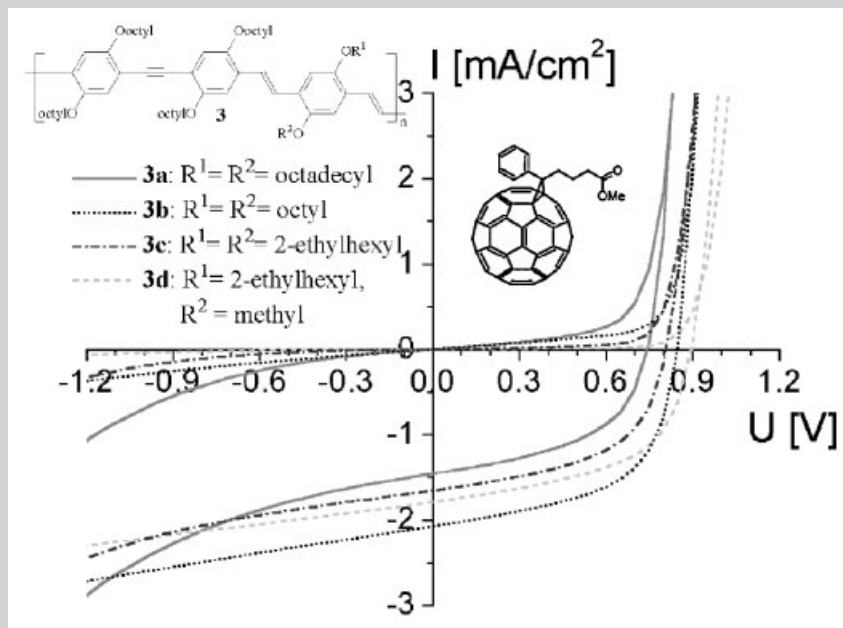


Summary: The electrochemical behaviour of four types of (phenylene ethynylene)-*alt*-(phenylene vinylene) hybrid polymers, **1**, **2**, **3**, and **4** have been investigated with respect to the influence of the grafted alkoxy side chains. In the case of the fully substituted polymers **2**, **3**, and **4**, the strong insulating nature of longer linear octadecyl or bulky branched 2-ethylhexyl side chains lowers the HOMO levels of the polymers thereby increasing the discrepancy, ΔE_g , between

the electrochemical, E_g^{cc} , and the optical, E_g^{opt} , bandgap energies. Thus it is not possible to establish a direct correlation between the open circuit voltage, V_{OC} , of bulk heterojunction solar cell devices of the configuration glass substrate/ITO/PEDOT:PSS/polymer **3**:PCBM(1:3, w/w)/LiF/Al and the HOMO energy levels of polymer **3** solely, as postulated in the literature. The photovoltaic (PV) parameters greatly depend on the grafted side chains.



Linear I - V curves of solar cell devices from polymers **3a-d**, measured in the dark and under $100 \text{ mW} \cdot \text{cm}^{-2}$ solar simulator illumination.

Side Chain Influence on Electrochemical and Photovoltaic Properties of Yne-Containing Poly(phenylene vinylene)s

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Introduction

To enable the solubility of conjugated polymers and their subsequent processability into thin films for various applications, it is useful to attach alkyl and/or alkoxy side chains.^[1,2] The grafted side chains play an essential role in the ordering of molecular self assembly; they also contribute to both the tuning of the optical as well as electronic properties of optoelectronic materials. For example, attaching hexyl side chains in a regioregular manner onto the backbone of poly(thiophene) (i.e., poly(3-hexylthiophene)) has led to a material exhibiting very high charge carrier mobility due to a high degree of intermolecular ordering, making it one of the best materials to date for the design of highly efficient solar cell devices and organic field-effect transistors.^[3,4]

To match the energetic scheme levels in photovoltaic devices, it is necessary to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the donor and acceptor components. Electrochemistry, and especially the combination of cyclic voltammetry (CV) and electrochemical voltage spectroscopy (EVS) has proven to be a powerful tool to this effect.^[5] Note that there is some similarity between the electrochemical processes and the movement of charges in light-emitting diodes and photovoltaic devices.

