

Light-induced ESR studies in conjugated polymer-fullerene composites

G. Zorinants^a, V. Dyakonov^b, M. Scharber^a, C.J. Brabec^a, R.A.J. Janssen^c, J.C. Hummelen^d and N. S. Sariciftci^a

^aPhysical Chemistry, Johannes Kepler University of Linz, A-4040, Linz, Austria

^bEnergy and Semiconductor Research, University of Oldenburg, D-26129 Oldenburg, Germany

^cLaboratory of Macromolecular and Organic Chemistry, TU Eindhoven, PO Box 513, 5600 MB Eindhoven, The Netherlands

^dOrganic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract

In this contribution we discuss photo-induced electron transfer in conjugated polymer/fullerene composites and compare this with light induced effects in pure components. Two overlapping LESR lines are observed, from positive polarons on the polymer chains and negative charges on the fullerene moieties. Microwave power saturation studies show different relaxation times for these two spins, giving clear evidence for independent spins. The unusually high relaxation rate of the fullerene monoanionic spins is of intrinsic origin and discussed in terms of a splitting of the T_{1u} level by a Jahn-Teller type distortion as proposed in the literature. We observed two distinct contributions to LESR signals, a prompt and a persistent one. Excitation light intensity dependence of the prompt contributions into P^+ and C_{60}^- ESR signals is of bimolecular type ($I^{0.5}$) and implies the mutual annihilation within ($P^+ \dots C_{60}^-$) pair. The persistent contribution is found to be excitation intensity independent and proposed to originate from deep traps due to disorder.

Keywords: Electron spin resonance, poly(phenylene vinylene), fullerene, heterojunctions

1. Introduction

Photoinduced electron transfer in composites of conjugated polymers and fullerenes is a recently discovered phenomenon on which the photovoltaic action of the electronic devices is based [1,2]. The charge transfer occurs within subpicosecond range and the separated state is metastable. This may be described as superfast formation of pairs of ($D^+ \dots A^-$) - type which have a high rate of dissociation and low rate of recombination. The analysis of the lineshape of the previously reported LESR signals [1] is difficult due to their strong overlap. Further, the assignment of the particular LESR signal to radical anions or radical cations requires the knowledge of g-factors. To get a closer look to photoexcitations in conjugated polymer/fullerene composites we performed systematic LESR studies.

2. Experimental

We used a Bruker EMX (X-Band) ESR spectrometer with variable temperature cryostats. In the following, the ESR signal will be referred to as: “dark” signal, “light-on” signal, “light-off” signal and “annealed” signal, respectively. Polymer reported here was: poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) which is soluble in xylene at elevated temperatures. The preparation and characterization of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{61} (denote as PCBM) is described elsewhere [3]. C_{60} (99.5%) was purchased from MER Corp. We studied films made of following

composites: MDMO-PPV/PCBM (1:3 weight ratio), MDMO-PPV/ C_{60} (3:1).

3. Results and discussion

Neither a “dark” ESR, nor LESR signals have been found in films of pure MDMO-PPV in the temperature range of 77-300K and at excitation power between 0.5 to 100mW. No “dark” ESR signal can be found in PCBM film, too. A dramatic enhancement of the LESR is observed when mixing both substances together. Two overlapping LESR lines with microwave power dependent intensities are observed. Fig. 1 shows an LESR spectrum of MDMO-PPV/ C_{60} at three values of the microwave power. By applying the microwave power of 200mW one can almost suppress the low-field LESR line due to microwave saturation (upper curve in Fig. 1). In contrast, the intensity of the high-field LESR signal vanishes to zero at 20 μ W. Thus, the different saturation behaviour enables us to separate two overlapping LESR lines from different paramagnetic species and to determine the individual g-values as $g=2.0025$ and $g=1.9995$. When the excitation light is switched off, the intensity of ESR signals in conjugated polymer/fullerene composites decrease significantly, but not completely. Therefore, we distinguish between the prompt component of LESR, which disappears after the light is off, and the persistent component, which remains for hours at low temperatures after the illumination is off. The persistent component, however, can be eliminated when one heats the films to room temperature (annealing). Prompt components of the two LESR signals are plotted in Fig. 2 as a function of the intensity of the excitation light. The prompt

LESR components originate from nearly equal amount of spins and show the $I^{0.5}$ power dependence on the intensity of excitation light for both LESR lines (see Fig. 1). Hence, we may conclude that the two photoinduced charges annihilate each other with bimolecular dynamics. In contrast, the persistent component is nearly independent on the intensity of previously applied light. The g-factor below 2 is supposed to be a distinct ESR feature of

