PHOTOINDUCED ELECTRON TRANSFER AND TRANSIENT STATES IN ORGANIC COMPOSITES STUDIED BY ESR

H.-K. Roth¹*, A. Konkin², V. I. Krinichnyi³ and M.Schroedner¹

¹ TITK Institute Rudolstadt, Department Functional Polymer Systems and Physical Research, Breitscheidstr. 97, D-07407 Rudolstadt, Germany (*e-mail: <u>roth@titk.de)</u>

²Ilmenau University of Technology, Institute for Micro- and Nanotechnologies, Gustav-Kirchoff-Str.7, D-98693 Ilmenau, Germany (e-mail: <u>alexander.konkin@tu-ilmenau.de</u>)

³Institute of Problems of Chemical Physics, Russian Academy of Sciences, N. N. Semenov Avenue 1, Chernogolovka 142432, Russia (e-mail: <u>kivirus@gmail.com</u>)

Introduction

By this contribution we will show how we can support by electron spin resonance (ESR or EPR) the development of polymer photovoltaic and related fields of organic electronics. Essential processes in organic photovoltaic are the excitation of molecules, the electron transfer, the generation of charge carrier pairs, and the motion of charges. To the study of all mentioned processes ESR can support.

The contributions of ESR are especially high if one has the possibility to use various measuring frequencies, that is, to employ besides the ordinary X-band with 9.5 GHz, for example, the K-band (24 GHz), and/or the Q-band (35 GHz), the W-band (94 GHz), or the D-band (140 GHz). The higher the frequency, the better is the spectral resolution [1-2]. In the solid state the ESR signals are usually influenced by inhomogeneous line broadening caused by unresolved hyper-fine structures and by anisotropic broadening connected with the anisotropy of the g-factor components. K-, Q-, W- and D-band measurements allow to determine the spectral parameters g_i and ΔB_i (line widths) with better accuracy.

As known in polymer electronics thin layers of semiconducting polymers are applied showing often strong anisotropic structures and properties. The ESR offers the opportunity to study the anisotropic behaviour direct on the polarons P^+ generated and moving in polymer chains. If the polymer chains in polymer films exhibit some degree of order and orientation the same is valid also for the polarons. The macroscopic anisotropy of polymer thin film morphology can be

confirmed by angular-dependent ESR experiments as made recently, for example, by K-band investigations on films of P3HT/PCBM blends [3].

LESR (light-induced ESR)

According to the topic of the paper especially <u>L</u>ESR spectra – that is ESR measured during <u>light</u> illumination - are in the center of interest. The following information can be obtained by analysis of LESR spectra [4]:

- 1. The main is the detection of cation and anion radicals during and after light excitation including the determination of the estimation of charge carrier concentration.
- 2. The analysis of the spectroscopic Zeeman splitting factor (g-factor) gives information about the localization of the paramagnetic centre and on the symmetry. The deviation of the average g-factor from the g-factor g_e of the free electron; $\Delta g = g - g_e = \lambda / \Delta E_g$, where λ is the spin-orbit coupling constant and ΔE_g is the polymer band gap, informs about the most probable position (or spin density maximum) of polaron localization on the polymer chain. This is possible because of the significant difference of the λ value for C-atoms of a conjugated polymer ($\lambda = 29 \text{ cm}^{-1}$ for C) from that of other atoms ($\lambda =$ 78 cm⁻¹ for N and 382 cm⁻¹ for S)
- 3. The LESR signal line-width analysis gives essential information about
 - (a) spin-lattice and spin-spin relaxation times T_1 and T_2 , respectively,
 - (b) exchange and dipole-dipole interactions,
 - (c) anisotropic broadening, connected with the anisotropy of g-factor components,
 - (d) inhomogeneous broadening due to unresolved hyperfine signal structure.
- 4. The time dependence of the signal amplitude gives information on the kinetics of charge generation and charge recombination processes.

Examples of LESR-spectra of a poly(3-dodecylthiophene){P3DDT} /PCBM {phenyl-C61butyric acid methylester} composite registered during laser irradiation at 77 K shows Fig. 1 [2]. The spectra of two overlapping ESR signals are seen where the left hand signals belong to diffusing polarons P^+ and the right hand signals are attributed to the PCBM anion radicals C_{61}^- .



Fig.1 <u>left</u>: X-band LESR spectra of polarons P^+ in P3DDT and of PCBM anion radicals, a) measured (S₁) + simulated (S₄) 1st derivative spectrum, b) absorption spectrum calculated from S₁, S₅ = extracted P^{+} signal, c) schematic representation of anisotropic absorption signals and g-factor components Fig.1 <u>right</u>: D-band ESR spectra

of polarons P^+ in P3DDT

LESR studies have been made also on PPV-PPE/PCBM and PPV-MDMO/PCBM at 77 K [4]. The strong saturation effect of the polaron signal gives the opportunity to investigate the PCBM anion radical de facto separately and in detail. Measured and calculated spectra dominated by the anion radicals are seen in Fig. 2. In the first step the absorption spectrum had been calculated



Fig. 2; LESR spectra of a 1:2 composite of PPV-PPE/PCBM registered during laser irradiation $(\lambda = 488 \text{ nm}, P = 15 \text{ mW})$ at 77 K (in the X-band) (a) measured and calculated first derivative spectrum, (b) constructed absorption spectrum, (c) schematic representation of the anisotropic absorption signal of the PCBM anion radical (calculated with a small line-width) and positions of the determined g-factor components PPV-PPE = poly(phenylene)vinylene)-poly(phenylene ethynylene)

by integration of the experimentally first derivative ESR signal. In the second step these absorption spectrum were simulated as a glass type spectrum with a Lorentzian line shape.