In this work, the effects of side chains in combination with the conjugation pattern on the electrochemical properties of four types of alkoxy-substituted phenylene ethynylene/phenylene vinylene hybrid polymers **1–4**^[6–8] together with three yne-free poly(phenylene vinylene)

(PPV) derivatives **5**^[7b,8] are presented and discussed (Figure 1). It has been shown that the open circuit voltage of polymer-fullerene bulk heterojunction solar cells depends linearly on the reduction potential of the fullerene used as the acceptor.^[9] Furthermore it has been postulated, as well as demonstrated,^[7a,10] that the open circuit potential is influenced by the donor-polymer HOMO-level. To check whether this applies to our hybrid systems, photovoltaic devices were designed with polymers of type **3**. The choice of the four polymers of type **3**, bearing different side chains at R¹ and R² (Figure 1) is based on two advantageous facts: (1) The polymers exhibit a similar degree of polymerisation of around 7 and polydispersity indexes between 2 and 3,^[6c] allowing a reliable comparison of their properties. (2) Their repeating unit consists of a 1:2 triple bond/double bond ratio which has proven to be more favourable for the intramolecular charge carrier mobility than a 2:2 ratio present in **1**, **2**, and **4**.^[11]

Experimental Part

Materials

The various chemicals were purchased from commercial suppliers (Fluka, Aldrich). The synthesis of the investigated polymers has been reported elsewhere.^[6–8]

Electrochemical Studies

All electrochemical experiments were carried out on dropcast polymer films at room temperature in a glovebox under argon

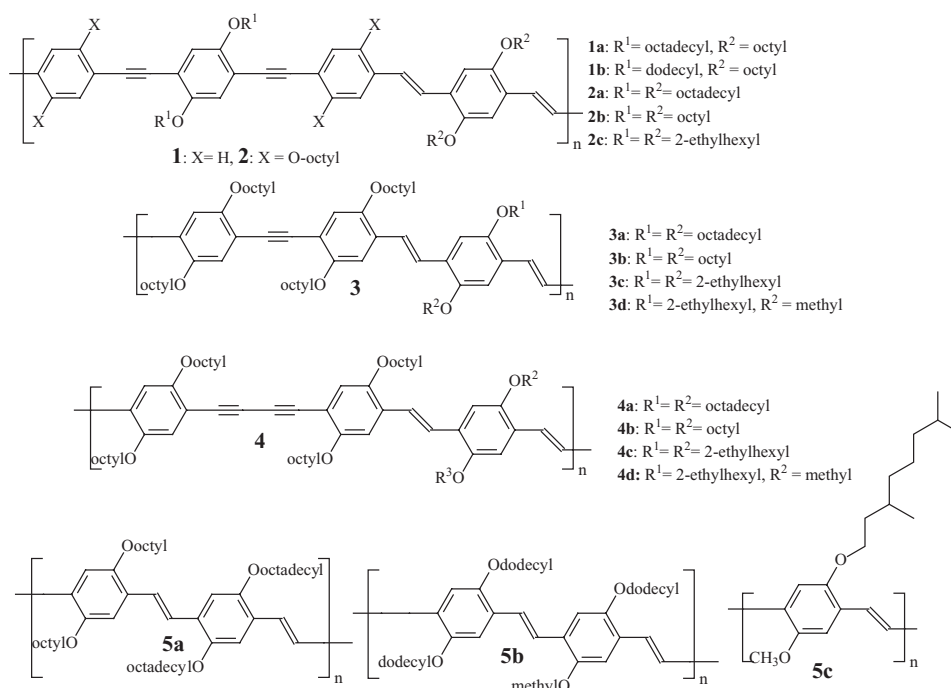


Figure 1. Chemical structures of the studied polymers.

atmosphere using a PC-controlled Jaislle 1002 T-NC potentiostat. The supporting electrolyte was tetrabutylammonium perchlorate (TBAClO₄) (98%, ~0.1 M, Aldrich) in anhydrous acetonitrile (Aldrich). For CV and EVS the working electrode (WE) as well as the counter electrode (CE) were platinum foils.

