binding energy and a maximized energy difference between the LUMO of the acceptor and the HOMO of the donor to obtain high open circuit voltage devices [2]. Moreover, the polymer should be soluble in common organic solvents to reach a high molecular weight, and should possess good processability and charge carrier mobility of the order of $10^{-3} cm^2/Vs$. In general, the synthesis strategy focuses mainly on the energy level positioning for instance by the alternation of electron rich and electron deficient units. The alkyl side chains that are necessary for the polymer solubility are often seen as an independent problem. In this work we will show that the alkyl chain type and position has a strong impact on the energy level positions and therefore that the synthesis strategy should include the backbone design but also the side chains type and position along the backbone. For this purpose, different polymers were synthesized with the same backbone, comparable molecular weights but different alkyl chain type and position. The frontier energy level positions were measured by cyclic voltammetry in solid state and the optical gap was estimated from the absorption spectrum in thin films. DFT calculations have been performed to estimate the influence of the side chains on the molecular conformation. The charge carrier mobility was extracted from transfer characteristics of organic field effect transistors. Finally, BHJ solar cells using the different donor polymers blended with $PC_{60}BM$ were elaborated and characterized. These experimental and theoretical results will be discussed to draw a general synthesis strategy for efficient electron donor polymers.

2. Results and Discussion

2.1. Experimental details

The synthesis description for most of the studied copolymers can be found elsewhere [4]. The different copolymers structures are represented in Figure 1 with equivalent backbones but different alkyl chains: linear dodecyl side chains (C12), branched 2-ethyl-hexyl side chains (CEH) and 2-ethyl-hexyloxy side chains (OEH). For sake of simplicity, we chose a non-conventional nomenclature for the side chain position as α and β when the chains are attached to the third or fourth position of the thiophene, respectively. In the following, the copolymers will be only designed by their chain nature and position as depicted in Figure 1.

UV-visible absorption spectroscopy measurements were done using a Shimadzu UV-2101 spectrophotometer. The absorption spectra were measured on polymer thin films spin-coated on glass substrates. Cyclic voltammetry analyses were carried out with a BioLogic VSP potentiostat using platinum electrodes at a scan rate of 20 mV/s. The measurements were performed on polymer thin film drop-casted from *o*-DCB solutions onto a platinum working electrode. A Pt wire was used as counter electrode and Ag/Ag^+ as reference electrode in a 0.1 $mol.L^{-1}$ solution of tetrabutylammonium perchlorate in acetonitrile. Ferrocene was used as internal standard to convert the values obtained with Ag/Ag^+ reference to the saturated calomel electrode scale.

In order to anticipate the influence of the alkyl side chain positioning on the copolymer optoelectronic properties, density functional theory at the B3LYP/6-311+G* level of theory in vacuum (using Spartan 10 [5]) was utilized to model the structural and electronic properties of relevant molecular structures. In particular, the HOMO and LUMO level positions and related electron distributions were calculated. To keep the computational time within a reasonable range, the alkyl chains were replaced by shorter chains. It is thereby assumed that the electronic coupling between alkyl chains and the π-electron system is negligible. CH_3 groups were placed at both ends and the dihedral angle between the last carbon atom and the methyl group was kept fixed in order to mimic the rigidity of the actual polymer.

Bottom contact field-effect transistors (FETs) were elaborated on commercially available pre-patterned test structures whose source and drain contacts were composed of 30 nm thick gold and 10 nm thick Indium Tin Oxide (ITO) bilayers. A 230 nm thick silicon oxide was used as gate dielectric and n-doped $(3 \times 10^{17} \text{ /cm}^3)$ silicon crystal as gate electrode. The channel length and channel width were 20 µm and 10 mm respectively. The test structures were cleaned in acetone and isopropyl alcohol and subsequently for 15 minutes in an ultra-violet ozone system. Then, hexamethyldisilazane (HMDS) was spin-coated (500 rpm for 5 s and then 4000 rpm for 50 s) under nitrogen ambient and followed by an annealing step at 130°C for 5 minutes. Finally, 4 mg/ml anhydrous *o*-DCB polymer solutions were spin-coated (1250 rpm for 60s and 2000 rpm for 120s) to complete the FET devices. The samples were then left overnight under vacuum ($<10^{-6}$ mbar) to remove residual solvent traces. Both, the FET elaboration and characterizations were performed in nitrogen ambient.

