The particular systems under investigation are poly(p-arylene-ethynylene)-alt-poly(p-arylene-vinylene)s (PAE-PAV) based copolymers. We used targeted side chain modification for manipulating the nanostructural properties of these materials in order to tune their photophysical and photovoltaic performance. Interchain interactions were systematically modified by decorating the conjugated polymer backbone with linear or branched or combinations of linear and branched alkoxy side chains. The effect of different side chain substitution has been discussed in another report. Here we would like to discuss the effect of the casting solvent by means of one of the polymers of this series. The chemical structure of the particular polymer is depicted in Figure 1.

X-ray scattering experiments on extruded fibers revealed that the polymer arranges in a stacked structure. This layered structure comprises \( \pi-\pi \) stacks of the backbones (\( \pi-\pi \) stacking distance \( d_{\pi-\pi} \)) which are separated by interlayers build by the side chains (distance \( d_{\text{inter}} \)). For details on the structural investigations on the bulk samples see Ref. ([1]).

![Figure 1: Left: chemical structure of the anthracene containing poly(phenylene-ethynylene)-alt-poly(phenylene-vinylene) copolymer: \( R^1=R^3= \) methyl and \( R^2=R^4= \) 2-ethylhexyl. Right: sketch of the layered structure.](image)

We performed grazing-incidence wide-angle x-ray scattering experiments on thin films of the pristine polymer as well as of its blends with different amounts of [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) spin coated from 1. chlorobenzene (CB), 2. chloroform (CF) and 3. from a (1:1) mixtures by weight fraction of CB and CF. Figure 3 shows the spectra obtained for films deposited from CB and from CB:CF mixtures, only. The pure polymer deposited from CB does not show significant signal indicating the absence of any longer ranged order. The isotropic rings
visible in the spectra of the polymer:PCBM blends deposited from CB correspond to the PCBM nearest neighbor distances of the rather weakly ordered PCBM domains. There is no preferred orientation of the PCBM domains relative to the substrate. Deposition out of CB:CF solutions leads to a significant improvement of the solar cell performance in terms of power conversion efficiency. For more details on the device characterization see Ref.([2]). This improvement originates from a better phase separation between polymer and PCBM as can be seen from the more pronounced isotropic scattering features originating from the PCBM phase. Furthermore a broad peak appears well visible in the spectrum obtained for the pristine polymer film. This peak corresponds to \( \pi-\pi \) stacks perpendicular to the substrate. For the performance of the solar cells, such an orientation is ideal for the charge carriers to be transported away from their generation point as well as for charge collection at the active layer/electrode interface. The corresponding peak originating from interlayer stacking parallel to the substrate is not observed in as deposited samples. However, annealing of the sample leads to a sharpening of the \( \pi-\pi \) stacking peak as well as to a well defined interlayer stacking parallel to the \( \pi-\pi \) stacking direction.

![Figure 3](image)

Figure 3: Representative two-dimensional detector pattern of the pure polymer and its mixtures with PCBM in (1:1) and (1:2) blends by weight fraction deposited from pure CB (top) and (1:1) CB:CF mixtures (bottom).

References