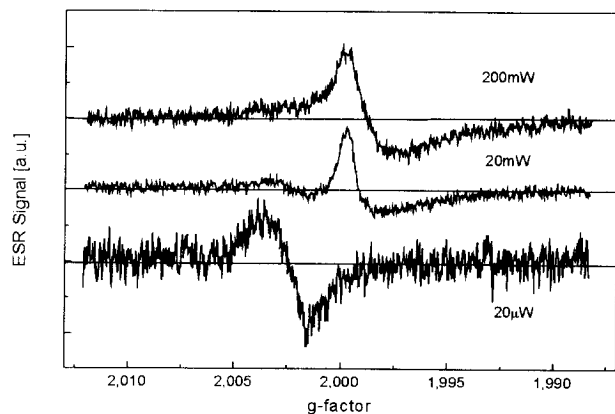


Fig.1. LESR spectrum of MDMO-PPV/C₆₀ composites at different values of microwave power. T = 100 K.

monoanionic fullerene molecule. The LESR signals at $g=1.9995$ was observed in all composites studied in this work. Therefore this line is assigned to the C₆₀⁻ radical. The LESR line with $g=2.0025$ is attributed to the positive polaron⁺ on the conjugated polymer backbone.

It is quite possible that in the radical pair of type (P⁺...C₆₀⁻) the two unpaired spins (1/2 each) are interacting. This is apparently the case in a number of fullerene containing salts, such as TDAE-C₆₀, where one ESR signal with the mean value of g-factors is observed instead of two ESR signals. [4,5]. In conjugated polymer/fullerene composites we did not find any difference in the lineshapes and g-factors despite of large variation of the relative concentrations of conjugated polymers and fullerenes from 1:3 to 3:1. On the other hand, the vast majority of the photoinduced spins are created as geminate pairs in close proximity which should interact with each other, either by exchange or by dipolar mechanisms. Since we do not see any of these interactions, it is safe to conclude that *the mobile polarons on the conjugated polymer backbone are moving away from the fullerene anions in a timescale faster than above mentioned exchange times, i.e. $t < 10^{-9}$ s.* This rapid spatial separation of the photoinduced charges is proposed to be responsible for the unusual long lifetime of the charge separated state in these systems. It is remarkable that the LESR line for the fullerene anions does not saturate within the experimentally available microwave power range. We state that the *high relaxation rate of the fullerene anion spin is an intrinsic property.* A Jahn-Teller type distortion on the fullerene molecule would split the T_{1u} level and result in two closely spaced energy levels available for the anion [6,7]. Thermal averaging over such states would provide a dominant relaxation channel for the spin and would

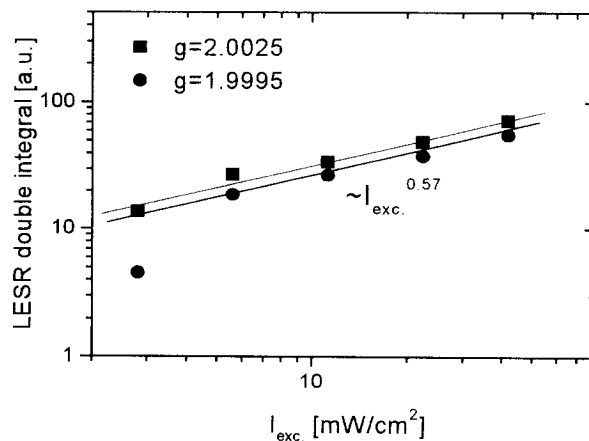


Fig.2. Dependencies of magnitude of the prompt LESR contributions of MDMO-PPV/PCBM composite on the intensity of the exciting light.

account for the linewidth effects as well as the non-saturation in our studies.

5. Conclusion

Different saturation behaviour of photogenerated paramagnetic species in composites allowed us to separate their contributions to the LESR spectrum. We distinguish between a fast decaying contribution into P⁺ and C₆₀⁻ LESR signals and a slowly decaying one. Excitation light intensity dependence of the prompt contributions into LESR signals is of bimolecular type and implies the mutual annihilation within the radical pairs. The unusually high relaxation rate of the fullerene anion spins is possibly arising from a Jahn-Teller type distortion on the fullerene molecule splitting the T_{1u} level.

6. Acknowledgements

We thank H. Neugebauer, E. Frankevich for valuable discussions. This work was supported by FWF, Austria, Project No: P 12680-CHE) and by a FWF Lise Meitner fellowship M00419-PHY for V. D.. Support by University Linz for G.Z. and by Russian Foundation for Basic Research, Grant 97-03-32164a are gratefully acknowledged.

7. References

1. N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 258: (1992) 1474.
2. N. S. Sariciftci and A. J. Heeger, in *Handbook of Organic Conductive Molecules and Polymers*, H. S. Nalwa (ed.), John Wiley & Sons, 1996.
3. J. C. Hummelen, B. W. Wright, F. Lepec and F. Wudl, *J. Org. Chem.*, 60 (1995) 532.
4. P. M. Allemand, et al., *J. Am. Chem. Soc.*, 113 (1991) 2780.
5. B. Gotschy, *Phys. Rev.*, B 52 (1995) 7378.
6. D. Dubois, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 114 (1992) 6446.
7. J. Stinchcombe, A. Penicaud, P. Bhyrappa, P. D. W. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 115: 5212, 1993.