

Investigation of Photoinduced Charge Transfer in Composites of a Novel Precursor PPV Polymer and Fullerenes

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ABSTRACT

Homogenous blends of a processable methanofullerene, [6,6]-Phenyl C₆₁-butyric acid methyl ester (PCBM), with poly (p-phenylene vinylene) (PPV) made from a novel non-ionic precursor route were investigated by optical spectroscopy and by photocurrent measurements. The conversion process of the precursor polymer to the PPV in the blends with PCBM was monitored by IR absorption. In composites of PPV/PCBM strong quenching of the PPV luminescence was observed. LESR (light induced electron spin resonance) and PIA (photoinduced absorption) studies confirmed the occurrence of photoinduced electron transfer from the PPV to PCBM. Photovoltaic devices made from PPV/PCBM blends showed monochromatic power conversion efficiencies of app. 0.3%. The spectral photocurrent was observed to follow the absorption profile of the PPV.

INTRODUCTION

Efficiencies of the first polymeric solar cells, based on hole conducting conjugated polymers (mainly polyacetylene) were rather discouraging [1]. Encouraging breakthrough to higher efficiencies was achieved by switching to different classes of electron donor type conjugated polymers (polythiophenes (PT), polyphenylenevinylenes (PPV) and their derivatives) and by mixing them with suitable electron acceptors [2]. The strongest hindrance to use organic polymeric semiconductors as the active component in photovoltaic devices during the last two decades was the rather inefficient charge

generation process as well as the unbalanced transport properties of the hole conducting polymers. Prototypes of photovoltaic devices based on a polymeric donor / acceptor network showed solar energy conversion efficiencies of around 1% [3]. Due to the application potential, the photophysics of conjugated polymer/fullerene solid composites have been well investigated in the last years [4].

From the conjugated polymers of the first generation, PPV was the most successful candidate for single layer polymer photovoltaic devices [5]. Unsubstituted PPV is generally produced from a soluble precursor polymer with subsequent heat conversion. Polymer electroluminescence (polymer light emitting diodes (LEDs)), which is close to market application now, was investigated for the first time in PPV and then optimized for soluble conjugated polymers [6, 7, 8, 9]. There are many important aspects with respect to the basic processes that control the life time of polymer devices, including substrate smoothness, barrier properties, presence of oxygen and moisture as well as the crystallinity and the morphology of two component blends [10, 11, 12]. Compared to the new generation of soluble, substituted PPVs, the PPV from the precursor polymer is therefore still interesting due to its environmental as well as mechanical stability, serving therefore as a model system for polymer devices.

With the observation of photoinduced charge transfer between non degenerate ground state polymers and fullerenes by Santa Barbara group and Osaka group [2, 4, 13, 14], new efforts were put again on the investigation of polymer based photovoltaic devices. Especially the long lifetime of the charge transferred state and the high quantum efficiency of this process (~100%) in conjugated polymer/fullerene composites compared to pristine conjugated polymer films favored the development of photocells.

In most cases, PPV was accessible via the Wessling precursor route [15]. Due to the water solubility of this precursor PPV, photovoltaic cells from PPV were mostly based on the pure polymer, as most fullerene acceptors could not be mixed into it. This solubility problem was attacked by the development of a new class of PPV precursor polymers which are soluble in common organic solvents [16].

In this paper we will investigate the photoinduced charge transfer properties of composites of this new precursor PPV with a highly soluble methanofullerene (PCBM). The successful observation of photoinduced charge transfer between these two molecules inside the bulk composite allowed the fabrication photovoltaic devices, which show higher efficiencies than reported for pristine PPV photovoltaic diodes.

