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Soluble Low Band Gap Polymers for Solar Cell Applications *via* Oxidative Polymerization.

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INTRODUCTION

Interpenetrating networks of conjugated polymers and derivatives of buckminsterfullerene (C₆₀) are receiving increasing attention in the field of thin film organic solar cells.^{1,2} In these devices an ultra fast photoinduced charge transfer takes place between the conjugated polymer as donor and the fullerene as acceptor. A large interfacial area between the donor and the acceptor in the active layer is required since the exciton diffusion length in polymers is only nanometers long and the charge transfer takes place at the donor-acceptor interface. In the second step the charges are transported to and collected at the electrodes. Since one of the limiting parameters for photovoltaic energy conversion is the mismatch of the absorption spectrum of the active layer and the solar emission, the optical band gap of the polymer used is of crucial importance for increasing the efficiency. Polymers with band gaps above 2 eV only absorb in the ultraviolet (UV) and green part of the visible range. Radiation at longer wavelengths (> 600 nm) passes through the solar cell and makes little contribution to the photocurrent. Therefore the design of new materials that absorb at higher wavelengths, e.g. low band gap polymers, is an ongoing issue for synthetic chemists.^{3,4}

Among the approaches towards low band gap polymers, the donor-acceptor route has received significant attention.⁵ The central concept forming the basis of this route is that the interaction between alternating electron rich donors and electron deficient acceptors will result in a compressed band gap. Furthermore, by changing the substituents of the polymer, the band gap can be fine-tuned. Various literature reports^{6,7} exist in which this route is used to electrosynthesize low band gap polymers containing cyanovinylene spacer (acceptor) units between two thiophene (donor) derivatives with reported band gaps ranging from 1.1 to 1.6 eV. However, for photovoltaic devices soluble low band gap polymers are needed since the conjugated polymer must be blended with a complementary acceptor to achieve a bulk heterojunction. One possibility to overcome this problem is using a precursor route towards low band gap polymers.⁸ Another method is the introduction of long flexible side chains as shown here.

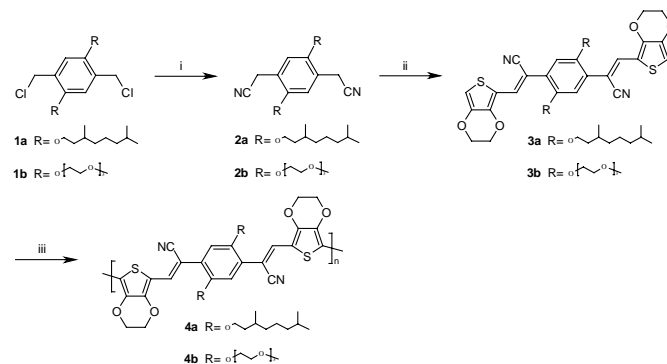
In this work, two soluble low band gap conjugated polymers are presented, which both have a *bis*-(1-cyano-2-(3,4-ethylenedioxythienyl)-vinylene)phenylene base structure. The polymers were synthesized *via* oxidative polymerization with FeCl₃. Solubility was introduced by incorporation of long alkoxy or oligo(oxyethylene) side chains. The electronic properties of the polymers were determined by means of UV-Vis absorption spectroscopy and cyclic voltammetry. Preliminary solar cell results are also reported here.

EXPERIMENTAL

Monomer Synthesis. The monomers were synthesized according to an earlier reported procedure.⁴ The cyanovinylene linkage is introduced using the well-known *Knoevenagel* condensation of 3,4-ethylenedioxy-2-thienylaldehyde with an aromatic acetonitrile moiety (**2a** and **2b**) in refluxing methanol containing potassium *t*-butoxide (Scheme 1). Compounds **2a** and **2b** are obtained *via* nucleophilic substitution of their corresponding chlorides (**1a** and **1b**) with sodium cyanide in DMF.

The overall yields from the starting compounds towards **3a** and **3b** is 50% and 60%, respectively.

Polymerization. Polymerization of compounds **3a** and **3b** to the corresponding conjugated polymers **4a** and **4b** is done *via* chemical oxidation of the monomers using anhydrous FeCl₃ in chloroform according to an adapted literature procedure (Scheme 1).⁹ The polymerization is carried out for 24h at 25°C. The soluble fraction is collected, purified and characterized.



