The Influence of Ordering on the Photoinduced Charge Transfer in Composites of Phenyl-type Substituted Polythiophenes with Methanofullerenes

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ABSTRACT

Regioregular polythiophenes baring 3-(p-methoxyethoxyethoxy)-phenyl substituents (PEOPT) show high photoluminescence efficiencies. Exposing thin films of this polymer to vapors of chloroform or annealing them by heat treatment results in a red shift of the absorption maximum due to solvent or heat induced ordering which gives rise to more planar conformations. The fact, that annealed thin films of PEOPT exhibit absorption edges at relatively low energies and thus have an enhanced spectral range makes them suitable for use in photodiodes / solar cells. The photoinduced charge generation efficiency in PEOPT is significantly enhanced by the addition of a strong electron acceptor like fullerene, as observed by quenching of the luminescence and by photoinduced absorption measurements in the infrared and UV-Vis regime. The efficiency of the photoinduced charge transfer from PEOPT to a methanofullerene is found to depend on the ordering of PEOPT in thin films.

INTRODUCTION

Polythiophenes were among the first conjugated polymers modified by attaching long solubilizing side chains to improve their processing properties. For some processible polythiophenes, among them the poly(3-alkylthiophenes), a thermochromic change was found rather early between a red and a yellow phase [1]. The origin of this thermochromism was extensively studied from structural point of view especially with

respect to the interplay between the effective conjugation length of the thiophene backbone and the conformational change of the alkyl side chains (i. e. flat trans vs. twisted gauche structures) [2, 3, 4]. Recently, emphasis was put again on the investigation of the two different phases in substituted polythiophenes, demonstrating photoinduced phase transformation in polyalkylthiophenes within the ns regime [5]. The regioregularity of the polythiophenes has an important influence on the effective conjugation length. For regioregular thiophenes, the π conjugation seems to be longer since the thiophene rings are less twisted due to steric hindrance [6].

Regioregular polythiophenes with enhanced absorption in the near infrared regime are also interesting for a second application. Since the discovery of an ultrafast photoinduced electron transfer [7] from many conjugated polymers onto fullerenes, this effect has been used to develop efficient photovoltaic devices [8]. Prototypes of photovoltaic devices based on a polymeric donor / acceptor networks show solar energy conversion efficiencies of around 1% [9]. A clear handicap of these cells is the relatively large band gap of the conjugated polymers, typically > 2.2. eV. Regioregular thiophenes with extended absorption in the < 2 eV regime are expected to enhance the efficiency of polymeric photovoltaic devices significantly.

In this paper we investigated a novel class of regioregular phenyl substituted polythiophenes [10] which show structural ordering upon heating (or solvent vapor treating), on the occurrence of photoinduced charge transfer with fullerenes. The difference between these two phases with respect to their efficiency in charge transfer will be evaluated.

EXPERIMENTAL

The chemical structure of various phenyl substituted polythiophenes which show an annealed / not annealed phase is shown in Figure 1. For the studies presented in this work PEOPT was used as the electron donor, while the electron acceptor was [6,6]-Phenyl C_{61} - butyric acid methyl ester [11] (PCBM). The enhanced solubility of PCBM compared to C_{60} allows a high fullerene - conjugated polymer ratio and strongly supports the formation of donor - acceptor bulk heterojunctions. The not annealed samples were produced by spincasting from 1 – 1.5 wt% solutions in chloroform at high spinning

