Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thin Solid Films 511–512 (2006) 328 – 332

thin solid films

www.elsevier.com/locate/tsf

Comparison of the electrical characteristics of four 2,5-substituted poly(p-phenylene vinylene) derivatives with different side chains

M. Breselge [a,*], I. Van Severen [b], L. Lutsen [a], P. Adriaensens [b],
J. Manca [a,b], D. Vanderzande [a,b], T. Cleij [b]

[a] IMEC, Division IMOMEC, Wetenschapspark 1, 3590 Diepenbeek, Belgium
[b] University Hasselt, Campus Diepenbeek, Agoralaan Bld D B-3590 Diepenbeek Belgium

Abstract

Semiconducting polymer thin film devices were prepared from three novel 2,5-substituted poly(p-phenylene vinylene) (PPV) derivatives and OC_1C_{10}–PPV. The novel PPV-derivatives, namely poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylene vinylene] (PEO-PPV), poly(2,5-bis-(triethoxymethoxy)-1,4-phenylene vinylene) (diPEO-PPV) and poly[2-(n-nonyloxy)-5-(triethoxymethoxy)-1,4-phenylene vinylene] ((PEO–OC_9)–PPV), were obtained through the "sulfinyl precursor route". The electrical properties of the new materials, i.e. permittivity, conductivity, charge carrier mobility, and solar cell parameters, were compared to the results obtained with the well-known OC_1C_{10}–PPV, showing that the introduction of PEO-side chains yielded a systematic increase of the relative permittivity, while the mobility remained unchanged.

Keywords: PPV-derivatives; Electrical characterisation; Bulk heterojunction solar cells

1. Introduction

Organic semiconductors have attracted a lot of interest over the past years. One of the most appealing advantages organic materials offer is the possibility to tailor their properties to suit a given application. In this paper we will discuss the impact of altering the two side groups of 2,5-substituted poly(p-phenylene vinylene) (PPV) on mobility, conductivity and permittivity of the materials. Additionally preliminary results of bulk heterojunction solar cells prepared from these material and PCBM are presented.

2. Synthesis

The various steps (indicated by numbers) of the synthesis of the three novel 2,5-substituted PPV derivatives are illustrated in Fig. 1.

The PPV-derivatives 7a–c were prepared via the sulfinyl precursor route. Whereas 7b and 7c, respectively, carry one or two polar oligo(ethylene oxide) side chains attached to the aromatic ring of a PPV analogue, 7a also carries a long hydrophobic alkyl side chain.

The monomers 5b–c were prepared from the respective 1,4-substituted benzene derivatives (1a–c). Subsequently 1 is chloromethylated using concentrated HCl and formaldehyde in acetic anhydride to give 2. The next steps involve the formation of the bissulfonium salt 3, followed by the reaction of 3 with an equimolar amount of an alkylthiolate anion. The resulting mono-substituted thioether 4 is selectively oxidised to the desired sulfinyl monomer 5. It should be noted that 4a–b and 5a–b are present in a 1/1 mixture of regio-isomers, which is used without further separation. Monomer 5 was polymerised according to the standard procedure as described in [1]. The final step in the PPV synthesis according to the sulfinyl precursor route is the thermal elimination of sulfenic acids in toluene as a result of which the precursor polymer converts into the conjugated structure 7. Yields, GPC results and absorption maximums of polymer 7 are presented in Table 1.

