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Time resolved photoinduced electron spin resonance studies on conjugated polymer fullerene mixtures in solution

M .C. Scharber, C. J. Brabec, V. Dyakonov[a], N. S. Sariciftci

Physical Chemistry, Johannes Kepler University Linz, 4040 Linz, Austria

Abstract

We report results of cw- and transient ESR investigations on mixtures of P3OT (poly-3-octylthiophene) and C_{60} in solution. In pristine C_{60} solutions with xylene or ODCB (*ortho*-dichlorobenzene) as solvent the dominant LESR signal is the C_{60} triplet. In solutions of P3OT and C60 in xylene a change of the decay dynamics of the C_{60} triplet state is observed. Photoinduced C_{60}^- has not been observed in the investigated solutions.

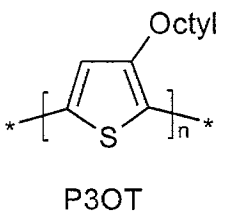
Keywords: Electron Spin Resonance, Polythiophene and Derivatives, Fullerenes and Derivatives

1. Introduction

Time resolved light induced electron spin resonance (TRLESR) is a useful technique for the investigation of paramagnetic intermediates produced by optical excitation. This method has been applied frequently to study the different steps of charge separation in photosynthetic reaction center.
We apply this method to investigate photoexcitation processes in conjugated polymer/fullerene mixtures. In these solid state composites a photoinduced charge transfer occurs on the timescale of 100fs and is one of the fastest ever reported [1]. The quantum efficiency of this process is therefore close to unity. As a consequence of this high quantum efficiency other relaxation paths for the photoexcitation like luminescence or triplet generation are quenched.

2. Experimental

The experiments were performed on P3OT / C_{60} mixtures (0.5mg/ml / 5 10^{-4}M) and C_{60} ($5\cdot10^{-4}$M) in xylene and ODCB.



P3OT

Fig. 1: Chemical Structure of P3OT

C_{60} (MER 99,5%) was used as received. Master solutions of C_{60} were filtered using 200nm RC-filters. Samples were deoxygenated in the ESR tube by subsequent freeze-pump-thawing cycles from argon bubbled solutions and sealed under vacuum.

The schematic experimental set-up is shown in Fig. 2. The measurements were carried out on a Bruker EMX spectrometer (X-band). The material under investigation is illuminated by a Nd-YAG pumped OPO (excitation wavelength 420-700 nm). The pulse duration is 3ns. The typical pulse energy is ~1mJ at a repetition rate 31.7 Hz. The signal is taken directly from the detection diode, amplified (6.5MHz bandwidth) and fed into a digital oscilloscope. In general several hundred transients are recorded and averaged to improve signal to noise ratio. All measurements were carried out at room temperature.

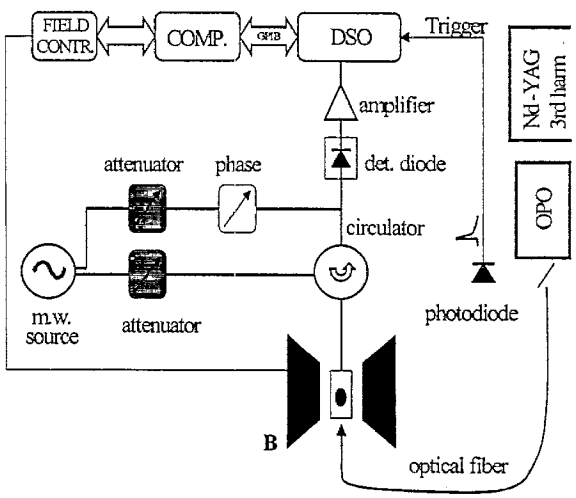


Fig. 2. Experimental set-up of the time resolved ESR (see text).

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Fig. 4. Time evolution of the $^3C_{60}$ ESR line intensity in xylene solutions of C_{60} and P3OT/C_{60}

3. Results and discussion

In solutions of P3OT in xylene (0.5mg/ml) no detectable light-induced ESR-Signal has been observed by cw as well as time resolved measurements. The main relaxation routes for the photoexcited P3OT are the radiative $(S_1)\rightarrow(S_0)$ relaxation (photoluminescence) and the $(S_1)\rightarrow(T_1)$ intersystem crossing. It is known from photoinduced absorption (PIA) studies, that polyalkylthiophenes undergo efficient intersystem crossing to a triplet state[2]. However we could not detect the polymer triplet LESR signal with direct observation.