Bulk heterojunction devices were elaborated using the studied copolymers as electron donor and $PC_{60}BM$ as electron acceptor. The standard device structure was the following: ITO/PEDOT:PSS(~40 nm)/polymer:$PC_{60}BM$(~100 nm)/Al(~120 nm). Indium Tin Oxide coated glass with a surface resistance lower than 20 Ω/sq was used as transparent substrate. ITO was cleaned sequentially by ultrasonic treatments in acetone, isopropyl alcohol, and deionized water. After an additional cleaning for 30 minutes under ultra-violet generated ozone, a highly conductive polyethylene dioxythiophene:polystyrene-sulphonate PEDOT:PSS was spin coated (1500 rpm: 40 nm) from an aqueous solution and dried for 30 minutes at 120°C under vacuum before being transferred to the nitrogen filled glove box. The dichlorobenzene polymer:$PC_{60}BM$ solutions were stirred at 70°C for 48 hours before spin-coating. The solution had a total concentration of 40 mg/ml with a polymer:fullerene weight fraction ranging from 1:1 to 1:4. Finally, a 120 nm thick aluminum layer was thermally evaporated and used as cathode. The device active area was 9 mm^2, while each sample included four independent diodes. Current density versus Voltage (J-V) characteristics were measured under darkness and under AM1.5 (100 mW/cm^2) illumination using an Oriel 150 W solar simulator.
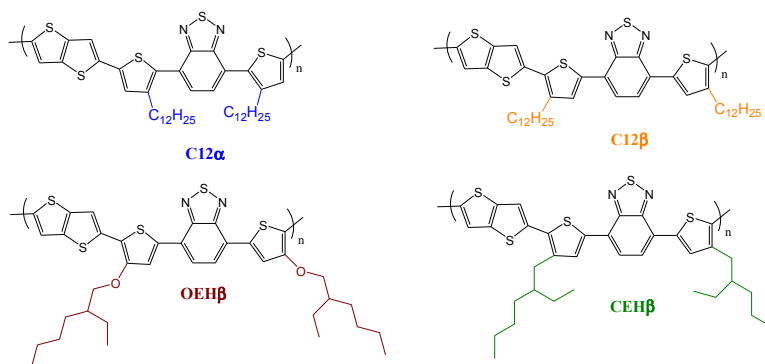

Fig. 1. Chemical structure of the different studied polymers.

2.2. Experimental results

The normalized absorption spectra for all copolymers measured on spin-coated thin films are reported in Figure 2. They all present two absorption bands as commonly observed on copolymers based on the alternation of donor and acceptor moieties. For all copolymers, the low energy absorption bands are red shifted when going from solution (not presented here) to solid state. This behaviour is expected when π-stacking interactions are enhanced in the solid state. The energy band gap as deduced from the onset of the solid-state absorption spectrum is also presented in Fig. 2.
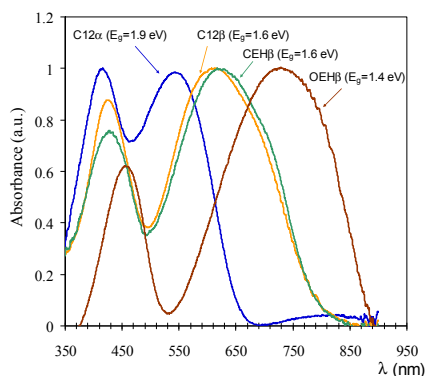

Fig. 2. Absorption spectra in solid state for all the studied polymers.