Scheme 1. Synthetic route towards the synthesis of the monomers **3a** and **3b** and polymers **4a** and **4b**. i: NaCN, DMF; ii: 3,4-ethylenedioxy-2-thienylaldehyde, NaOtBu, MeOH; iii: FeCl₃, CHCl₃.

RESULTS AND DISCUSSION

Synthesis. The polymerization reaction proceeds with the formation of an initial dark-blue color and a subsequent black precipitate. After the polymerization, the polymers contain residual iron(III)salts which can be reduced in concentration by rigorous purification. Subsequent precipitation in MeOH and MeOH/Hydrazine not only removes residual FeCl₃, it also dedopes the polymers. Further traces of iron(III)salts are removed by Soxhlet extraction with methanol. During this step also unreacted monomer is being removed. Further extraction with acetone removes oligomeric and low molecular weight fractions from the polymer. The soluble fraction was eventually collected by extraction with chloroform.

Polymerization results are shown in Table 1. The weight-average molecular weights (M_w) of the polymers have been determined by analytical SEC in THF (**4a**) and DMF (**4b**) using polystyrene standards. The reported overall yields (Y1) were determined after extraction with acetone and the soluble polymer yield (Y2) indicates the soluble fraction of the polymer in chloroform. From these results it is evident that polymerization of **3a** with alkoxy side chains gives rise to a high molecular weight polymer, this in contrast to **3b** which under the same conditions only results in low molecular weight and oligomeric material. However one must be careful when interpreting these data. In view of the differences in solubility, molecular weights of both polymers were measured in different solvents. Hence, a straightforward comparison is impossible. Notwithstanding, these observed molecular weights suggest that the introduction of the more flexible oligo(oxyethylene) side chains makes the monomer significantly less reactive. This may be the result of a difference in steric hindrance or solvation/aggregation effects.

Table 1. Polymerization Results

| Polymer | M _w (x 10 ⁻³) | M _n (x 10 ⁻³) | PD | Y1 (%) | Y2 (%) |
|-----------|--------------------------------------|--------------------------------------|-----|--------|--------|
| 4a | 79 | 46 | 1.7 | 56 | 20 |
| 4b | 16 | 9 | 1.7 | 61 | 50 |

Electronic properties. All spectroscopic properties were measured both as thin films on quartz substrates and in chloroform solution (Figure 1). UV-Vis absorption spectroscopy shows that the absorption maximum of **4a** in a thin film ($\lambda_{\text{max}} = 630$ nm) exhibits a 60 nm red shift as compared to **4b** ($\lambda_{\text{max}} = 570$ nm). In solution this difference is only 10 nm ($\lambda_{\text{max}} = 580$ nm for **4a** and $\lambda_{\text{max}} = 570$ nm for **4b**). Another interesting fact is that λ_{max} of **4b** in a thin film is the same as in solution. The reason for this behavior is related to the difference in conformation of the conjugated backbone imparted by the oligo(oxyethylene) side chains, *i.e.* the planarity of the conjugated backbone is modified. The high energy shoulder, seen for **4a** in film ($\lambda_{\text{max}} = 720$ nm) and the absence thereof for **4b** provides further evidence of strong π stacking interactions for the former polymer and more disorder for the latter. Apparently the flexible oligo(oxyethylene) side chains prevent **4b** from closely packing in a thin film. The band gap as derived from UV-Vis spectroscopy is 1.6 eV.

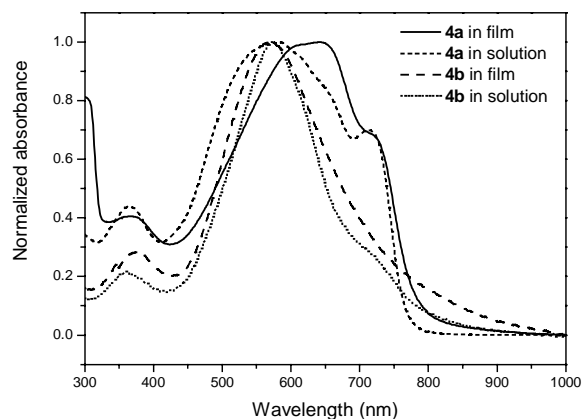


Figure 1. UV-Vis spectra of **4a** and **4b** measured both in a thin film and in solution (solvent CHCl_3).