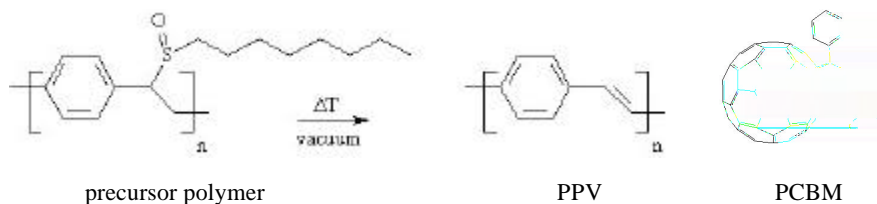


Figure 1: Chemical structure of the precursor polymer, of PPV and of PCBM. The conversion from the precursor polymer to PPV is shown schematically.

EXPERIMENTAL

The chemical structures of the compounds investigated in this study are shown in Figure 1 together with a scheme of the conversion process of the precursor polymer to the PPV. For the studies presented in this work, a n-octyl sulfinyl precursor polymer was used as the electron donor, while the electron acceptor was [6,6]-Phenyl C₆₁-butyric acid methyl ester [17] (PCBM). The enhanced solubility of PCBM compared to C₆₀ allows a high fullerene - conjugated polymer ratio and strongly supports the formation of donor - acceptor bulk heterojunctions. Samples for investigations were produced by spin casting from a 1% toluene solution either on KBr pellets (for IR investigations, but also for UV/Vis absorption and luminescence measurements) or on glass substrates (for luminescence, UV/Vis absorption and PIA measurements). The conversion of the cast precursor polymer films to PPV was performed typically at 180° C for 4 hours. IR absorption and 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 with 20 mW/cm². 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.

A HP UV/VIS spectrometer with a CCD array and a Hitachi luminescence spectrometer with a photomultiplier was used to measure the room temperature absorption and luminescence respectively.

Photovoltaic devices were produced by spin casting 1:1 ratios of PCBM : precursor polymer from xylene solution at ambient conditions onto ITO coated glass. The aluminum top electrode was evaporated thermally. Photocurrents were measured at room temperature under active vacuum in an optic cryostat. Illumination through the

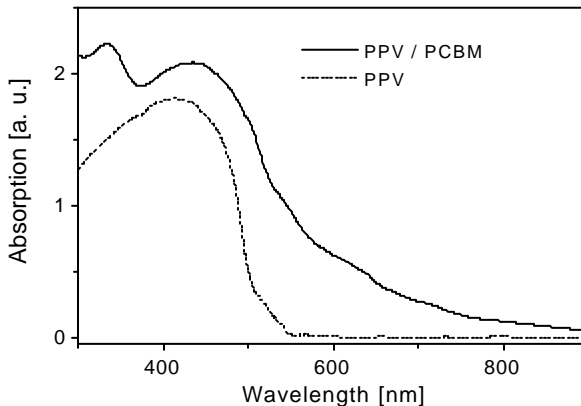


Figure 2: Absorption spectrum of PPV and PPV/PCBM (1:1 wt. ratio) after 3 hours conversion at 180° C.

transparent ITO side was provided by either a defocused Ar⁺ laser beam at 488 nm or by a Xe arc lamp with a Czerny-Turner single pass monochromator. For the spectrally resolved photocurrent measurements the illumination intensity was kept constant at 1mW/cm² at each wavelength in the range between 400 and 700 nm. Light intensities were measured by a calibrated Si photodiode. I/V curves were recorded by a Keithley 2400 Source Meter, typically by averaging 200 measurements for every point.

RESULTS AND DISCUSSION

UV/Vis absorption spectroscopy was used to give a first evaluation of the conversion of the PPV precursor with and without PCBM. This step was necessary to verify that the presence of PCBM inside the composites does not hinder the complete conversion of the precursor. Figure 2 shows the absorption spectrum of PPV compared to PPV/PCBM after elimination of 4 hours at 180° C. A clear color change of the samples was observed after conversion, from transparent to an intense yellow. A broad absorption band peaking around 425 nm with an onset of ~ 520 nm proves the build up of conjugation for the pristine PPV. The situation looks more complicated for the compounds with PCBM. PCBM itself is absorbing in the region from 750 nm to 500 nm, making it difficult to determine the onset of the PPV absorption within the composite. However, the maximum at 440 nm is clearly observed, and shows that the precursor polymer was converted. The absorption feature at 330 nm again is assigned to PCBM. The observance of a slight red shifted absorption maximum in the case of the PPV/PCBM composite is not clear. Photoluminescence was measured for the same samples, and at room temperature the PL of the PPV/PCBM sample was found to ~3 orders of magnitude smaller than for the pristine PPV sample. The photoinduced absorption IR spectrum of the PPV drop cast film on KBr is shown in

