



The influence of side chains on solubility and photovoltaic performance of dithiophene–thienopyrazine small band gap copolymers

Arjan P. Zoombelt^{a,b}, Mark A.M. Leenen^a, Marta Fonrodona^{a,b}, Yohann Nicolas^{a,b},
Martijn M. Wienk^a, René A.J. Janssen^{a,*}

^a Molecular Materials and Nanosystems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 18 April 2009

Received in revised form

15 July 2009

Accepted 16 July 2009

Available online 22 July 2009

Keywords:

Polymer synthesis

Polymer composite materials

Photovoltaics

ABSTRACT

Three small band gap copolymers based on alternating dithiophene and thienopyrazine units were synthesized via Yamamoto coupling and applied in bulk heterojunction solar cells as donor together with PCBM ([6,6]-phenyl C₆₁ butyric acid methyl ester) as acceptor. The polymers have an optical band gap of about 1.3 eV in the solid state and only vary by the chemical nature of the solubilizing side chains. The nature of the side chain has a major effect on solubility and processability of the polymer. Using *n*-butoxymethyl side chains a soluble, easy to process polymer was obtained that gave the best photovoltaic performance. With short-circuit currents up to 5.2 mA/cm² an efficiency of 0.8% was achieved under estimated standard solar light conditions (AM1.5G, 100 mW/cm²) with spectral response up to 950 nm.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, many small band gap polymers have been synthesized and applied in bulk heterojunction solar cells [1–11]. The most widely used strategy to obtain small band gap polymers involves the alternation of electron-rich and electron-deficient units along the polymer chain. These *p*-type semiconducting polymers are designed to absorb a large part of the solar spectrum and with *n*-type materials like methanofullerenes (i.e. the [6,6]-phenyl C₆₁ and C₇₁ butyric acid methyl esters; [60]PCBM and [70]PCBM) have already provided solar cells with power conversion efficiencies that approach 6% [7,9,11]. Judicious positioning of the energy levels of the polymer with respect to those of the fullerene acceptor is crucial for the ultimate photovoltaic performance. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the polymer determine the optical band gap and thereby the fraction of solar photons absorbed and the maximum photocurrent. To ensure quantitative electron transfer to the acceptor, it has been suggested that the LUMO of the polymer must be 0.3–0.4 eV above the LUMO of the acceptor [12,13]. However, raising the HOMO and LUMO levels of the polymer with respect to the levels of the acceptor, reduces the open-circuit voltage (V_{oc}) that is governed by the energy difference between the HOMO of the donor and the LUMO of the acceptor

[14,15]. Following these rules, a successful small band gap polymer combines a low lying HOMO for high voltage and a high-lying LUMO level for good electron transfer, and therefore needs a carefully optimized compromise to maintain a small band gap.

When designing polymers for bulk heterojunction solar cells, solubility is an important parameter. Solubilizing side chains are incorporated to allow the synthesis of monomers and high molecular weight polymers. While side chains do not absorb light or transport charges, and do not contribute to the photocurrent, they generally strongly influence the morphology and charge carrier mobility. Bulky substituents may reduce or even prevent three-dimensional ordering of the polymer in the solid state. Generally, replacing linear alkyl side chains by branched chains reduces charge carrier mobility by preventing close packing and crystallinity, and therefore possibly lowers photovoltaic performance [16–20]. It is thus preferred to keep the amount of bulky side chains to minimum, but still ensure adequate solubility to enable obtaining high molecular weight polymers that are beneficial for obtaining efficient solar cells [21,22] and can be solution processed.

Here we report the synthesis and photovoltaic performance of three small band gap copolymers comprising alternating dithiophene and thienopyrazine units (Fig. 1). Incorporation of these units in an alternating fashion results in a reduction of the band gap [1,23–27], and we explore the use of different side chains to tune the solubility and photovoltaic properties. PBOTT contains four linear octyl side chains per repeat unit, while in PBEHTT the two octyl chains on the pyrazine ring are replaced by branched 2-ethyl-

* Corresponding author. Tel.: +31 40 2473597; fax: +31 40 2451036.
E-mail address: r.a.janssen@tue.nl (R.A.J. Janssen).

