

Anthracene-containing PPE-PPV copolymers: Effect of side-chain nature and length on photophysical and photovoltaic properties

Rupali Jadhav^{1,2}, Stefan Türk³, Florian Kühnlenz¹, Vera Cimrova⁴, Silke Rathgeber⁵, Daniel A. M. Egbe^{*,2,3}, and Harald Hoppe^{**1}

¹Institute of Physics, Ilmenau University of Technology, Weimarer Str. 32, 98693 Ilmenau, Germany

²Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria

³Institute for Print and Media Technology, Chemnitz University of Technology, Reichenhainer Str. 70, 09126 Chemnitz, Germany

⁴Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

⁵Johannes Gutenberg-University Mainz, Staudingerweg 7, 55128 Mainz, Germany

Received 21 June 2009, revised 23 October 2009, accepted 28 October 2009

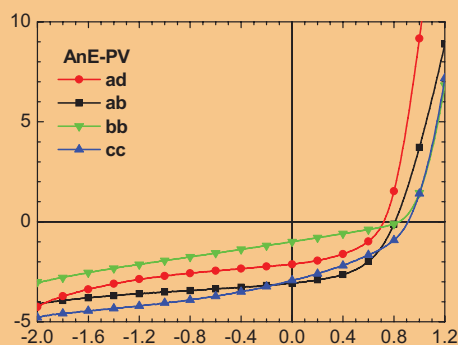
Published online 30 November 2009

PACS 72.40.+w, 73.61.Ph, 73.61.Wp, 78.40.Me, 78.66.Qn, 88.40.fh

* Corresponding author: e-mail daniel_ayuk_mbi.egbe@jku.at, Phone: +43 732 2468 8398, Fax: +43 732 2468 8770.

** e-mail harald.hoppe@tu-ilmenau.de

High-molecular weight anthracene containing poly(*p*-phenylene-ethynylene)-*alt*-poly(*p*-phenylene-vinylene) (PPE-PPV) copolymers bearing linear and/or branched alkyl side chains have been synthesized and investigated for use in polymer–fullerene bulk heterojunction solar cells. By variation of the nature and length of alkyl side chains the ordering in thin films could be tuned. Besides the basic photophysical characterization, small-angle X-ray scattering on extruded fibers and cyclovoltammetry measurements are reported. The photovoltaic characterization indicates that improved ordering due to linear side chains on the arylene–ethynylene segment as well as lower side-chain volume fraction yield higher photocurrents. Power conversion efficiencies of nearly 2.5% are reported for the best devices with a polymer:fullerene composition of 1:1 by weight.

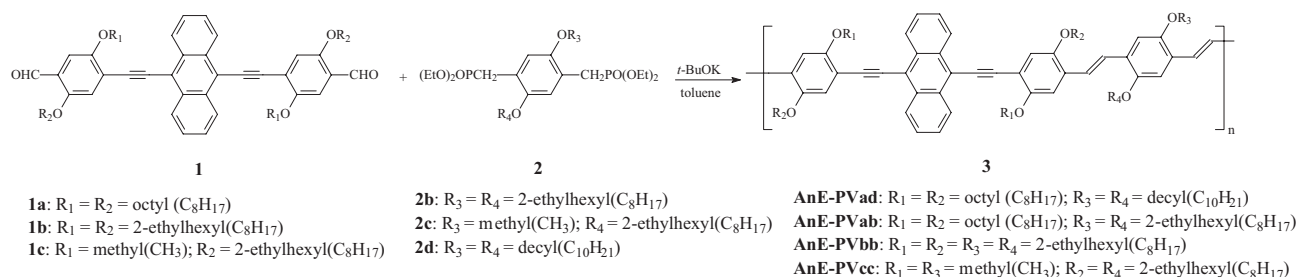


IV-characteristics of partly optimized photovoltaic devices based on [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) blends with a blending ratio of 1:1 under solar simulator illumination.

© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Poly(arylene-ethynylene)-*alt*-poly(arylene-vinylene)s PAE-PAVs are a subclass of poly(-*p*-phenylene-vinylene)s (PPVs) exhibiting enhanced electron affinity due to the incorporation of triple bond into the conjugated backbone [1–6]. They show tunable backbone rigidity and tunable highest occupied molecular orbital (HOMO)- and lowest unoccupied molecular orbital (LUMO)-levels through variation of the triple bond and

double bond ratio. They have proven their value as donor [7–9] and acceptor [10, 11] materials in the design of organic solar cells. Based on this class of materials, we were able to show that the volume fraction of solubilizing alkoxy side chains can be used in the control of the nanoscale morphology of polymer–fullerene bulk heterojunction solar cells, which can be assigned to their hydrophobic nature [9, 12]. It is well known that π – π stacking of rigid conjugated polymers can



Scheme 1 Synthesis of the polymers.

be controlled by the nature (linear or branched) of the side chains [13].

With the aim to establish a correlation between π - π stacking distance, photophysical properties and photovoltaic performance, we have carried out a study on four anthracene-containing PPE-PPV with general constitutional unit: $(-\text{Ph}-\text{C}\equiv\text{C}-\text{Anthr}-\text{C}\equiv\text{C}-\text{Ph}-\text{CH}=\text{CH}-\text{Ph}-\text{CH}=\text{CH}-)_n$ whereby linear and/or branched side chains were grafted in order to tune the π - π stacking distance.

2 Experimental The polymers *AnE-PVi* ($i = ab, ad, bb, cc$) were synthesized through the Horner-Wadsworth-Emmons olefination reaction of dialdehydes *1a, 1b, 1c* with bisphosphonates *2b, 2c, 2d* in a similar way as described elsewhere as illustrated in Scheme 1 [7, 14]. Gel permeation chromatography (GPC) was performed on a set of Knauer using THF as eluent and polystyrene as standard. Thermogravimetric analysis (TGA) was performed on a Mettler TA-300-thermal analyzer operating under air atmosphere. The π - π stacking distance, $D_{\pi-\pi}$, was determined from wide-angle X-ray scattering measurements on extruded filaments as described elsewhere [15]. The solid state absorption spectra were recorded on Varian UV/Vis spectrophotometer. Solid state emission spectra were recorded on a home-built photoluminescence setup. Thin films were spin coated on glass substrates using mostly chlorobenzene-based solutions (0.6–0.8 wt.%). Solar cell device preparation involved etching part of ITO-layer on glass (Merck KgaA, Darmstadt) for selective contacting of back electrode followed by spin casting of PEDOT:PSS at 3000 rpm (Baytron/Clevios PH H.C. Starck). Then the photoactive layer was spin cast from polymer: [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM, Solenne 99.5%) blend (1:1 blending ratio). A thermally sublimed aluminum top

electrode completed the solar cell. Solar cells with an active area of 0.5 cm² were characterized by current voltage measurements under AM1.5 solar spectrum simulator.

3 Results and discussion Scheme 1 shows the synthetic path to the polymers *AnE-PVi* ($i = ab, ad, bb, cc$). They were synthesized in about 90% yield by the Horner-Wadsworth-Emmons olefination reaction based on well established protocol [7, 14]. Linear (methyl, octyl, decyl) and/or branched (2-ethylhexyl) alkoxy side groups have been grafted in order to tune the π - π stacking distance with the goal to correlate π - π stacking ability with photophysical behavior and photovoltaic performance. The chemical structures were confirmed by NMR, IR, and elemental analysis. The materials are soluble in common organic solvents such as chloroform, toluene, chlorobenzene, THF, and dichlorobenzene and can readily form smooth films. The data from GPC, TGA, and the X-ray scattering measurements are provided in Table 1. The number-average molecular weight, M_n were between 15 000 and 48 000 g/mol, leading to a degree of polymerization, DP, between 13 and 48. The polydispersity indexes, $\text{DPI} = M_w/M_n$ (M_w = weight-average molecular weight), were found between 2 and 3.5 after extraction of the final product with hot diethyl ether [16]. TGA shows that the polymers are thermostable up to 300 °C. The start of the thermal degradation under air lies between $T_{5\%} = 306$ and 330 °C, where 5% weight loss was recorded. X-ray scattering experiments on extruded fibers reveal that the polymers *AnE-PVab* and *AnE-PVad*, bearing linear octyl side chains at R₁ and R₂ on the more rigid part of the conjugated backbone, i.e., arylene-ethynylene segment arrange in a stacked structure. This layered structure comprises π - π stacks of the backbones (π - π stacking distance $D_{\pi-\pi}$) which are

