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Studies of Photoinduced Charge Transfer in Conjugated Polymer-Fullerene Composites by Light-Induced ESR

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Abstract. In this work we present comparative studies of the photoinduced electron transfer (PIT) in a number of conjugated polymer/fullerene composites and in pure components by using light-induced electron spin resonance. PIT from the polymer onto fullerene in the composites results in the appearance of two LESR lines: i) $g=2.0025$, attributed to the positive polaron on the polymer chain and ii) $g=1.9995$ originating from the fullerene anion-radical. These signals have different spin-lattice relaxation times with different temperature dependencies, the low field line possessing the longer relaxation time. The amount of light induced charges is proportional to the square root of the excitation light intensity, which indicates bimolecular recombination of polarons. Both lines have reversible light-induced ESR components and persistent light-induced contribution attributed to trapped polarons.

INTRODUCTION

Photoinduced electron transfer (PIT) in composites of conjugated polymers (CP) and fullerenes is a recently discovered phenomenon enabling the production of photovoltaic (PV) devices. Upon addition of few percent of a strong electron acceptor, such as fullerene into conjugated polymer, the following effects have been found: photoluminescence quenching in the subpicosecond range (1), dramatic increase of photo-conductivity (2), and improved photovoltaic effect (3). These effects are interpreted within a model of ultrafast electron transfer from polymer onto fullerene molecules with the formation of pairs of $(D^+...A^-)$ - type which have a high rate of dissociation and small rate of recombination. To demonstrate the electron transfer in

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alkoxy-PPV/C₆₀ and alkyl-PT/C₆₀ composites, light-induced ESR (LESR) has been applied in (4) and revealed the appearance of two signals. These signals were attributed to radical anions of the fullerene and positive polarons (P⁺) on the polymer. LESR spectra of composites made from fullerenes and thiophene oligomers consist also of two signals (5). However, the LESR spectrum of CP/fullerene composites is not clearly understood. First, the line shape is not very well described. Therefore g-factors cannot be precisely determined. Second, the origin and the fate of polarons in this charge separation process is not clear. In undoped PPV film, a dark ESR was observed additional to a LESR signal and attributed to positive polarons (6). The CT in pristine PPV films was observed by using sensitive PL-detected magnetic resonance (PLDMR) techniques (7). Therefore, one would expect in the ESR spectrum of a pristine CP a correlated amount of photoinduced negative and positive charged radicals. In contrast to (6), the PPV used in (7) did not show any dark or light induced ESR signal. Further, the amount of photoinduced spins of each type is not well determined. Integration of the LESR curve (4) implies an equal amount of C₆₀⁻ and P⁺ photoinduced paramagnetic species in MEH-PPV/C₆₀. The presence of P⁺ on the chain is therefore ruled out.

EXPERIMENTAL

We used a commercial Bruker EMX (X-band) ESR spectrometer with nitrogen-flow cryostat, allowing measurements between 77K to 300K. Excitation light was provided from an Ar⁺-ion laser. Different CPs and their composites with pure and functionalized fullerenes were investigated. Polymers studied were: 3,7-dimethyloctyloxy-methyloxy-poly-p-phenylene-vinylene (PPV) and poly-(3,4-di-[(R,S)-2-methylbutoxy]thiophene (PMBT). PPV is soluble in xylene at elevated temperatures. The fullerenes were: 1-(3-cholestanoxycarbonyl)-propyl-1-phenyl-[6,6]C₆₁ (denoted as PCBM) and C₆₀ (99.5%) purchased from MER Corp. Films were produced from solutions with the following ratios: PPV/PCBM (1:3 weight ratio), PPV/C₆₀ (3:1) and PMBT/PCBM (1:1). Further experimental details are described elsewhere (8). We distinguish between a prompt LESR signal ("light-on" signal corrected on "light-off" and "dark" signals), and a persistent one ("light-off" corrected on the "dark", and/or "annealed" signals). Correction on the "annealed" ESR is necessary to ensure that no irreversible photochemical process occurred in the sample. Note that the composites we studied here were also used for the fabrication of the solar cells (9).

RESULTS AND DISCUSSION

Pristine PPV films do not show any dark or light-induced ESR signal. This indicates a high degree of purity of the polymer and a low concentration of paramagnetic defects. Films of PCBM do not show any dark ESR signal either, but exhibit a very weak LESR signal. The nature of this signal is not yet clear. A possible explanation could be a PIT of intramolecular type. Addition of PCBM to PPV gives

rise to a dramatic increase of the LESR signal (Fig. 1). Since the particular lineshapes cannot be deduced from the spectrum, we can only speculate that the LESR spectrum may correspond to two paramagnetic species with different g-factors.