As a reference electrode (RE), a silver wire coated with AgCl was used. After each measurement the RE was calibrated with ferrocene ($E^0 = 400$ mV vs. a normal hydrogen electrode (NHE)) and the potential axis was corrected to NHE according to the difference of E^0 (ferrocene) and the measured $E^{1/2}$ (ferrocene).

In this work, EVS^[5] was solely used to determine the onset potentials of oxidation and reduction. It was considered that oxidation or reduction started when the initial peak current reached 1 μ A relative to the baseline. The so determined onset potentials were corrected to NHE as described above, and recalculated to eV vs. vacuum level using a value of -4.75 eV for the NHE, which is well supported by photoelectron spectroscopic measurements.^[12]

Experimental Conditions for Solar Cells

Blend solutions of polymers **3a–d** as donor component and the C₆₀-derivative 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C₆₁ (PCBM) as acceptor at a weight ratio of 1:3 were prepared in chloroform at a concentration of 10 mg polymer \cdot mL⁻¹. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron PH, Bayer Germany) was spin-coated on top of indium-tin oxide (ITO) (Merck, Germany) coated glass ($\sim 25 \Omega \cdot \text{cm}^{-2}$), which had been cleaned in an ultrasonic bath with acetone and isopropyl alcohol after etching part of the ITO glass. The active layer (polymer:PCBM blend) was then spin-coated onto the annealed PEDOT:PSS layer (about 80 nm thick). Lithium fluoride (LiF, 6 Å) was first deposited on the blend, and then a 80 nm thick Al electrode was deposited on top of the LiF by thermal evaporation at $\sim 5 \times 10^{-6}$ mbar. All current-voltage (I - V) characteristics of the photovoltaic devices were measured using a Keithley SMU 2400 unit under inert atmosphere (argon) in a dry glove box. A Steuernagel solar simulator under AM 1.5 conditions was used as the excitation source with an input power of 100 mW \cdot cm⁻² white light illumination.

Results and Discussion

Figure 2 illustrates the CV curves of polymers **2a–c** and **3a–d**. The vertical lines show the onset oxidation and reduction values as obtained by EVS. All the polymers show reversible or partially reversible redox behaviour but are not stable to repeated cycling. Table 1 summarizes the electrochemical data as obtained from CV and EVS. For the purpose of comparison, the optical bandgap energies, E_g^{opt} (calculated from $\lambda_{10\% \text{ max}}$, the longer wavelength at which the extinction coefficient has dropped to 10% of the absorption peak value),^[6] are also listed. Several ways to evaluate the HOMO and LUMO energy levels from the onset potentials have been proposed in the literature.^[5,13,14]

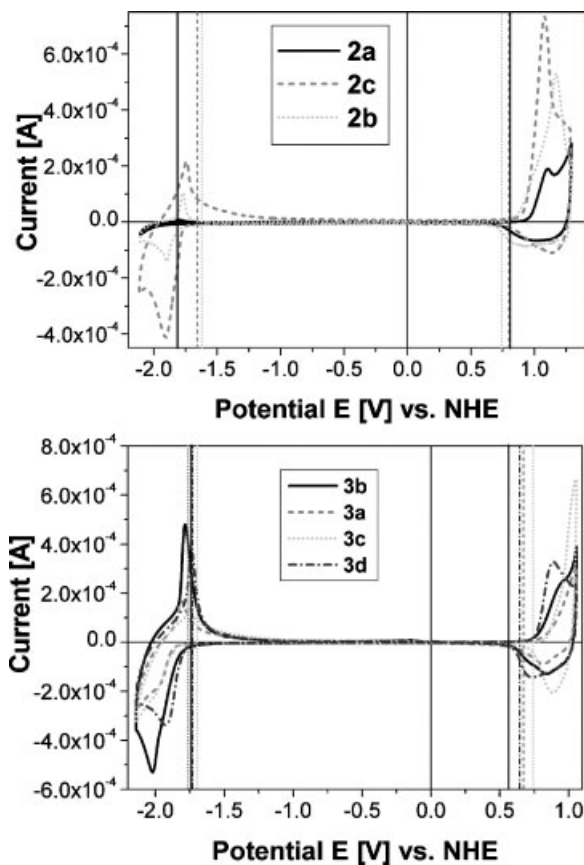


Figure 2. CV curves of polymers **2a–c** (top) and **3a–d** (bottom). The vertical lines show the redox onset values as obtained by EVS.

