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LESR study on PPV–PPE/PCBM composites for organic photovoltaics

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Abstract

Photoinduced charge carrier generation and charge transfer in the new conjugated poly(phenylene vinylene)–poly(phenylene ethynylene) (PPV–PPE) copolymers mixed with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) were studied by LESR technique at 77 K. The effective charge separation has been verified by two ESR signals belonging to positive polarons on the polymer chains and to radical anions of PCBM molecules, respectively. The relaxation times T_1 and T_2 of the anion radical of PCBM were estimated by anisotropic linewidth analysis and microwave power saturation studies. The low temperature recombination of long living charge carrier pairs after cessation of photoexcitation was studied and described by a tunnel model in which the recombination time depends on the distances between charge carrier pairs. Results on PPV–PPE/PCBM were compared with those of a poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO–PPV)/PCBM composite.

Keywords: Electron spin resonance; Conjugated polymers; Fullerene derivatives; Charge recombination; Tunnel model; Polymer solar cells

1. Introduction

In polymer solar cells the dominating processes are the generation of charge carriers by light, the separation of charge carrier pairs, and the motion of charge carriers to the electrodes. An effective method for investigation of the light-induced charge carrier generation, of the separation and the recombination of charge carrier pairs is the electron spin resonance (ESR). Such ESR application is called light-induced ESR or LESR [1]. This method strongly differs from time-domain measurements during light induced formation of transient free radicals in the liquid state [2] and in solids [3] because in the topical LESR study we cannot made use of the signal enhancement by chemically induced dynamic electron polarisation (CIDEP). Different important information can be obtained by analysis of LESR spectra of light induced anion/cation radicals. Firstly, the main is the registration of appearance of cation/anion radicals after light excitation and hence, the charge separation processes with the estimation of charge carriers concentration. Secondly, the analysis of spectroscopic Zeeman splitting factor (g-factor) gives information about the symmetry of the paramagnetic centre and the average g-factor value on the deviation from free electron g-factor $\Delta g = g - g_e = \lambda/\Delta E_g$, where λ is the spin-orbit coupling constant and ΔE_g is the polymer band gap, and hence about the most probable position (spin density maximum) of polaron localisation on the polymer chain. This is really possible because of the significant difference of λ magnitude for main chain atoms of conjugated polymer (29 cm^{-1} for C, 78 cm^{-1} for N and 382 cm^{-1} for S) and ΔE_g may be directly estimated by the light absorption experiment. Thirdly, the LESR signal linewidth analysis gives essential information about: (a) spin–lattice and spin–spin relaxations, (b) exchange and

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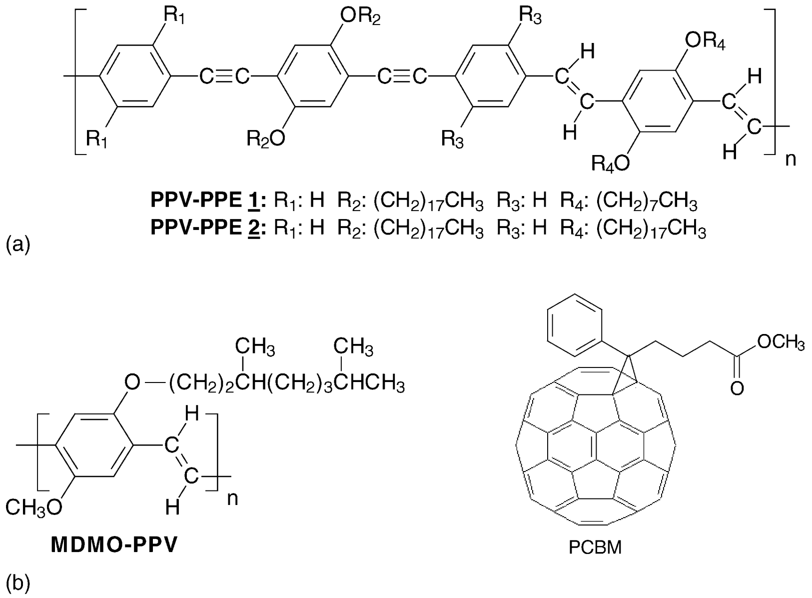

Fig. 1. (a) Chemical structures of poly(phenylene vinylene)–poly(phenylene ethynylene) copolymers **1** and **2**. (b) Structure of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and MDMO–PPV.

dipole–dipole interactions, (c) anisotropic broadening, connected with the anisotropy of *g*-factor components and slow molecular rotational motion, (d) inhomogeneous broadening connected with unresolved hyperfine LESR signal structure and so on. Fourthly, the time dependence of the signal amplitude gives information on the charge separation kinetics after light on and intrinsical charge recombination kinetics after light off.

In the present paper, we report on results of LESR studies of the two derivatives **1** and **2** of poly(phenylene vinylene)–poly(phenylene ethynylene) copolymers (PPV–PPE) (Fig. 1a) with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) applied as composites with a weight ratio of 1:2, and compare them with the data of MDMO–PPV/PCBM with the same weight ratio. MDMO–PPV and PCBM (Fig. 1b) are the well-known materials for plastic solar cells, for example, reviewed by Brabec et al. [4]. Apart from poly(3-hexylthiophene) MDMO–PPV/PCBM shows the best efficiency in donor–acceptor polymer composite materials in plastic solar cells [4–6].

Generally, the main intention of our study is a comparison of the microscopic properties of the different systems prepared on identical conditions. This is a first step to estimate the suitability and perspective of these polymer types components of solar cell devices.

2. Experimental

The PPV–PPE copolymers have been synthezised by Egbe et al. [7] and their chemical structures are shown in the Fig. 1a. The optical and cyclovoltammetric characterisation of the PPV–PPE copolymers have been done earlier and were reported in paper [8]. MDMO–PPV was purchased from Aldrich and PCBM came from the laboratory of Hummelen [9]. The composite films were prepared via drop casting using chlorobenzene as solvent and polyester foil as substrate. The samples have been dried under vacuum at room temperature. The ESR spectra were recorded by a Bruker X-band spectrometer ELEXYS E500 without and with illumination by an Argon ion laser at 488 nm. All measurements have been carried out at 77 K.

3. Results and discussion

3.1. Spectroscopic and relaxation parameters

The effective charge separation has been verified by two LESR signals, which were observed only under light excitation. In the case of the PPV–PPE (**1** or **2**)/PCBM composites the signals can be attributed to positive polarons (P^+) on the polymer chain with a *g*-factor $g_{\mathrm{iso}} \approx 2.0028$ and to radical anions of PCBM molecules with $g_{\mathrm{iso}} \approx 1.9995$ (Fig. 2). Polaron LESR spectra were observed only at a significant low microwave power of a few μW and can be recorded only with a low signal/noise ratio (see also in [10]). Contrary to the situation in P3DDT/C_{60} [11a,b] dark signals were absent in all experiments with PPV–PPE/PCBM for both types of radicals. Consequently the fact of the charge separation processes after light excitation of PPV–PPE was clearly detected. Because of the saturation of the LESR signal of polarons in all three studied composites the belonging signals are very weak and cannot disturb the signal of the PCBM radical anions by an overlap. An example is given in Fig. 2. (The spectra of the PPV–PPE **2**/PCBM composite are similar