

Poly(5,6-dithiooctylisothianaphtene), a new low band gap polymer: spectroscopy and solar cell construction

L. Goris^{a,*}, M.A. Loi^{c,1}, A. Cravino^c, H. Neugebauer^c, N.S. Sariciftci^c, I. Polec^a,
L. Lutsen^a, E. Andries^b, J. Manca^a, L. De Schepper^{a,b}, D. Vanderzande^{a,b}

^aDepartment of IMOMEC, IMEC v.z.w., Wetenschapspark 1, Diepenbeek B-3590, Belgium

^bLimburgs Universitair Centrum (LUC), Universitaire Campus, Building D, Diepenbeek B-3590, Belgium

^cLinz Institute for Organic Solar Cells (LIOS), Johannes Kepler University, Altenbergerstrasse 69, Linz A-4040, Austria

Abstract

To enhance the efficiency of polymer photovoltaics, much effort is put into synthesis of novel compounds which show a better harvesting of solar light. In this respect, a new low band gap polymer, namely, poly(5,6-dithiooctylisothianaphtene), was synthesised. This work focusses on the spectroscopic characterisation of the material. The dynamics of the photoexcitations were studied by monitoring the dependence of the photoinduced absorption band on the laser modulation frequency and indicated dispersive recombination kinetics in this material. An appropriate model was used to describe the observed behaviour. To investigate the nature of the photogenerated species more profound, photoinduced absorption spectroscopy in the infrared was performed, showing an infrared active vibrational pattern (IRAV). Solar cells were constructed with an active layer consisting of the pristine material or a mixture with an electron accepting moiety. For this purpose, (6,6)-phenyl-C₆₁-butyric-acid (PCBM) in 1:1 a (w/w) ratio with respect to the polymer was used. A clear improvement of the diode behaviour was observed going from the pristine material to the mixture. Photocurrent action spectra of the solar cells with the polymer:PCBM-mixture indicated an active contribution of the polymer to the photocurrent.

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1. Introduction

Increasing the light harvesting properties of the active layer in composite solar cells—consisting of a bi-continuous network or a “bulk heterojunction” of an electron donating and an electron accepting organic material—is a route which is receiving an increasing amount of attention in order to achieve higher power conversion efficiencies. Recently, very attractive power conversion efficiencies, up to 2.5% under A.M. 1.5 solar irradiation, could be reached with a combination of a soluble derivative of poly-*p*-phenylenevinylene (PPV), poly(2-methoxy-5-(3',7'-dimethyl-octyloxy))-*p*-phenylenevinylene (MDMO-PPV) as electron donating material and a soluble fullerene, (6,6)-phenyl-C₆₁-butyric-acid (PCBM) as electron accepting molecule [1]. The working principle of this class of solar cells is based on an ultrafast electron transfer between the optically excited conjugated

material and the C₆₀-derivative, yielding a nearly 100% quantum yield for charge generation [2]. This already points out the importance of the nanoscopic nature of the bulk heterojunction, as the diffusion length of an exciton in the polymer is limited up to a few nanometres. The lifetime of the resulted charge separated state is in the order of milliseconds and permits the charge carriers to be transported to and collected at the electrodes yielding photocurrent [3]. In improving the power conversion efficiency of bulk heterojunction solar cells, one can focus on three main aspects: (i) the spectral overlap of the constituting donor and acceptor compounds with respect to the solar irradiance; (ii) charge carrier generation; (iii) transport and collection properties. This work focusses on improving the absorbance of the donor in the Donor–Acceptor-blend, by developing a soluble and therefore processable polyisothianaphtenederivative, poly(5,6-dithiooctylisothianaphtene). This polymer indeed shows a very low band gap as can be seen from the UV-Vis absorption spectrum (Fig. 1).

Photoinduced absorption spectroscopy proved to be a very useful tool to investigate the nature of the photogenerated species in conjugated materials. To study the dynamics of

* Corresponding author. Tel.: +32-11-268826; fax: +32-11-268899.