As seen in Fig. 2, the position of the alkyl side chains has a significant impact on the absorption properties of the polymer (C12α and C12β). On the other hand, the impact of the alkyl side nature on the absorption spectra is limited (C12β and CEHβ), except for the hexyloxy side chain copolymer that has a much smaller energy band gap (1.4 eV) than the other polymer studied. This energy band gap of 1.4 eV is well adjusted for the polymer photon harvesting properties.

The HOMO levels as deduced from cyclic voltammetry measurements and the LUMO levels as deduced from the optical gap (Fig. 2) are summarized in Fig. 3. We chose to present the deduced LUMO levels as they are more representative than the cyclic voltammetry LUMO levels for photovoltaic properties.
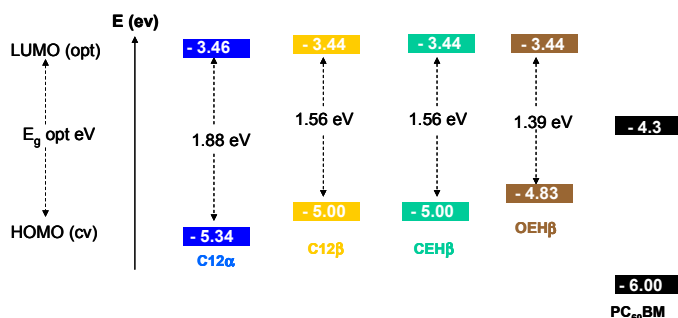

Fig. 3. HOMO levels measured by cyclic voltammetry and LUMO levels as deduced from the measured optical energy band gap. The PC$_{60}$BM levels are taken from Ref. 2.

As seen in Fig. 3, while the LUMO levels are rather unaffected by the nature and the position of the alkyl side chains, the HOMO levels differ substantially from the α to the β position (C12α and C12β) and the hexyloxy side chain induces a strong reduction of the copolymer ionization potential. The OEHβ copolymer anticipated as a good candidate for photon harvesting properties appears as a poor candidate for photovoltaic applications. Indeed, the open circuit voltage (V_{oc}) estimated from the energy difference between the $PC_{60}BM$ LUMO and the copolymer HOMO minus 0.3 V (empirical value from Ref. 2) should be as small as 0.23 V.

Simulations were carried out using DFT on copolymers with the structure depicted in Figure 4. From these calculations, the dihedral angles (Table 1) and the HOMO and LUMO levels (Figure 5) were deduced. Note that using this simple structure, C12β and CEHβ copolymers are equivalent.
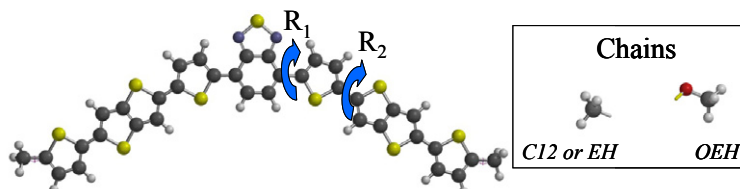

Fig. 4. Chemical structure of the copolymer used in the simulations

As seen in Table 1, the alkyl chains in α position induces a strong torsion between the 2,1,3-benzothiadiazole and the thiophene moieties. On the other hand, the influence of the chain position on R_2 is rather limited. This dihedral angle between the thieno[3,2-*b*]thiophene and the thiophene moieties is sensitive to the presence of hexyloxy side chains. This observation is consistent with the fact that, as reported in polythiophenes, the alkyl group exhibits bigger steric hindrance to the adjacent units than the alkoxy group [6].

Table 1. Calculated dihedral angles.

Copolymer Name	R_1 (°)	R_2 (°)
C12α	45-48	14-15
C12β	1-2	16-18
CEHβ	1-2	16-18
OEHβ	1-2	0-1

We performed calculations on a structure similar to CEHβ but with the dihedral angles found as the equilibrium position for OEHβ in order to check the influence of the lowering of R_2 on the calculated HOMO and LUMO values. It turned out that the low value of R_2 found for OEHβ has no influence on the calculated HOMO and LUMO values.