Table 1 Data from GPC, TGA, and X-ray scattering on extruded filaments.

polymer <i>AnE-PV</i>	M_n (g/mol)	M_w (g/mol)	PDI	DP	Yield (%)	$T_{5\%}$ (°C)	$D_{\pi-\pi}$ (nm)
<i>ad</i>	19 300	54 000	2.79	15	90	330	0.380 ± 0.002
<i>ab</i>	40 000	141 600	3.54	32	83	306	0.386 ± 0.002
<i>bb</i>	15 800	47 200	2.98	13	94	325	–
<i>cc</i>	47 500	91 900	1.9	48	86	309	–

Table 2 Data from thin film photophysical and electrochemical investigations.

polymer <i>AnE-PV</i>	λ_a (nm)	E_g^{opt} (eV)	λ_e (nm)	HOMO (eV)	LUMO (eV)	E_g^{elc} (eV)
<i>ad</i>	552, 590	1.91	620	5.12	3.46	1.66
<i>ab</i>	508, 583	1.80	623	5.12	3.43	1.64
<i>bb</i>	527	2.02	599	5.15	3.45	1.70
<i>cc</i>	532	1.84	617	5.10	3.35	1.75

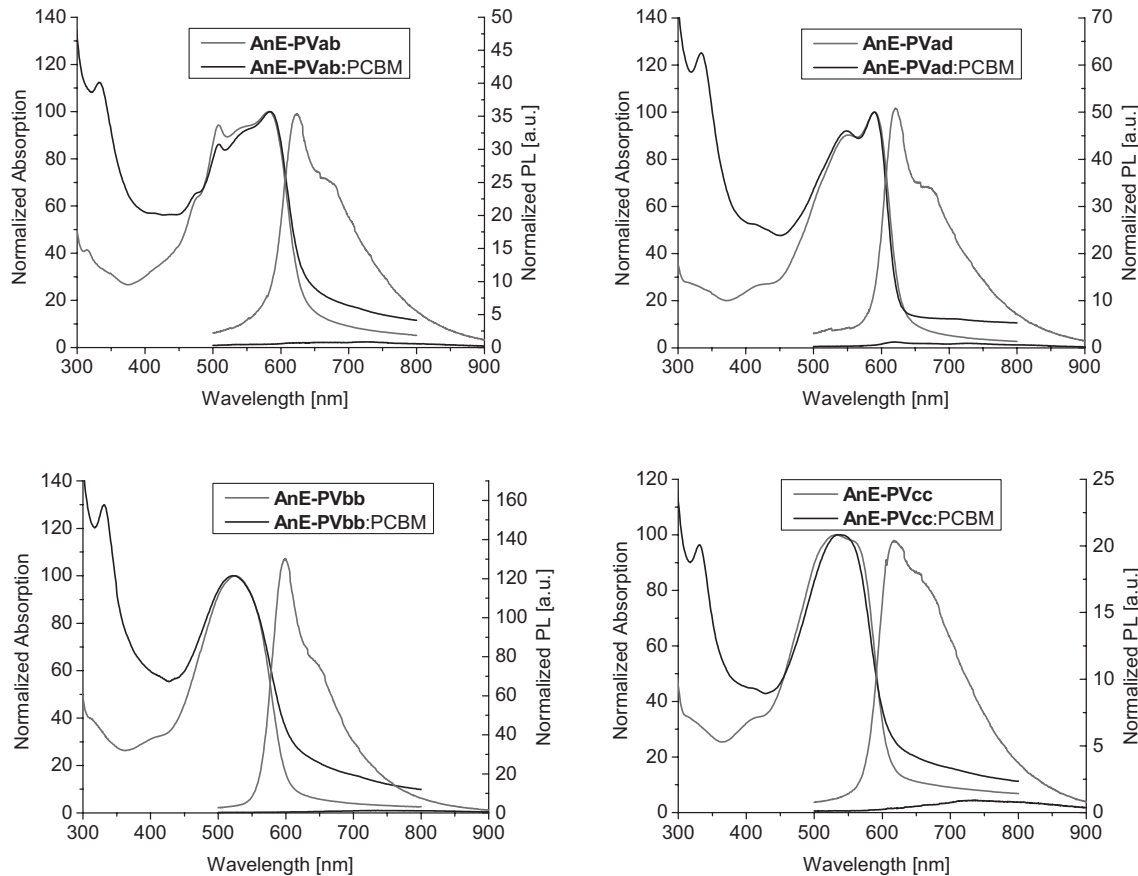
separated by interlayers built by the side chains. For details on the structural investigations including a sketch of the structure see Refs. [15, 16]. These findings are in accordance with previous results showing that placement of anthracene between two double bonds (within the PPV units) leads to a distortion of the backbone. However, when the anthracene is placed between two triple bonds (ethynylene groups), no such distortion occurs and the backbones are well able to stack [17, 18]. In contrast, the polymers *AnE-PVbb* and *AnE-PVcc* with bulky branched 2-ethylhexyl attached on the arylene-ethynylene moiety show no long range order. The scattering spectra reveal no indication for π - π stacking of the backbones.