POPT   PEOPT   POOPT
   WM-98
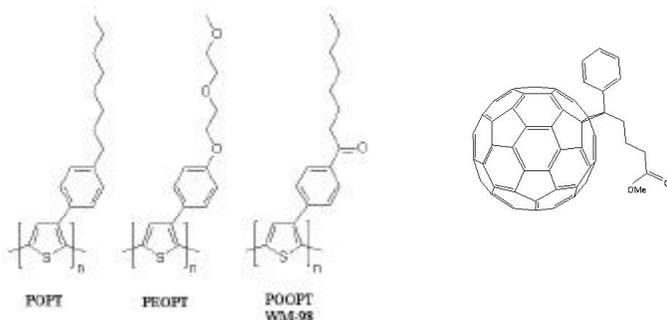
speed, resulting in orange brownish films. The annealing of the cast films was performed typically at a temperature of 100 ° C, giving deep purple films. Casting ODCB solutions directly results in the annealed form without heat treatment. A HP UV/VIS spectrometer with a CCD array was used to measure the room temperature absorption. Photoinduced FTIR spectra were recorded on a Bruker IFS 66S spectrometer with a liquid nitrogen cooled MCT detector. The photoinduced changes in the infrared absorption spectra of the conjugated polymer were observed by measuring 10 single beam spectra under illumination of the polymer sample and referencing them to 10 single beam spectra taken in the dark. The samples were illuminated by the 488 nm line of an Ar^+ laser. For a better signal-to-noise ratio 200 repetitions of the measuring sequence described above were accumulated. The vacuum during all measurements was better than 10^{-5} mbar. Photovoltaic devices were produced by spin casting 1:1 ratios of PCBM : PEOPT from chloroform or ortho-dichlorobenzene (ODCB) solution at ambient conditions. The transparent aluminum top electrode was evaporated thermally. Photocurrents were measured at room temperature in vacuum. Illumination through the transparent ITO side was provided by white light from a halogen lamp with 60 mW/cm^2. I/V curves were recorded with a Keithley 2400 Source Meter, typically by averaging 200 measurements for one point.
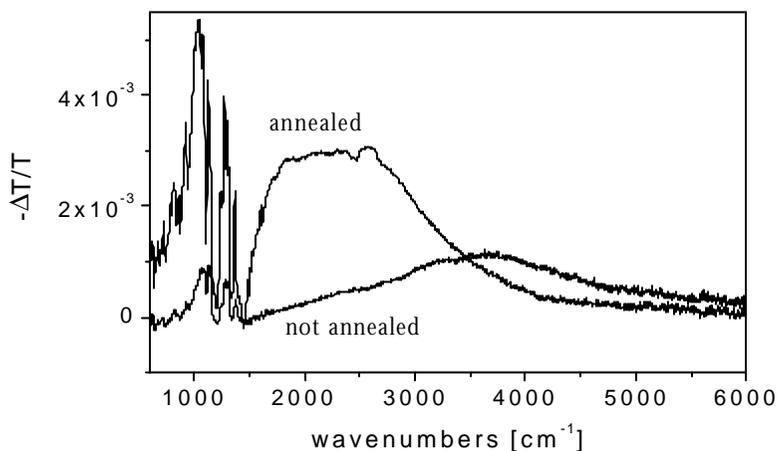
RESULTS AND DISCUSSION