The evaluation in this work was done according to Equation (1) and (2) after the correction of the onset potentials vs. NHE with ferrocene (see Experimental Part).

$$\text{HOMO} = (-E_{\text{onset}}^{\text{ox}} - 4.75) \text{ eV} \quad (1)$$

$$\text{LUMO} = (-E_{\text{onset}}^{\text{red}} - 4.75) \text{ eV} \quad (2)$$

Higher electrochemical bandgap energies, E_g^{cc} , than the corresponding optical bandgap energies, E_g^{opt} , were obtained. The difference, $\Delta E_g = E_g^{\text{cc}} - E_g^{\text{opt}}$, may be caused by the interface barrier present between the polymer film and the electrode surface. This interface barrier is related to the insulating (or shielding) effects of the side chains.^[15,16] ΔE_g tends to zero in the case of polymers **1**, having alternate phenyl rings with side chains and phenyl rings without side chains. Among the fully substituted polymers **2** and **3**, ΔE_g increases by a factor of more than two, when the side chains length, R¹ and R², increases from octyloxy (in **2b** or **3b**) to octadecyloxy (in **2a** or **3a**). Similarly, an increase of ΔE_g is observed when 2-ethylhexyloxy (in **3c** or **4c**) replaces methyloxy (in **3d** or **4d**) at R². The HOMO levels are consequently lowered in the presence of 2-ethylhexyloxy or octadecyloxy. Moreover, there is an upward shift of the LUMO level of 0.12 eV going from **2b** (octyloxy) to **2a**

Table 1. Electrochemical data as obtained from CV and EVS and optical bandgap energies. All potential values are shown vs. NHE, the NHE level used for the calculation of HOMO-LUMO levels was -4.75 eV.

Code	$E_{\text{onset}}^{\text{ox}}$ mV	$E_{\text{onset}}^{\text{red}}$ mV	$E_{\text{peak}}^{\text{ox}}$ mV	$E_{\text{peak}}^{\text{red}}$ mV	HOMO eV	LUMO eV	E_{g}^{cc} eV	$E_{\text{g}}^{\text{opt}}$ eV	ΔE_{g} eV
1a	+795	-1620	+1176	-1973	-5.54	-3.13	2.41	2.39	0.02
1b	+815	-1615	+958	-1973	-5.56	-3.13	2.43	2.43	0.03
2a	+800	-1810	+1100	-	-5.55	-2.94	2.61	2.21	0.40
2b	+740	-1630	+1160	-1900	-5.49	-3.12	2.37	2.23	0.14
2c	+800	-1640	+1075	-1910	-5.55	-3.11	2.44	2.24	0.20
3a	+665	-1765	-	≈ -1980	-5.42	-2.99	2.43	2.18	0.25
3b	+565	-1725	$\approx +1000$	-2010	-5.32	-3.03	2.29	2.17	0.12
3c	+740	-1695	-	≈ -2000	-5.49	-3.06	2.45	2.23	0.22
3d	+645	-1725	+885	-1930	-5.40	-3.03	2.37	2.19	0.18
4a	+760	-1590	+1215	-	-5.51	-3.16	2.35	2.19	0.16
4b	+710	-1570	+1125	-	-5.46	-3.18	2.28	2.17	0.11
4c	+760	-1590	-	-	-5.51	-3.16	2.35	2.19	0.16
4d	+710	-1560	+1095	-	-5.46	-3.19	2.25	2.21	0.04
5a	+680	-1730	+945	-	-5.43	-3.02	2.41	2.10	0.31
5b	+630	-1760	+865	-	-5.38	-2.99	2.39	2.08	0.31
5c	+510	-1750	+670	-	-5.26	-3.00	2.26	2.12	0.14