E-mail address: ludwig.goris@luc.ac.be (L. Goris).

¹ Present address: ISMN-C.N.R., Via P. Gobetti, 101, I-40129 Bologna, Italy.

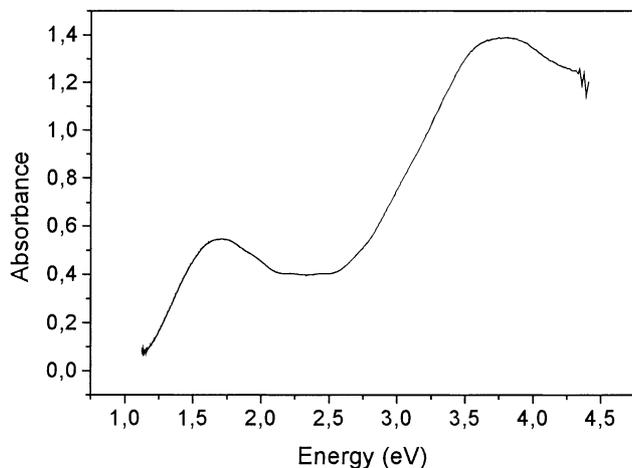


Fig. 1. UV-Vis spectrum of poly(5,6-dithiooctylisothianaphtene) in chlorobenzene solution.

the photoexcitations, one can follow the dependence of the absorption features on the modulation frequency of the exciting laser pump. Due to the inhomogeneous character of some conjugated polymer thin films, it is often the case that relaxation kinetics are not effectively described by a single lifetime. On the contrary, they are described by a broad distribution of relaxation times, reflected in a gentle fall-off in the modulation frequency dependent behaviour of the photoinduced absorption feature [4]. Distribution profiles are often used to describe relaxation processes in amorphous and glassy materials [5,6]. In this respect, there are two phenomenological relaxation functions that are used to describe this kind of behaviour: the Kohlraush–Williams–Watts function, which is defined in the time domain and the Havriliak–Negami function, applied in the frequency domain [7]. For this work, photoinduced absorption spectroscopy was performed on poly(5,6-dithiooctylisothianaphtene). To investigate the dynamics of the photoinduced absorption feature, the dependence of the signal on the modulation frequency of the pump laser was checked and evidence for dispersive relaxation behaviour was found. Successfully, an attempt was made to extract the lifetime distribution function, using a simplified Havriliak–Negami relaxation model.

Photoinduced absorption spectroscopy was also performed in the infrared. A second broad absorption feature arises at lower energies and a distinctive infrared active vibration pattern could be seen, from which unambiguously can be concluded that upon photoexcitation charges are created in the conjugated material.

In conclusion, the construction of solar cells with this low band gap polymer as active material is reported. Because of the presence of charges upon illumination of the material, as evidenced from the photoinduced absorption spectra, an attempt was made to make solar cells with the pristine material. Although a clear photovoltaic effect was obtained, adding a strong electron acceptor to the polymer clearly improved the diode behaviour of the cell.

2. Experimental

To spectroscopically characterise the material, films of poly(5,6-dithiooctylisothianaphtene) were prepared by dropcasting from a chlorobenzene solution (1.5% (w/v)) onto precleaned microscopic glass substrates. The optical absorption was measured by a Varian Cary 3G UV-Vis spectrophotometer.

To perform photoinduced absorption spectroscopy (PIA), samples were mounted on a cold finger of an optically accessible cryostat under dynamic vacuum, at a constant temperature of 90 K. The material was excited with the 488 nm line of an Ar⁺ laser. The laser beam was chopped mechanically with a frequency of about 35 Hz providing the reference for a lock-in amplifier (SR 830, Stanford Research Systems), which both records the in-phase (IP) and out-of-phase (OP) components of the measured signal. A 120 W tungsten halogen lamp provided the light for the transmission measurements. The transmission signal (with and without laser light on the sample) was detected with a Si–InGaAsSb photodiode after passing through a monochromator. The spectral dependence of the negative ratio of the photoinduced changes in sample transmission ($-\Delta T$), corrected for the weak photoluminescence, is plotted after normalisation to the transmission (T). To study the recombination kinetics, the dependence of the observed photoinduced absorption feature on the modulation frequency of the laser was checked. For simple mono- and bimolecular recombination processes, the IP-component of the signal is a monotonic decreasing function of the modulation frequency, resulting in half its zero frequency value at $\omega = \tau^{-1}$. At this value, the OP-component reaches its maximum.