The photophysical characteristics of the polymers were studied by UV-Vis absorption and photoluminescence in

dilute chloroform solution (absorbance around 0.05) and in thin films obtained from chlorobenzene solution (concentration 0.6–0.8 wt.-%).

The polymers exhibit almost identical photophysical behavior in dilute solution. The absorption maximum is found around 540 nm and the emission around 580 nm with a fluorescence quantum yield of $\sim 50\%$ [7]. Data from thin film photophysical investigation and electrochemical studies are summarized in Table 2, namely the absorption maxima, λ_a , the optical band gap energy, E_g^{opt} (calculated from $\lambda_{10\%,max}$ taken from lower energy side) [14], the emission maximum, λ_e , the HOMO and LUMO energy levels and the electrochemical band gap energy, E_g^{elc} .

Figure 1 depicts the absorption and emission spectra of the pristine polymers and their blends with PCBM. There is a

**Figure 1** Thin film absorption and emission spectra of the polymers and their blends with PCBM.

splitting of the absorption peak of the octyloxy based polymers *AnE-PVab* and *AnE-PVad*, which is an indication of better ordering, *i.e.*, better π - π stacking. This correlates well with the X-ray findings (Table 1). The structure-less absorption spectra as exhibited by *AnE-PVbb* and *AnE-PVcc* are an indication of comparably lower order in the bulk. There is a discrepancy between the optical (1.80–2.02 eV) and electrochemical (1.64–1.75 eV) band gap energies as obtained from the onset value of the redox potentials in cyclic voltammetry measurements due to quasi-donor (arylene-vinylene segment)-acceptor (arylene-ethynylene segment) nature of the polymers [14]. Overall the optical properties – especially the absorption and emission ranges – are comparable due to the fact that all polymers exhibit the identical chemical structure of the back-bone.

Normalized photoluminescence spectra demonstrate strong exciton quenching – indicating an efficient charge transfer – for all blends investigated. The 0–0 transition photoluminescence peak appears to be less pronounced for *AnE-PVcc*, which might be an indication of excimer-like emission contributions.