(octadecyloxy), of 0.04 eV going from **3b** to **3a**, and of 0.02 eV going from **4b** to **4a**. These results imply that increasing the side chain length or grafting of bulky branched 2-ethylhexyloxy will increase the energy barrier for the anodic reaction, i.e., the p-doping process, and in some cases (e.g., **2a**, **3a**, **4a**) for the cathodic reaction, i.e., the n-doping process. Another reason is that the charge transport from the polymer to the electrode (or vice versa) will be arduous for longer or bulky side chains. A side chain dependent ΔE_{g} also occurs with PPV “homopolymers” **5**. It is less pronounced in polymers **4**, compared to polymers **3**, where the “wider opening” introduced by the insertion of a second yne-unit leads to an improvement of the movement of charges during the electrochemical process.

Among the polymers with shorter side chains (i.e., less side chain influence), the following applies: the higher the number of the weak electron-withdrawing triple bonds ($-\text{C}\equiv\text{C}-$) per repeating unit, the lower the LUMO and HOMO levels. This means that polymers **2b**, **4b**, and **4d** have a more enhanced electron accepting strength than polymer **3b**, which in turn has a higher electron affinity than the PPV “homopolymer” **5c**.

Linear and semilogarithmic $I-V$ curves of solar cells built as: glass substrate/ITO/PEDOT:PSS/polymer **3**:PCBM (1:3, w/w)/LiF/Al are shown in Figure 3. The photovoltaic device parameters are given in Table 2. The theoretical values of the open circuit voltage, $V_{\text{OC}}^{\text{theor.}}$, postulated as the difference between the HOMO of the donor polymer and the LUMO of the acceptor, PCBM,^[10] is also given in Table 2 for the purpose of comparison with the experimental value, $V_{\text{OC}}^{\text{exper.}}$. The LUMO of PCBM was assumed to be -4.3 eV as determined by EVS.^[13]

In addition to the influence of the polymer-PCBM blend morphology on the PV parameters,^[17] it can be ascertained from the data in Table 2 that the PV parameters of polymers

3 are side chain dependent. For instance, the discrepancy, ΔV_{OC} , between $V_{\text{OC}}^{\text{theor.}}$ and $V_{\text{OC}}^{\text{exper.}}$ increases with the length

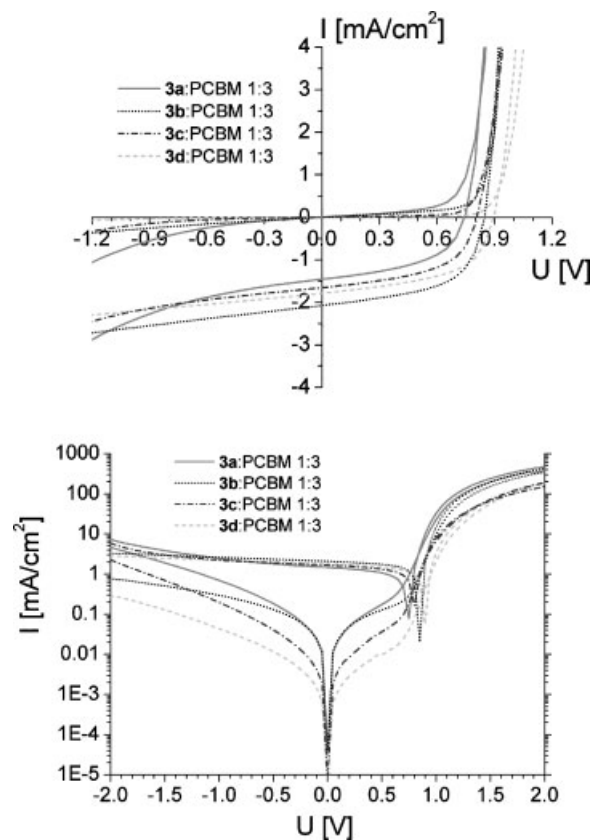


Figure 3. Top: Linear $I-V$ curves of solar cell devices from polymers **3a-d**, measured in the dark and under $100 \text{ mW} \cdot \text{cm}^{-2}$ solar simulator illumination. Bottom: Semilogarithmic $I-V$ curves of solar cell devices from polymers **3a-d**, measured in the dark and under $100 \text{ mW} \cdot \text{cm}^{-2}$ solar simulator illumination.