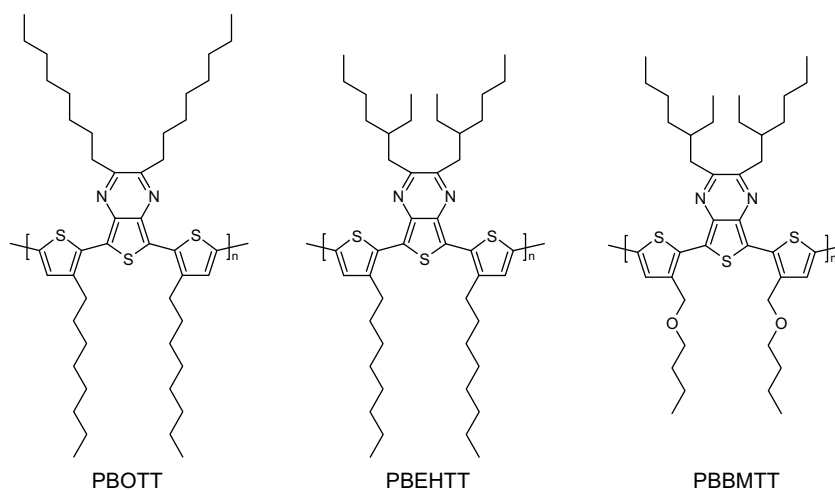


Fig. 1. Structure of PBOTT, PBEHTT and PBBMTT.

hexyl chains to increase solubility. In PBBMTT also the octyl side chains on the thiophene rings are replaced. The *n*-butoxymethyl chains used in PBBMTT are known to substantially enhance solubility and also increase the oxidation potential of the polymer via an inductive effect, that may increase V_{oc} [28,29].

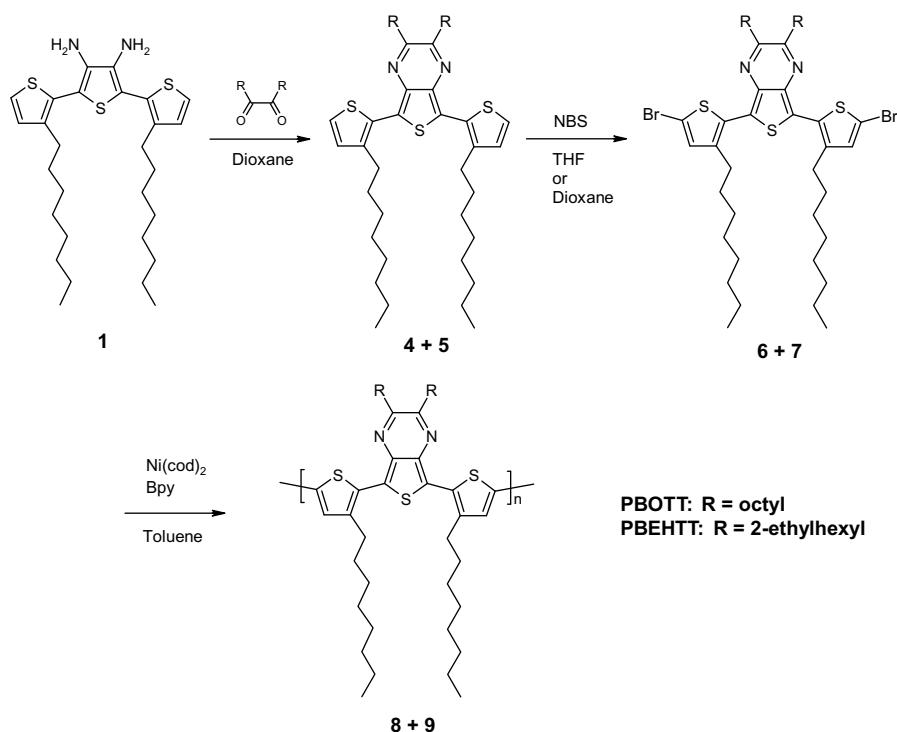
2. Experimental section

The synthetic procedures for preparing monomer and polymers, and their characterization by ^1H and ^{13}C NMR are described in detail in Supporting Information. Molecular weights were determined using size exclusion chromatography in HPLC-grade *o*-dichlorobenzene (ODCB) at 80 °C against polystyrene standards on a Polymer Laboratories-GPC 120 high temperature chromatograph, a PD 2040 high temperature light scattering detector, and

a Midas autosampler. A mixed-C 300 × 7.5 mm column was used, together with a pre-column. The flow rate was 1 ml/min and the injection volume was 100 μl .

UV–vis absorption spectra were measured with a Perkin–Elmer Lambda 900 spectrometer. Cyclic voltammetry (scan rate = 100 mV/s) was performed on an Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell using ODCB containing 0.1 M TBAPF₆ (Fluka) as electrolyte. The working electrode was platinum disk, the counter electrode a silver rod, and the reference electrode Ag/AgCl. Potentials are relative to Fc/Fc⁺ as internal standard.

Photovoltaic devices were made by spin coating PEDOT:PSS (Baytron P, VP Al 4083, HC Starck) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square). The photoactive layer was deposited by spin coating from the appropriate



Scheme 1. Synthetic route towards PBOTT (8) and PBEHTT (9).

Download English Version:

<https://daneshyari.com/en/article/5184680>

Download Persian Version:

<https://daneshyari.com/article/5184680>

[Daneshyari.com](https://daneshyari.com)