An estimation of the relative position of HOMO/LUMO levels was determined with cyclic voltammetry (CV). The HOMO/LUMO levels are determined from the onsets of oxidation and reduction, respectively. In the anodic scan, the onset of oxidation of **4a** occurs at 0.10 V vs. Ag/Ag^+ , which corresponds to a HOMO energy level of -5.0 eV. The onset of the reduction is at -1.59 V vs. Ag/Ag^+ and a LUMO energy level of -3.3 eV. Oxidation of **4b** starts at -0.02 V vs. Ag/Ag^+ ; reduction at -1.50 V vs. Ag/Ag^+ . This means a HOMO energy level of -4.9 eV and a LUMO energy level of -3.4 eV.

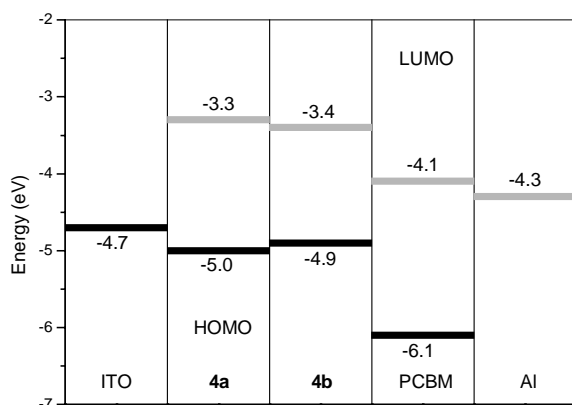


Figure 2. Energy band diagram with HOMO/LUMO levels of **4a**, **4b** and PCBM in relation to the work function of the common electrode materials ITO and Al.

Figure 2 exhibits the resulting energy band diagram in relation to the relative energy levels of the most frequently employed acceptor in organic solar cells, (6,6)-phenyl- C_{61} -butyric-acid (PCBM), and the workfunction of indium tin oxide (ITO) and aluminium (Al), which are usually applied as electrodes in polymer solar cells. The HOMO of the polymers is distinctively higher in energy than that of PCBM. However, not the HOMO energy levels but the relative positions of the donor LUMO and the acceptor LUMO are important for the intended charge transfer. The difference between the LUMO of **4a** and **4b** and PCBM is in the range of 0.5 eV, which is sufficiently high to enable an unrestricted and directed charge transfer.

Solar Cells. A first attempt was made to construct two bulk heterojunction solar cells with either polymer **4a** or **4b** as a donor and PCBM as an acceptor in a 1:2 ratio. The active layer was casted from a chlorobenzene solution on a thin indium tin oxide (ITO) layer on glass, which is covered by a 70 nm spincoated layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulphonic acid) (PEDOT:PSS). As back electrode an Al-layer was evaporated. A thin LiF-layer (0.5 nm) was introduced as an interface between the active layer and the back electrode. Dark and illuminated IV-characteristics were measured under AM1.5 conditions. Preliminary solar cell characteristics for **4a** found under these measurement conditions are: $I_{\text{sc}} = 0.88$ mA/cm^2 , $V_{\text{oc}} = 0.29$ V, FF = 45%, eff = 0.14%. Similar characteristics were found for **4b**: $I_{\text{sc}} = 0.67$ mA/cm^2 , $V_{\text{oc}} = 0.20$ V, FF = 42%, eff = 0.07%.

Additionally charge carrier mobility measurements were carried out in a field effect transistor. However, the observed hole mobility for both polymers was below 10^{-6} cm^2/Vs , which may well be an explanation for the low efficiency. This low mobility possibly originates from residual traces of iron(III)chloride, but may also be a result of the backbone structure in which either the ethylenedioxythiophene (EDOT) units or the cyanovinylene linkers act as trapping sites. Further research is being done to investigate the factors that affect the mobility in these polymers and to ultimately improve the mobility.

CONCLUSION

The synthesis of two low band gap polymers was successfully carried out *via* oxidative polymerization. It was shown that **4a** and **4b** both have a low band gap (1.6 eV) as derived from UV-Vis absorption spectroscopy. However preliminary results indicate that solar cells made of these polymers displayed low efficiencies due to a low charge carrier mobility.

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