Photovoltaic devices based on 1:1 (polymer:PCBM) blends have been prepared and optimized by variation of solution concentration and film thickness. Since the compounds showed different solution viscosities upon preparation of identical solid content solutions, individual optimization of the polymer concentration was necessary. This resulted in concentrations varying between 0.6 and 0.8 wt.% for the various polymers investigated. The film thickness has been varied by changing the spin frequency between 500 and 4000 rpm, resulting in thicknesses of smaller than 100 nm for the optimized devices. In the following only the best photovoltaic results are reported in Figure 2 and Table 3, which summarize the IV-results of all polymer:PCBM blends with a weight ratio of 1:1 under solar simulator illumination. As expected from the electrochemical characterization, the *AnE-PVcc*:PCBM blend exhibits the highest open circuit voltage V_{OC} corresponding to the

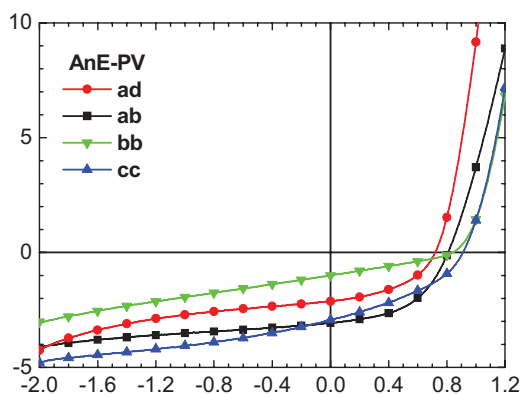


Figure 2 (online colour at: www.pss-a.com) IV-characteristics of partly optimized photovoltaic devices based on polymer:PCBM blends with a blending ratio of 1:1 under solar simulator illumination.

Table 3 Photovoltaic parameters of the polymer solar cells are summarized.

<i>AnE-PVi</i> :PCBM (blend ratio 1:1)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	η (%)	R_S (Ω)	R_P (Ω)
<i>ad</i> :PCBM	4.24	0.72	44.6	1.36	11.3	1361
<i>ab</i> :PCBM	6.13	0.81	49.08	2.44	22.2	1480
<i>bb</i> :PCBM	1.99	0.84	29.23	0.49	16	1012
<i>cc</i> :PCBM	5.86	0.91	37.5	2.00	12.8	625

lowest LUMO level. Only the *AnE-PVad*:PCBM blend shows smaller V_{OC} values than 0.80 V, which can be related to its long side chains resulting in a resistive voltage loss during charge transfer as has been shown earlier by us [8, 12]. The other two compounds, *AnE-PVab* and *AnE-PVbb* give open circuit voltages of slightly more than 0.8 V.

The relatively low fill factors (FF), and relatively high series resistances, R_S , in all blends may stem from a non-balanced charge transport, indicating the need for further increasing the fullerene content. Only the short circuit current densities, J_{SC} , from solar cells based on the *AnE-PVab* and *AnE-PVcc* polymers reach reasonable values around 6 mA/cm², which corresponds to more than 50% of what can be expected based on the corresponding absorption spectra. Especially polymer *AnE-PVbb* shows only inferior currents, which may indicate incomplete or hindered charge separation efficiency after transfer. Under application of an increasing reversed electric field, the photocurrent of *AnE-PVbb* keeps on increasing linearly limited by either the initial charge separation step or the morphology dependent charge transport.

Furthermore, the larger current densities of *AnE-PVab* as compared to *AnE-PVbb* may be related to a better ordering due to π - π stacking, leading to improved charge transport properties in blends with PCBM. The high photocurrent densities of photovoltaic devices based on *AnE-PVcc* may be related to a lower side-chain density as compared to *AnE-PVbb*, yielding higher charge transfer efficiency [12]. In general, smaller parallel resistances, R_P , lead to smaller FF. The high photocurrents in case of *AnE-PVab* and *AnE-PVcc* promote relatively high power conversion efficiencies of $\eta \geq 2\%$.