The general trend observed in Fig. 3 is well reproduced using DFT calculations (Fig. 5) even if the absolute values are wrong due to the limited amount of aromatic cycles taken into account. The strong value of R_1 in the case of C12α influences the HOMO and LUMO values with a reduction of the energy band gap from C12α to C12β and CEHβ. On the other hand, the presence of hexyloxy side chains

reduces the copolymer ionization potential as already observed on other polymers [7] due to the strong electron-donating effect of the alkoxy groups.

Hole mobility was extracted from FET measurements (bottom contact) in the saturation regime using post-elaboration annealing conditions similar to the one optimized for photovoltaic measurements. The values are reported in Table 2.
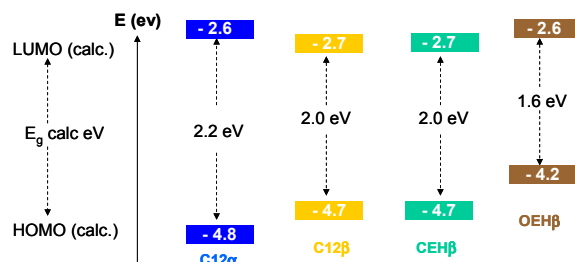

Fig. 5. HOMO and LUMO levels as calculated using DFT.

Table 2. Measured hole mobility.

Copolymer Name	Annealing conditions	μ_h (cm^2/Vs)
C12α	pristine	5×10^{-4}
C12β	150°C, 15 minutes	1×10^{-5}
CEHβ	130°C, 15 minutes	2×10^{-4}
OEHβ	pristine	6×10^{-4}

Except for C12β, the measured hole mobilities are within the acceptable range for moderately efficient photovoltaic devices. The low hole mobility for C12β remains rather unclear and further structural studies are necessary to understand this behavior.

Photovoltaic devices were elaborated and characterized using the four copolymers blended with PC$_{60}$BM. The optimum post elaboration thermal annealing conditions are similar to the one depicted in Table 2. According to Scharber et. al. [2], the open circuit voltage (V_{oc}) can be estimated using equation (1) where the LUMO energy of the acceptor is taken as equal to -4.3 eV:

$$V_{oc} \approx \frac{1}{e}\left[\left|E_{HOMO}^{donor}\right| - \left|E_{LUMO}^{acceptor}\right|\right] - 0.3 \quad V \tag{1}$$

As seen in Fig. 6(a), the measured open circuit voltages are in good agreement with the estimated ones from [2] (equation (1)) using the measured electron donor HOMO values. The power conversion efficiency (PCE) for OEHβ was too low to be plotted in Fig. 6(b) but the measured PCE as a function of the copolymer:PC$_{60}$BM weight ratio are represented on Fig. 6(b) for the other copolymers. It appears clearly that for linear alkyl side chains (C12α and C12β), the PCE increases with the PC$_{60}$BM load while on the other hand, for branched side chains (CEHβ), the PCE is higher for smaller PC$_{60}$BM fractions. A possible explanation is that the steric hindrance induced by bulky side chains lowers the minimal PC$_{60}$BM

needed fraction to induce electron acceptor percolation paths as suggested by McGehee [8]. Further structural studies on copolymer:$PC_{60}BM$ blends are needed to confirm this hypothesis.
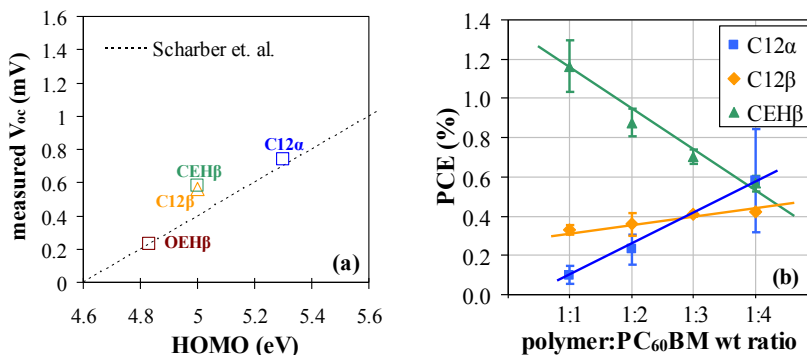