In addition, photoinduced absorption spectroscopy was also performed in the IR-region. For this purpose, the material was dropcast from a chlorobenzene solution (1.5% (w/v)) on a ZnSe substrate. In the same way as described previously, the dried polymer film was mounted in a optically accessible cryostat and cooled down to liquid nitrogen temperature. The sample was excited using the 488 nm line of an Ar⁺ laser. The photoinduced absorption was determined by measuring a sequence of 300 repetitions of recording 10 co-added single beam spectra under illumination and 10 co-added single beam spectra in the dark. Combining the resulting spectra the negative differential transmission $-\Delta T/T$ was calculated. For these experiments a Bruker IFS 66S with nitrogen cooled MCT-detector spectrometer was used.

The applicability of the poly(5,6-dithioisothianaphtene) for conversion of solar light into electricity, as well the pristine material as a 1:1 mixture with a soluble fullerene derivative, PCBM ((6,6)-phenyl-C₆₁-butyric-acid), was used as photovoltaic active layer in a state-of-the-art architecture for organic solar cells. For this purpose, the active layer was sandwiched between a transparent anode consisting of a thin indium tin oxide (ITO) layer on glass, which is covered by a 70 nm spincoated layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulphonic acid) (PEDOT:PSS) and an

aluminium electrode. An interfacial thin layer of LiF (0.5 nm) was provided between the active layer and the Al-back electrode, which has been proven to have a favourable effect on the characteristics of bulk heterjunction solar cells [8]. Dark and illuminated IV-behaviour was measured, using a Keithley 2400 source meter. Solar cells were illuminated using a 80 mW/cm² light source, provided by a Steuernagel solar simulator. All measurements were done in N₂ atmosphere.

3. Results and discussion

Poly(5,6-dithiooctylisothianaphthene) was synthesised by non-oxidative, thermal polymerisation of 5,6-dithiooctyl-dithiophthalide, resulting in a polymer material ($M_w = 4950$; 11 units), which has a comparable bandgap of that of polyisothianaphthene itself (1.2 eV). The UV-Vis spectrum of the polymer in solution shows two broad features peaking around 3.88 and 1.85 eV, of which the last one is corresponding to the $\pi \rightarrow \pi^*$ transition (Fig. 1). From the onset of absorption a bandgap of 1.16 eV was determined.

Photoexcitation of poly(5,6-dithiooctylisothianaphthene) in the high energy region resulted in the spectrum displayed in Fig. 2. Two broad spectral features can be distinguished: (i) a bleaching of the ground state absorption around 1.15 eV, which is in excellent agreement with the bandgap determined by UV-Vis spectroscopy; and (ii) a broad absorption band peaking around 0.75 eV due to photogenerated energy states, probably related to the existence of charged excitations. Fig. 3 displays the in phase and out of phase component of the measured signal as a function of laser modulation frequency. Two distinctive aspects strongly indicate the dispersive nature of the recombination behaviour of the excitation: (i) at low frequencies, the IP-component does not level off; (ii) at high frequency, both IP- and OP-components show a very gentle decrease with modulation frequency according to a power law: ω^α ($\alpha_{IP} = -0.73$; $\alpha_{OP} = -0.46$) [4]. Therefore, it was chosen to apply an appropriate model,