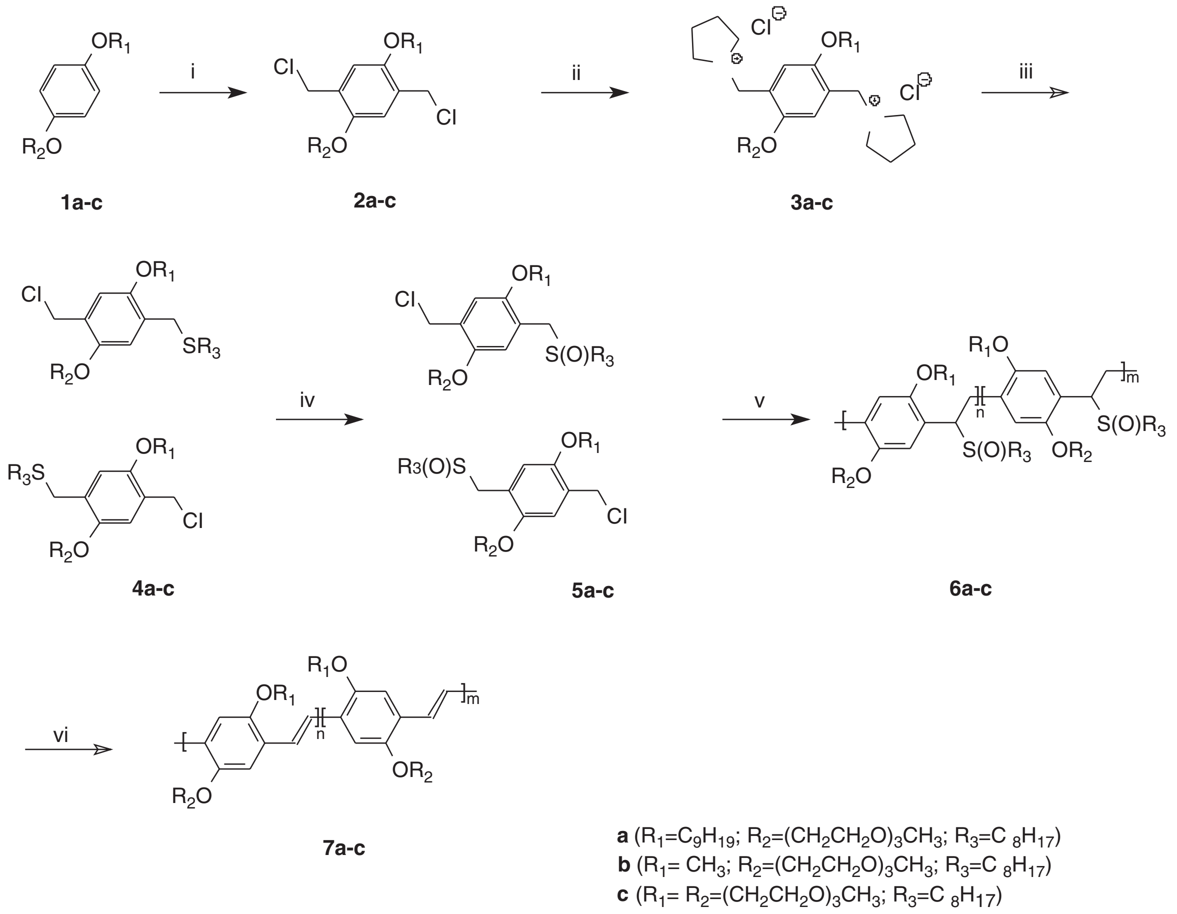
3. Experimental

All samples were prepared and measured in a glove box system in an inert nitrogen atmosphere with less than 1 ppm

---

* Corresponding author. Tel.: +32 11 268842; fax: +32 11 268892.
E-mail address: Martin.Breselge@uhasselt.be (M. Breselge).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.12.036



a (R_1=C_9H_{19}; R_2=$(CH_2CH_2O)_3CH_3$; R_3=C_8H_{17})
b (R_1= CH_3; R_2=$(CH_2CH_2O)_3CH_3$; R_3=C_8H_{17})
c (R_1= R_2=$(CH_2CH_2O)_3CH_3$; R_3=C_8H_{17})

Fig. 1. Synthesis of the sulfinyl monomer and polymers 1–7. (i: *p*-CH_2O, Ac_2O, HCl, 70 °C; ii: THT, MeOH; iii: RSH, Na*t*BuO, MeOH; iv: H_2O_2, TeO_2, HCl_{cat}, 1,4-dioxane; v: Na*t*BuO, 2-BuOH; vi: toluene (reflux)).

oxygen and water. The four considered PPVs were suspended in chlorobenzene and stirred and heated at 50 °C on a hotplate until they were completely dissolved. Films of different thicknesses were than prepared by spin coating. In case of the sandwich structures, used for impedance spectroscopy, an aluminium contact was evaporated.

4. Relative permittivity

The relative permittivity was obtained from spectral impedance measurements of ITO/polymer/aluminium sandwich structures. The samples consisted of a glass substrate with two indium tin oxide (ITO) strips acting as electrodes, a spin coated polymer layer acting as dielectric and four evaporated aluminium contact acting as counter-electrodes (see Fig. 2). The intersections of the metal electrodes and the ITO-strips defined capacitors of different sizes. The four polymers were spin coated with varying film thicknesses to extend the number of different capacitor geometries.

The complex impedance of the samples was measured with a HP4284 LCR-meter by applying a bias voltage of 0.8 V superposed by an oscillating voltage of 25 mV. Assuming the equivalent circuit in Fig. 3, with a capacitance C, a parallel resistance R_p and a serial resistance R_s the capacitance can be determined from the constant region of the susceptance. Plotting the capacitances C against the geometric factor A/d, the relative permittivity ε_r can be extracted from the slope of the graph, following the equation:

$$C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d} \tag{1}$$

where A is the capacitor's size defined by the intersection of an ITO-strip and an aluminium electrode, d is the distance of the two electrodes determined by the thickness of the polymer film and ε_0 is the permittivity of free space.

The results for the four PPV-derivatives are depicted in Fig. 4 and listed in Table 2. The reference material OC_1C_{10}–PPV gives a relative permittivity of ~3. Replacing the –$OC_{10}H_{23}$-side chain (OC_1C_{10}–PPV) by a –$(CH_2CH_2O)_3CH_3$-side chain (PEO-PPV) increases the permittivity by 1 to

Table 1
Overview of yield, molecular weight M_w, polydispersity PD and maximum of the optical absorbance $\lambda_{a,max}$ of the conjugated polymer 7 in a thin film

Polymer	Yield [%]	M_w [g/mol]	PD	$\lambda_{a,max}$ (film) [nm]
OC_1C_{10}–PPV	n. a.	920 000	9.1	480
(PEO–OC_9)-PPV (7a)	63	60 000	3.8	524
PEO-PPV (7b)	59	300 000	3.2	504
diPEO-PPV (7c)	57	650 000	3.1	511