Optical and ESR studies on poly(3-alkylthiophene)/fullerene composites for solar cells


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Abstract

Optical measurements (absorption coefficients, photoluminescence) and light-induced electron spin resonance (ESR) techniques were used to study photoinduced charge generation and charge transfer in conjugated polymer / fullerene composites. The quenching of fluorescence by C60 gives a first indication of an effective charge transfer from P3DDT to C60. At 77 K two kinds of ESR signals were identified, one of polaron (P+) on the polymer chain and one of radical anion (C60−) of fullerene. The relaxation rates of generated paramagnetic centres were estimated by microwave power saturation studies. Moreover for the first centre (P+) two contributions to the ESR signal were observed: a permanent and a photoinduced one. The light intensity dependence of the photoinduced P+ and C60− ESR signals is of bimolecular type (I−2). Solar cells based on P3DDT/C60 and P3DDT/PCBM are prepared and characterised.

Keywords: solar cells, polythiophene, conjugated polymers; fullerene, light-induced electron spin resonance (ESR)

1. Introduction

Conjugated polymers like poly(3-alkylthiophenes) are a subject of great research interest due to their wide range of applications in polymer electronic devices such as light-emitting diodes (LEDs), field effect transistors (FETs), lasers and organic solar cells [1]. The discovery of ultrafast charge transfer in p-conducting polymer/fullerene composites by Sariciftci and Heeger in 1992 [2] brought an crucial milestone in the field of polymer solar cells.

LESR is a promising method to investigate charge transport mechanisms in conducting polymers and polymer-acceptor composites, which play a central role in the photophysics of polymer solar cells [3]. In this paper poly(3-dodecylthiophene) (P3DDT)/C60-fullerene composites are investigated.

2. Experimental

C60-fullerene (98%) and regioregular poly(3-dodecylthiophene) (P3DDT) were purchased from Aldrich, PEDOT:PSS (poly(3,4-ethylenedioxythiophene)) doped with poly(styrenesulfonate) is a commercial product of Bayer AG. PCBM ([6,6]-phenyl-C61-butaic acid methyl ester) comes from the laboratory of J.C. Hummelen at the University of Groningen.

The absorption coefficients were obtained from the analysis of ellipsometric spectra, measured with a Woollam VSAE® variable angle spectroscopic ellipsometer with rotating analyser.

The photoluminescence spectra were measured by exciting the samples with the 459 nm line of an Ar+ laser at 80 K. For ESR experiments films of following composites were studied: P3DDT/C60 2:1 and 3:1 wt. ratio. The EPR experiments were carried out using a BRUKER X-band spectrometer ELEXSYS E500 at 77K. Photolysis was performed with ILA 120-1 Ar+ laser operating at λ = 488 nm. For the solar cells a layer from PEDOT:PSS (~100 nm) followed by the photoactive layer of P3DDT/C60 (2:3 wt.}

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ratio) or P3DDT/[6,6]-PCBM (1:2 wt. ratio) were spincoated (80-100 nm) onto an ITO polyester foil.

Intermediate drying steps after each layer were inserted. The cells were completed by an aluminium top electrode deposited by vacuum evaporation. A source monitor unit (SMU) HP 4142 was used to record the I/V curves by illuminating with 14 mW/cm² white-light of a xenon lamp.

3. Results and Discussion

The absorption coefficients of pure P3DDT compared with that of a blend of P3DDT/C₆₀ (1:1 wt. ratio) are presented in Fig.1b. The optical absorption is a simple superposition of the optical absorption spectra of the two components. That means there is no ground state doping by C₆₀.

The film photoluminescence spectra of P3DDT, P3DDT/C₆₀ and P3DDT/PCBM are depicted in Fig.1a. The spectra of the blends show clearly a photoluminescence quenching effect caused by the presence of fullerences. This is an indication of the charge transfer from P3DDT to fullerene as described by Sariciftci [1,2,4] for composites of p-conducting polymers and fullerenes derivatives.

At 77 K two LERS signals were observed with light excitation at different light intensities. Typical ESR spectra with two relative concentrations of donor and acceptor are shown in fig.2a. The g-factor of the low field signal has a weak anisotropy with an average value of 2.0024. It can be attributed to positive polarons at the polymer chains (P⁺) [5]. The g-factor of the high field component is about 2.000 which is typical for C₆₀ radical anion. It was also found dramatic differences in values of microwave power saturation for both radicals (for C₆₀ radical it is more than 10 times higher ). Spin-lattice and transverse relaxation times were determined by the saturation method. We obtained T₁ ≈ 8·10⁻⁹ sec. for P⁺. We then estimated that C₆₀ spin-lattice relaxation time is at least 10 times shorter than T₁ of P⁺. In general the light intensity dependence of the light-induced P⁺ and C₆₀ LERS signals is described by a function S ∝ I^α where S is the double integrated ESR signal intensity and α is an independent parameter. One example is shown in fig.2b.

Fig.3 shows the I/V characteristics of two solar cells based on P3DDT/C₆₀ or PCBM in a logarithmic scale. Cell I has an open circuit potential V_{oc} ≈ 580 mV, short circuit current I_{sc} ≈ 0.46 mA/cm², fill factor FF~0.3 and overall energy conversion efficiency η ~ 0.65 %. Cell II gives V_{oc}~525 mV, I_{sc}~1.2 mA/cm², FF~0.38 and η ~ 1.7 %.

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References