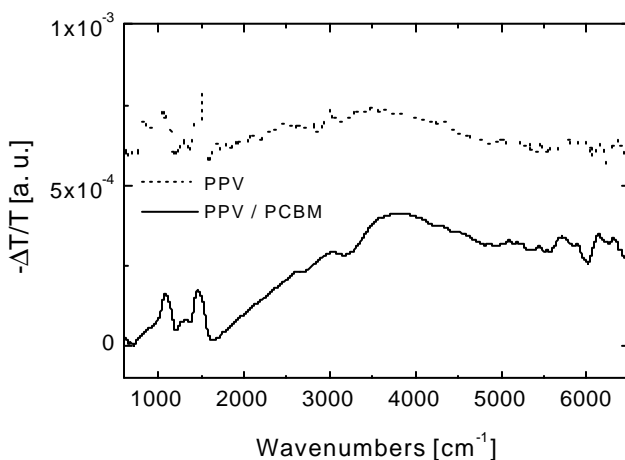


Figure 3: FTIR PIA spectrum of PPV (---) and PPV/PCBM (—) pumped at 488 nm with 20 mW/cm².

Figure 3 together with the spectrum of a composite film of PPV/PCBM. The spectrum reveals a subgap electronic absorption band at 3800 cm^{-1} , which is enhanced by a factor of 4 compared to the pristine PPV sample. Additional, strong IRAV bands are seen at 1112 cm^{-1} , 1276 cm^{-1} , 1313 cm^{-1} , 1413 cm^{-1} and 1479 cm^{-1} for the PPV /PCBM sample. Again, these IRAV bands are much weaker in the pristine PPV sample and confirm the enhanced generation of long living photoinduced charges within these composites. Photovoltaic devices were produced from PPV / PCBM (1:1) solutions as described in the experimental section. Figure 4 shows the spectrally resolved photocurrent of a PPV / PCBM (1:1) device under constant illumination intensity of 1 mW/cm^2 together with the room temperature absorption spectrum taken from a drop casted PPV film on a glass substrate. At higher energies, the photocurrent tends to fall slightly. The photocurrent spectra are in good agreement with the optical absorption of PPV. The rise of the photocurrent follows the onset of the optical absorption and shows its maximum close to a shoulder in the PPV absorption spectrum around 470 nm . The monochromatic efficiency was calculated with $\sim 0.3\%$.

CONCLUSION

This novel PPV precursor is a promising material for devices. Charge transfer within the bulk of a PPV / PCBM composite was evidenced clearly. The spectrally resolved photocurrent of photovoltaic devices prepared from solutions of precursor polymer / PCBM (1:1 wt. ratio) showed excellent agreement with the optical absorption.

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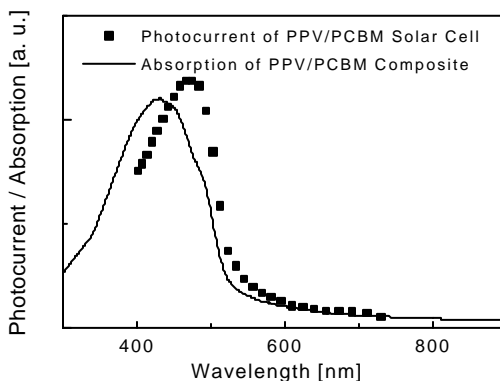


Figure 4: Spectral photocurrent of a PPV / PCBM solar cell compared with the absorption. Curves were normalized to their onset.

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