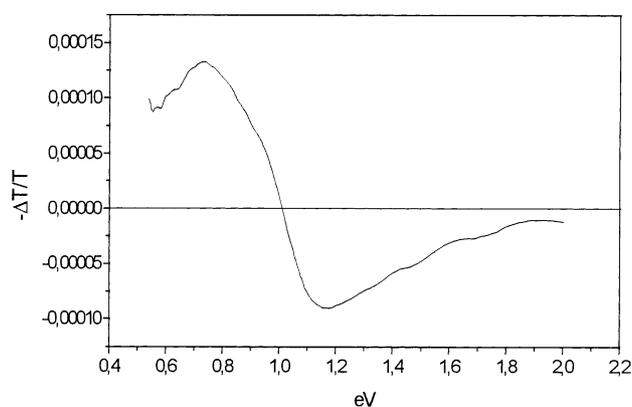


Fig. 2. PIA-spectrum of poly(5,6-dithiooctylisothianaphthene) in film, obtained by dropcasting from chlorobenzene solution.

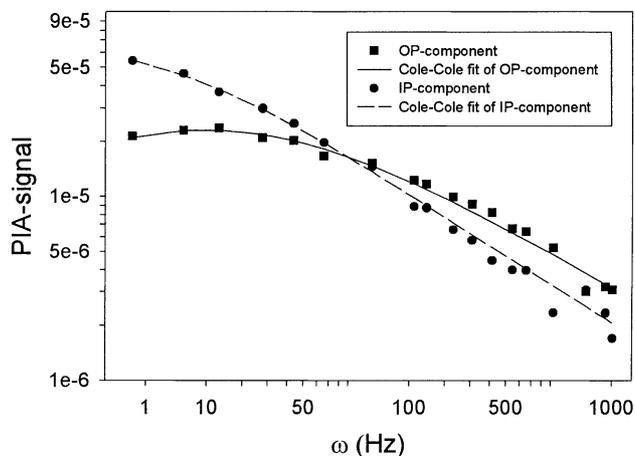


Fig. 3. In phase (IP: circles) and out of phase (OP: squares) component of the PIA-signal as a function of modulation frequency of the laser and their Cole–Cole fits (solid lines).

assuming a distribution function for the recombination times, which all contribute to the overall recombination process following the photoexcitation. In this respect, a Cole–Cole distribution function, a simplified form of the Havriliak–Negami description, was used to describe the observed frequency dependence of the PIA-signal Eq. (1).

$$R(\omega) = \frac{R_0}{1 + (i\omega\tau_0)^\alpha} \quad (1)$$

where $\alpha < 1$ and τ_0 is the mean lifetime of the photoexcited state. $R(\omega)$ represents the density the photogenerated species created upon a modulated photoexcitation at frequency ω . As a consequence, R_0 is the steady-state photoexcitation density at zero frequency. Now, assuming that this relaxation/recombination distribution function is composed of a superposition of a series of independent Debye-like processes, with a continuous normalised distribution of recombination lifetimes, Eq. (2) can be written [6].

$$R(\omega) = \int_{-\infty}^{+\infty} \frac{G(\ln(\tau))}{1 + i\omega\tau} d(\ln(\tau)). \quad (2)$$

The lifetime distribution function G can thus be extracted by experimental determination of $R(\omega)$ and performing the transform, described in Eq. (2). The results of the fits of the IP- and OP-behaviour with increasing modulation frequency, according to the Cole–Cole approximation are displayed in Fig. 3. From this a value of $\alpha = 0.66$ could be retrieved and a mean lifetime $\tau_0 = 50$ ms could be determined. The very good quality of the fit indeed confirms the initial assumption about the dispersive nature of the excitation dynamics in this material. The lifetime distribution function could be extracted and is displayed in Fig. 4.