In P3OT in ODCB (0.5mg/ml) we observe one very weak LESR line in cw-detection with a g-value of $g \approx 2.0026$. From cw PIA studies [2] it is known that polarons are photogenerated in this system. We therefore attribute the LESR signal to the polaron on the polymer chain. In contrast to the findings for the P3OT in ODCB, we do not observe a LESR signal for a P3OT solution in xylene (0.5mg/ml). This result indicates that the polarity of the solvent plays an important role in the photoinduced charge generation process. The charge transfer can either be of intrachain character, or into the solvent.

The dominant photoinduced signal in C_{60}/xylene or C_{60}/ODCB solutions is the fullerene triplet. This signal, arising from the triplet ESR, can be detected by cw- as well as by transient LESR studies. In Fig. 3 the reconstructed ESR spectrum of the C_{60} triplet, 3 μs after the laser flash, is shown. The bandwidth of the signal is 0.3 G and its g value of $g \sim 2.0015$ is in accordance with literature[3][4].

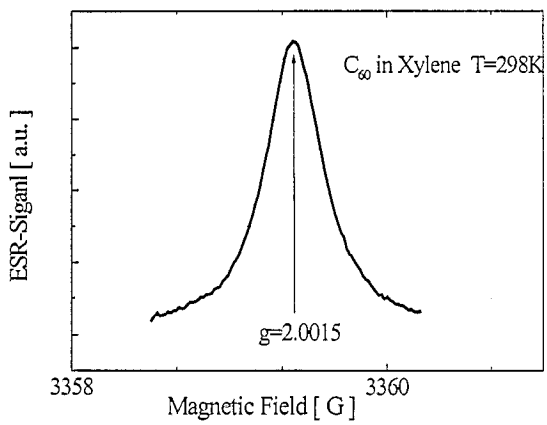

Fig. 3. ESR-spectrum of the photoexcited C_{60} triplet, detected using TRESR for the time delay of 3μs after the laser flash.

The signal recorded in a mixture P3OT/C_{60} in Xylene (0.5mg/ml, $5\,10^{-4}$M) by cw- and transient technique is assigned again to the C_{60} triplet state (g=2.0015) [3],[4]. Fig. 4 shows the time evolution of the photoexcited $^3C_{60}$ state in P3OT/C_{60} solution as compared to the results obtained in pristine C_{60} solutions. The presence of polymer changes the decay characteristic significantly. Single exponential fits to the decay of the transient signal of the transient signal give a relaxation time of 22 μs for the signal of the P3OT in xylene and 2.3 μs for P3OT/C_{60} in xylene.

We also investigated the photoexcited response of P3OT/C_{60} in ODCB (0.5mg/ml, $5\,10^{-4}$M) by ESR measurements. Although ODCB supports charge transfer due to its high polarity no light induced ESR signal of C_{60}^- has been observed. At a g value of g=2.0015 a weak photoinduced signal with a linewidth of appr. 0.3 G is observed. This line is again interpreted as the $^3C_{60}$ signal.

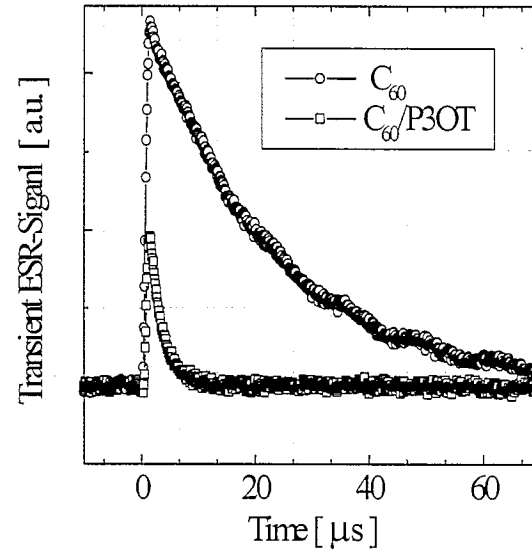

Fig. 4. Time evolution of the $^3C_{60}$ ESR line intensity in xylene solutions of C_{60} and P3OT/C_{60}

4. Conclusion

Our cw-ESR results are in good agreement with PIA studies on P3MBET[2]. In solutions of P3OT/C60 investigated here photoexcited C_{60}^- has not been observed by the LESR method. Addition of P3OT to C_{60} in xylene or ODCB accelerates the decay of the C_{60} triplet transient LESR signal.

5. References

[a]New address: Energy and Semiconductor Research, Carl von Ossietzky University Oldenburg, 26111 Oldenburg, Germany

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