UV/Vis absorption spectroscopy was used to give a first evaluation of the annealing of PEOPT with and without PCBM. This step was necessary to verify that the presence of PCBM inside the composites does not hinder the complete structural reorganization of the PEOPT. Figure 2 shows the absorption spectrum of PEOPT compared to PEOPT/PCBM before and after the annealing step. Annealing was preformed by a temperature step. Treating the thin films with solvent vapor was found to give less complete ordering. A clear color change of the samples was observed during the
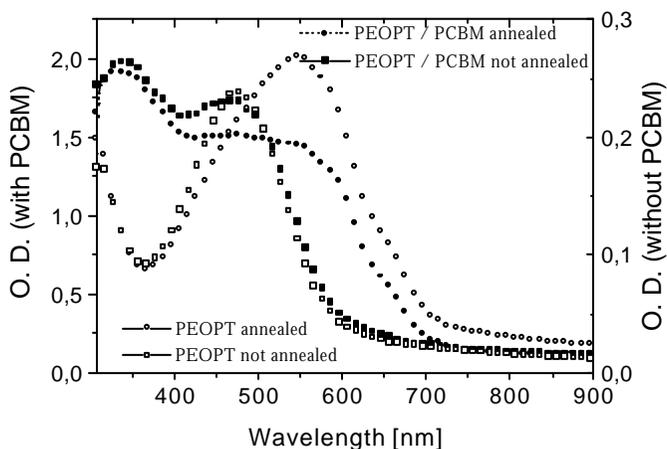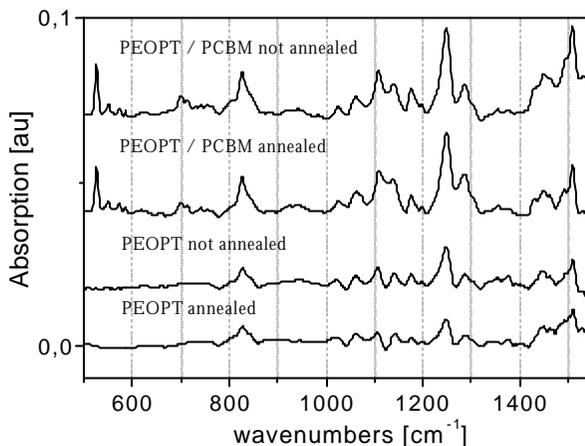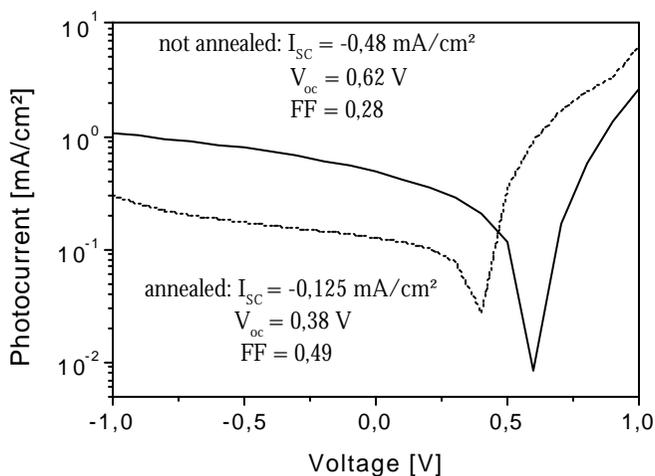
annealing step, from orange/brownish to a deep purple red. The absorption data show, that annealing takes place successfully also in the presence of PCBM. The absorption maximum, located around 475 nm for the not annealed form, is shifted by ~ 75 nm to it's maximum in the annealed form around 550 nm. The presence of PCBM in the fullerene loaded composites broadens the absorption, but even without deconvolution the maximum around 550 nm for the PEOPT / PCBM annealed composite can be recognized. The IR absorption and the PIA IR spectrum of the four samples is shown in Figure 3 for spin cast films on a KBr pellets. IR absorption shows clearly, that no new IR bands are formed during the annealing step. This is in agreement with the assumption, that the annealing is triggered by a macroscopic ordering phenomenon. The photoinduced IR absorption spectrum (Figure 4) reveals, that the lower polaronic absorption of the PEOPT is shifted by app. $1500 \, cm^{-1}$.(~ 0.18 eV), which is half the value of the bandgap shift. The IRAV bands were found to be at comparable energies for the annealed and the not annealed form. Interestingly, the signal of the annealed form is stronger than the one from the not annealed form. Further investigations are necessary to explain this increase of the signal intensity.

Photovoltaic devices were produced from PEOPT / PCBM (1:1) solutions as described in the experimental section. Figure 5 shows the logarithmically plotted I/V curves of annealed and not annealed PEOPT/PCBM devices. Annealed devices were produced directly by spin casting from ODCB solutions, which gives the annealed form. The I/V curves presented in Figure 5 were recorded on devices with semitransparent Al electrodes. It is worth to note, that the annealed device shows an unusual high filling factor (FF ~ 0.49). FF of this magnitude are usually only observed in organic bilayer structures. The V_{oc} of the not annealed device (~ 0.65 V) can not be explained by a simple metal isolator metal picture, since the difference in the work functions between the ITO and the Al is app. 0.4 eV. More sophisticated models are necessary to explain this observation [9].

-ΔT/T

4×10^{-3}

2×10^{-3}

0

annealed

not annealed

1000   2000   3000   4000   5000   6000

wavenumbers [cm^{-1}]

CONCLUSION

This novel class of regioregular thiophenes is a promising candidate for photovoltaic devices. Charge transfer within the bulk of the annealed phase PEOPT / PCBM composite was shown, however I/V characteristics of photovoltaic cells show higher photocurrents and photovoltages for the not annealed form. Further optimization of the PV devices in the annealed form is necessary to utilize the red shifted absorption of this material.

10^1

10^0

10^{-1}

10^{-2}

Photocurrent [mA/cm²]

not annealed: I_{SC} = -0,48 mA/cm²
V_{oc} = 0,62 V
FF = 0,28

annealed: I_{SC} = -0,125 mA/cm²
V_{oc} = 0,38 V
FF = 0,49

-1,0   -0,5   0,0   0,5   1,0

Voltage [V]

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