Fig. 6. (a) Measured open circuit voltage (V_{oc}) as a function of the measured donor polymer HOMO. (b) The estimated variation from [2] is the dotted line. Power conversion efficiency (PCE) as a function of the polymer:$PC_{60}BM$ weight ratio.

3. Conclusions

In this work, we synthesized a series of low band-gap copolymers with the same backbone but with different side chain nature and position. The impact of the side chains on the optoelectronic properties of the copolymers is important and a systematic study of these properties allows us to put forward general rules on the side chains design.

The side chains should be placed so that the rotation of the adjacent units is minimized. Otherwise, they hinder an efficient hybridization of the molecular orbital and tends to increase the energy gap in the case of low band gap copolymers based on the alternation of electron rich and electron poor moieties. The impact of such rotation is also expected to play a role in the structural ordering of the copolymer.

In the case of a low density of alkyl side chains, bulky side chains should be preferred rather than linear ones. Otherwise, a large fraction of $PC_{60}BM$ might be necessary for the formation of percolation paths of electron acceptor material.

Alkoxy side chains result in poor photovoltaic performances due to the strong electron-donating effect of the alkoxy groups that reduces the copolymer ionization potential and as a consequence the open circuit voltage.

Acknowledgements

References

[1] Boudreault P.-L.T, Najari A. and Leclerc M. Processable Low-Bandgap Polymers for Photovoltaic Applications. *Chem. Mater.* 2011;**23**:456-469.

[2] Scharber M.C., Mühlbacher D., Koppe M., Denk P., Waldauf C., Heeger A.J., Brabec C.J. Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10% Energy-Conversion Efficiency. *Adv. Mater.* 2006;**18**:789-794

[3] Shockley W., Queisser H.J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.*, 1961;**32**:510-9

[4] Binek L., Chochos C.L., Leclerc N., Hadziioannou G., Kallitsis, J.K., Bechara R. et al. A [3,2-b]thienotiophene-alt-benzothiadiazole copolymer for photovoltaic applications: design, synthesis, material characterization and device performances. *J. Mater. Chem.*, 2009;**19**:4946-4951. Binek L., Chochos C.L., Hadziioannou G., Leclerc N., Lévêque P., Heiser T. Electronic properties and photovoltaic performances of a series of oligothiophene copolymers incorporating both thieno[3,2-b]thiophene and 2,1,3-benzothiadiazole moieties. *Macromol. Rapid Commun.*, 2010;**31**:651-6. Biniek L., Fall S., Chochos, C.L., Anokhin D.V., Ivanov D.A., Leclerc N. et al. Impact of the alkyl side chains on the optoelectronic properties of a series of photovoltaic low-band-gap copolymers. *Macromolecules*, 2010;**43**:9779-9786.

[5] See www.wavefun.com.

[6] Somanathan N., Radhakrishnan S., Optical properties of functionalized polythiophenes. *Int. J. Mod. Phys. B*, 2005;**19**:4645-4676.

[7] Hou J., Chen H.Y., Zhang S., Yang Y. Synthesis and Photovoltaic Properties of Two Benzo[1,2-b:3,4-b′]dithiophene-Based Conjugated Polymers. *J. Phys. Chem. C*, 2009;**113**:21202–21207.

[8] Mayer A.C., Toney M.F., Scully S.R., Rivnay J., Brabec C.J., Scharber M., et al. Bimolecular Crystals of Fullerenes in Conjugated Polymers and the Implications of Molecular Mixing for Solar Cells. *Adv. Funct. Mater.*, 2009;**19**:1173–1179.