Table 2. Photovoltaic parameters from solar cell devices of configuration: ITO/PEDOT:PSS/polymer **3**:PCBM(1:3 w/w)/LiF/Al.

Code	Active area	$V_{OC}^{theor.a)}$	$V_{OC}^{exper.}$	$\Delta V_{OC}^{b)}$	I_{SC}	FF	$\eta_{AM1.5}$
	mm ²	mV	mV	mV	mA · cm ⁻²	%	%
3a	12	1 120	750	370	1.46	49.5	0.54
3a	13.6	1 120	750	370	1.33	49.9	0.50
3b	12	1 020	850	170	1.96	60.3	1.00
3b	18	1 020	850	170	2.11	60.2	1.08
3c	12	1 190	800	390	1.66	53.6	0.71
3c	18	1 190	800	390	1.63	48.5	0.63
3d	10	1 100	900	200	1.79	54.1	0.87
3d	16.5	1 100	900	200	1.81	52.7	0.86

a) Theoretical open circuit voltage, $V_{OC}^{theor.} = LUMO_{PCBM} - HOMO_{polymer\ 3}$.

b) $\Delta V_{OC} = V_{OC}^{theor.} - V_{OC}^{exper.}$.

or bulkiness of the side chains. This is due to a decrease of the $V_{OC}^{exper.}$ with increasing length or bulkiness of the side chains, which is quite the opposite of the expected $V_{OC}^{exper.}$ considering the HOMO values given in Table 1. The widely accepted rule for the V_{OC} of the polymer-fullerene solar cells^[10] only applies when the backbones of the donor conjugated polymers are in better contact with the acceptor components, as in the case of the three PPV derivatives, which were the subject of a study of Lee and his group.^[10] The V_{OC} of the investigated devices in the present work was found to depend much more strongly on the length and nature of the grafted alkoxy side chains than on the HOMO energy levels. Polymers **3b**, **3c**, and **3d** with shorter side chains exhibit better PV parameters than their longer side chain counterpart **3a**. Longer side chains not only contribute to limiting the interfacial area between the donor conjugated backbone and the acceptor components, but might also favour an easy recombination of the photo-generated charges by elongating the percolating path as well as hampering the transfer of charges to the electrodes. Moreover, the low short circuit current, I_{SC} , in **3a** might be related to the above-mentioned insulating nature of the longer side chains, which would partially hinder the migration of charges to the electrodes.

An enhancement of the PV parameters of all four polymers is possible through morphological optimisation and eventually using post-production treatments of the polymer-PCBM blends. This aspect is under study.

Conclusion

Side chain dependent electrochemical behaviour has been demonstrated for the fully substituted (phenylene ethynylene)-*alt*-(phenylene vinylene) polymers **2**, **3**, **4** as well as the PPV homopolymers of type **5**. Longer linear octadecyl or bulky branched 2-ethylhexyl enhance the interface energy barrier, ΔE_g , due to their strong insulating nature. ΔE_g is minimal in the case of diyne-containing polymers **4**

compared to their yne-counterpart **3**, as a result of a wider opening introduced by the insertion of a second yne-unit in **4**. Thus a better migration of generated charges to the electrodes and vice versa is enabled. In our study, no correlation could be established between the HOMO energy levels and the V_{OC} of the solar cell devices from polymers **3**. As has been demonstrated in the literature,^[10] the PV parameters were found to be rather strongly dependent on the structure of the side chains. Thus not only the HOMO-LUMO levels of the donor-acceptor system, but also the side chain architecture of conjugated polymers has a considerable impact on the open circuit voltage, V_{OC} , of bulk heterojunction solar cell devices.

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