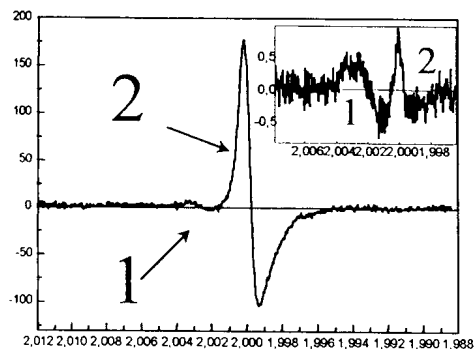


FIG. 1. LESR of Alkoxy-PPV/PCBM composite. 1 - Polymer⁺ line, 2 - Fullerene⁻ line. (inset - 20 μW)

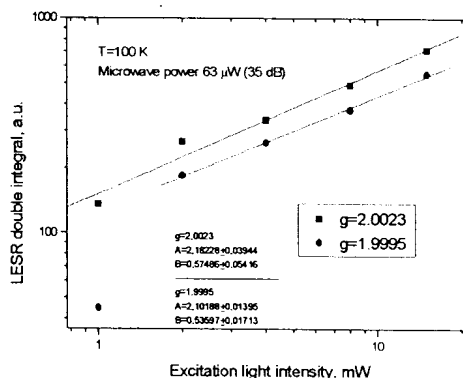


FIG. 2. Light intensity dependence of prompt component of LESR in Alkoxy-PPV/PCBM.

Spectra with similar parameters were also found for the other composites, PMBT/PCBM and PPV/C₆₀.

The lineshape distortion, in general, can be due to different mechanisms. Explanations for this lineshapes are: g-factor anisotropy in randomly oriented samples or the Overhauser effect. These assumptions are not yet ruled out, and will be a subject of future work. However, the very existence of two distinct light-induced species is proved by the following set of experiments.

The inset to Fig. 1 shows the LESR spectrum at $P_{\mu\omega} = 20 \mu\text{W}$. A different microwave power saturation behaviour of the two LESR signals is clearly observed. The saturation of the low-field line occurs at much lower microwave power, which indicates a slower relaxation. Increasing the temperature from 90 to 200 K shifts the saturation towards higher microwave powers, which means shorter spin relaxation times and is an indicative for a phonon-assisted relaxation. Therefore, the difference in the microwave saturation behaviour allows to distinguish between the two overlapping lines: at high power of 200 mW we only see the high-field line, at power lower than 20 μW the low-field signal is observable only. Detailed studies of the saturation behaviour of this spectrum (8) revealed g-factors for particular lines as: 2.0023 (low-field line) and 1.9995 (high-field line). The high-field line is attributed to the fullerene anion-radical, and the low-field line is attributed to P⁺ on the polymer chain.

A further consequence of the described difference in saturation behaviour is that the amounts of light-induced spins responsible for the LESR, as deduced by double integration of LESR spectrum, will only be valid at lowest microwave powers, when both lines are not saturated, i.e. below 50 μW.

After illumination, the LESR signals do not disappear completely. At $T < 200$ K some of the paramagnetic species remain detectable for many hours. Only heating up (annealing) the sample to room temperature in the dark eliminates these ESR signals. Therefore, we distinguish between the prompt, or reversible, component, which disappears immediately after the light is off, and the persistent component of LESR signal. Fig. 2 presents the dependency of the prompt contribution on the power of the excitation light. First, one can see that nearly equal amounts of P^+ and C_{60}^- are contributing to the prompt LESR signal. Second, they depend on the illumination power I as $I^{1/2}$. This is a clear evidence for bimolecular relaxation, i.e. for a process of mutual recombination within the photoinduced radical pairs. Contrary, the persistent components ("light-off" corrected on the "dark") of ESR signals do not depend on the light intensities, and the amount of persistent P^+ species is much higher than that of persistent C_{60}^- (for details see (8)). The independence on the excitation light intensity indicates that these contributions to the ESR signal originate from spins trapped by some defect states. Therefore it is related to the amount of the defects in the samples. Thermally assistant escape from the traps is responsible for the annealing of persistent LESR signals. Non-equal amount of persistent spins clearly points to the presence of some other kind of charge carriers in the system, for instance, negative polymer polarons.

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