4 Conclusions We have synthesized four different anthracene containing PPE-PPV copolymers bearing linear and/or branched alkyl side chains in order to tune the π - π stacking behavior. Polymers bearing linear octyl side chains on the arylene-ethynylene segment (*AnE-PVab*, *AnE-PVad*) exhibit a better ordering as confirmed by photophysical and X-ray scattering experiments. An asymmetrically substituted polymer (*AnE-PVcc*) reaches similar large photocurrents as a well-ordered one (*AnE-PVab*) presumably due to a lower side-chain density promoting efficient charge transfer. In this study only 1:1 blend ratios by weight have been carried out, however, the IV-characteristics indicate some charge transport limitations. Thus, upon increase of the

fullerene content we expect further improvement of the photovoltaic performance.

Acknowledgements Silke Rathgeber, Harald Hoppe, and Daniel A. M. Egbe are grateful to the DFG for financial support in the framework of SPP1355. HH gratefully acknowledges financial support from the Thuringian Ministry of Culture in the frame of FIPV.

References

- [1] G. Brizius, G. N. Pschirer, W. Steffen, K. Stitzer, H.-C. zur Loye, and U. H. F. Bunz, *J. Am. Chem. Soc.* **122**, 12435 (2000).
- [2] D. A. M. Egbe, H. Tillmann, E. Birckner, and E. Klemm, *Macromol. Chem. Phys.* **202**, 2712 (2001).
- [3] A. M. Ramos, M. T. Rispens, J. K. J. van Duren, J. C. Hummelen, and R. A. J. Janssen, *J. Am. Soc.* **123**, 6714 (2001).
- [4] A. P. H. J. Schenning, A. C. Tsipis, S. C. J. Meskers, D. Beljonne, E. W. Meijer, and J. L. Brédas, *Chem. Mater.* **14**, 1362 (2002).
- [5] Q. Chu, Y. Pang, L. Ding, and F. E. Karasz, *Macromolecules* **36**, 3848, (2003).
- [6] M. Tong, C. X. Sheng, C. Yang, Z. V. Vardeny, and Y. Pang, *Phys. Rev. B* **69**, 155211 (2004).
- [7] H. Hoppe, D. A. M. Egbe, D. Mühlbacher, and N. S. Sariciftci, *J. Mater. Chem.* **14**, 3462 (2004).
- [8] D. A. M. Egbe, L. H. Nguyen, K. Schmidtke, A. Wild, S. Günes, C. Sieber, and N. S. Sariciftci, *J. Polym. Sci., Part A: Polym. Chem.* **45**, 1619 (2007).
- [9] H. Hoppe, N. S. Sariciftci, D. A. M. Egbe, D. Mühlbacher, and M. Koppe, *Mol. Cryst. Liq. Cryst.* **426**, 255 (2005).
- [10] D. A. M. Egbe, T. Kietzke, B. Carbonnier, D. Mühlbacher, H.-H. Hörhold, D. Neher, and T. Pakula, *Macromolecules* **37**, 8863 (2004).
- [11] K. Kietzke, D. A. M. Egbe, H.-H. Hörhold, and D. Neher, *Macromolecules* **39**, 4018 (2006).
- [12] D. A. M. Egbe, L. H. Nguyen, H. Hoppe, D. Mühlbacher, and N. S. Sariciftci, *Macromol. Rapid Commun.* **26**, 1389 (2005).
- [13] D. A. M. Egbe, C. P. Roll, E. Birckner, U.-W. Grummt, R. Stockmann, and E. Klemm, *Macromolecules* **35**, 3825 (2002).
- [14] D. A. M. Egbe, C. Bader, J. Nowotny, W. Günther, and E. Klemm, *Macromolecules* **36**, 5459 (2003).
- [15] B. Carbonnier, D. A. M. Egbe, E. Birckner, U.-W. Grummt, and T. Pakula, *Macromolecules* **38**, 7546 (2005).
- [16] S. Rathgeber, D. Bastos de Toledo, E. Birckner, H. Hoppe, and D. A. M. Egbe, *Macromolecules*, in press (2009).
- [17] R. O. Garay, H. Naarmann, and K. Müllen, *Macromolecules* **27**, 1922 (1994).
- [18] A. Wild, D. A. M. Egbe, E. Birckner, V. Cimrova, R. Baumann, U.-W. Grummt, and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **47**, 2243 (2009).