To get more insight in the nature of the species that are generated upon photoexcitation, photoinduced absorption spectroscopy was performed in the infrared (IR). The resulting spectrum is displayed in Fig. 5. A second broad absorption

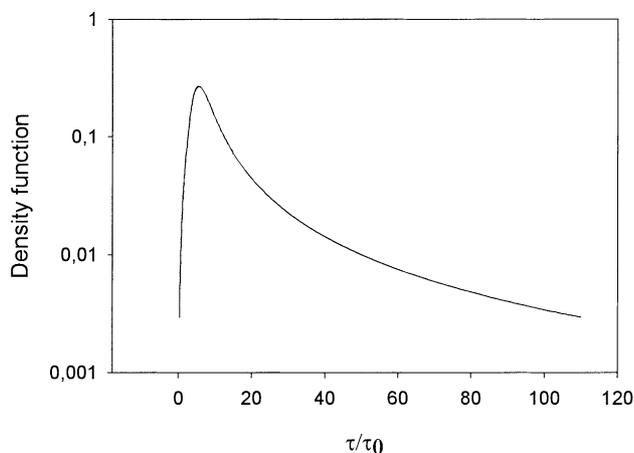


Fig. 4. Lifetime density distribution function, obtained by performing transform, described by Eq. (7).

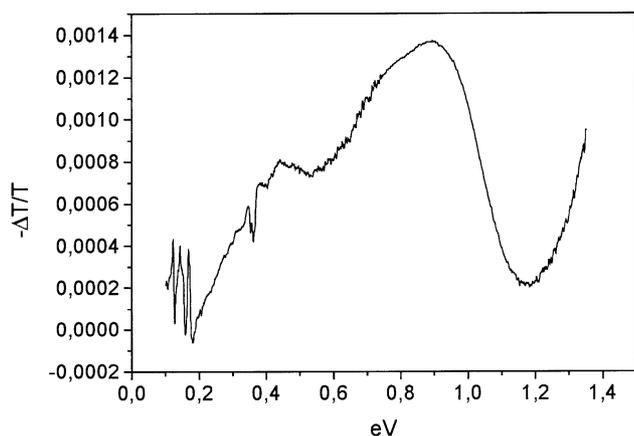


Fig. 5. FT-IR PIA-spectrum of poly(5,6-dithiooctylisothianaphtene) in film, obtained by dropcasting from chlorobenzene solution.

band, peaking around 0.44 eV appears, which is ascribed to the characteristic absorption of the formed excitations. Infrared active vibration bands are observed in the vibrational part of the spectrum, which strongly indicates

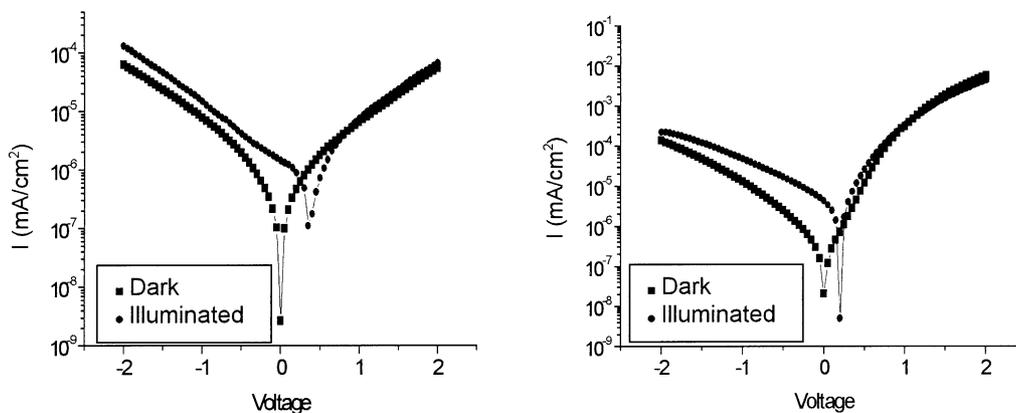


Fig. 6. (Left) Dark (squares) and illuminated (circles) behaviour of the solar cell, with a poly(5,6-dithiooctylisothianaphtene) film as active layer. (Right) Dark (squares) and illuminated (circles) behaviour of the solar cell, with a poly(5,6-dithiooctylisothianaphtene):PCBM (1:1) film as active layer.

the creation of charged species upon illumination. From the absorption pattern, we have solid evidence that the photogenerated species are from polaronic or bipolaronic nature [9].

As the primary aim for the synthesis of conjugated polymers with enhanced absorbing properties, is to build more efficient solar cells, we constructed solar cells using poly(5,6-dithiooctylisothianaphtene) as active material. As the presence of free charge carriers was clearly proven by photoinduced absorption spectroscopy, an attempt was made to build solar cells with only the pristine material, in assumption that both electron and hole mobilities are sufficient to assure a good transport of carriers to the electrodes. As can be observed from the dark IV-behaviour, no rectification could be obtained (Fig. 6). This is mainly caused by the poor film forming properties of the material, leading to shunts and preventing a typical diode behaviour. Despite the low rectification, a clear photovoltaic behaviour can be seen, when illuminating the cell with 80 mW/cm² of white light, of AM 1.5 spectral irradiance (Fig. 6). An open circuit voltage (V_{oc}) of 350 mV and a short circuit current $I_{sc} = 14.25 \mu\text{A}/\text{cm}^2$, could be determined. The latter can be explained by a limited mobility of holes and, especially electrons in poly(5,6-dithiooctylisothianaphtene). Adding PCBM ((6,6)-phenyl-C₆₁-butyric-acid), as a strong electron acceptor, in a 1:1 ratio by weight with respect to the polymer, a clear improvement is obtained in the diode behaviour of the cell, as can be concluded from Fig. 6. The cell yields a lower $V_{oc} = 200$ mV, compared to its PCBM-free analogue. The I_{sc} , on the contrary, increases by a factor of three, attaining a value of $42.07 \mu\text{A}/\text{cm}^2$. This effect can be explained by a better transport of electrons in the PCBM-part of the bulk heterojunction network, following a plausible electron transfer from the excited conjugated polymer to the fullerene derivative. Finally, the photocurrent action spectrum was recorded from the poly(5,6-dithiooctylisothianaphtene):PCBM (1:1) solar cell and plotted together with the UV-Vis absorption spectrum of the polymer (Fig. 7). Despite the low external quantum efficiencies that could be

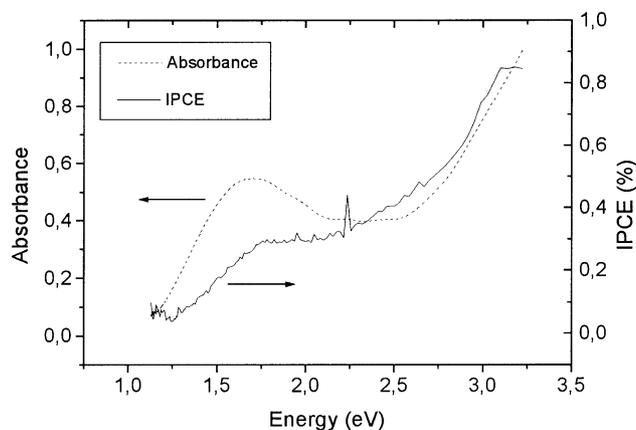


Fig. 7. IPCE-spectrum of the solar cell with a poly(5,6-dithiooctylisothianaphthene):PCBM (1:1) as active layer (solid line) and UV-Vis absorption spectrum of poly(5,6-dithiooctylisothianaphthene) (dotted line).

reached, a clear contribution of the photocurrent can be attributed to the polymer as evidenced from the simultaneous onset of optical absorption and photocurrent.

4. Conclusions

Poly(5,6-dithiooctylisothianaphthene), a low band gap polymer, was investigated by means of photoinduced absorption spectroscopy. Evidence was found that the photo-generated species are from polaronic or bipolaronic nature, characterised by dispersive recombination properties, which

can be described by a lifetime distribution function. Solar cells, constructed with the pristine material and a mixture with PCBM, as active layer showed a photovoltaic effect, however, adding a strong electron acceptor clearly improved the diode behaviour.

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