The complete analysis allows to eliminate the anisotropic line width broadening and to estimate the effective spin-spin relaxation time T_2 (and by means of it also the spin-lattice relaxation time T_1). T_1 of the anion radical is significantly influenced by the surrounding structure. (In MDMO-PPV $T_1=7.4 \ \mu s$, $T_2=68 \ ns$; in PPV-PPE $T_1=9.4 \ \mu s$, $T_2=65 \ ns$.) That in MDMO-PPV T_1 is shor-

ter than in PPV-PPE composites means that the exchange of spin energy with the surrounding occurs in MDMO-PPV faster than in PPV-PPE composites.



Fig. 3; Rise and decay of the LESR signal of PCBM anion radicals C_{61} in two different 1:2 composites measured at 77 K

The upper signal amplitude belongs to MDMO-PPV / PCBM composite and the lower one to a PPV-PPE composite

MDMO-PPV = poly[methoxy (dimethyloctyloxy)-phenylene vinylene

In Fig. 3 is to see that also the kinetics of the PCBM anion radical depends strongly on the polymer surrounding. The decay curves can be described successfully by a tunnel model in which the recombination frequency depends only on the distance between the charge carriers. The same model has been used before for the study of organic solar cell composites [6].

The generation of radical pairs normally occurs in the femto- to nano-second time domain. There -fore the time dependence of the ESR signal intensities is mainly caused by their recombination. Different activation energies obtained for P^+ and C_{61}^- are evidences for independence of the motion of the polarons and C_{61} anion radicals [5]. There are also different spin dynamics in this system, namely the polaron diffusion along and between the polymer chains and the dominant rotational diffusion of the PCBM anion radicals.



Similar LESR studies on thin films of M3EH-PPV with the fullerene dimmer PCBM- $C_{120}O$ as electron acceptor have been carried out by X- and K-band ESR at 77 and 120 K [7].



Fig.5 ; (Light-dark)-LESR spectra of an 1:1 M3EH-PPV/PCBM- $C_{120}O$ composite film registered during Xelamp illumination Left: X-band, 9.4 GHz Right: K-band, 24 GHz S₀ measured and simulated spectra, S₁ – S₃ spectra extracted from S₀, S₁ - spectra of polaron P^{+.} S₂ - spectra of C₁₂₀O anion radical, S₃ spectrum of PCBM-C₆₁ anion radical

It was found that the isotropic g-factor $g_0 = (g_x+g_y+g_z)$ of the PCBM-C₁₂₀O anion radical obtained in this blend is with $g_0 = 1.9996$ close to the g-factor of PCBM and of the electrochemical reduced $(C_{120}O)^{-}$, but it does not coincide with the analogous parameter of the triplet state radical $(C_{120}O)^{2-}$ [8].

ESR give also the opportunity to study the spin and charge dynamics in conjugated polymers like P3DDT [2] and also in P3DDT/PCBM composites with photo-generated radical pairs [5] especially if measuring at various frequencies [9] and as a function of temperature.

TR-ESR (time-resolved ESR)

If we would like to know

- what happens in detail after the absorption of light quanta in the polymer blends,
- from which excited state the photo-induced electron transfer will be introduced,
- the mechanism of the generation of charge carrier pairs and their motion, separation and energy exchange,

in that case the time-resolved ESR is a suitable measuring method. Such TR-ESR studies of the photo-induced electron transfer in poly(3-dodecylthiophene){P3DDT}/maleic anhydride {MA} blend in THF solution have been carried out [10]. The blends have been excited by laser flashes of about 20 ns and the ESR spectra were registered between 100 ns and 10 μ s after the flash.

By TR-ESR investigations a great part of the information on the photo-induced ET (electron

transfer) and with it on the formation of radical ion pairs we get from the irregular population of energy levels which are below 1 μ s far away from the population in the thermal equilibrium. The reason for the unusual level population is the so-called Chemically Induced Dynamic Electron Spin Polarization (CIDEP).

One reason for CIDEP is the Triplet Mechanism (TM). Absorption of a photon by a donor molecule M yields an excited singlet state ${}^{1}M^{*}$ which undergoes intersystem crossing to an excited triplet state ${}^{3}M^{*}$ whose Zeeman levels T_{+1} , T_{0} and T_{-1} have different energy in the magnetic field of the ESR spectrometer. The ISC is spin selective and creates spin polarization in the triplet state molecule. If the ET and the radical pair formation from a triplet state takes place more quickly than the deactivation by phosphorescence or by the spin-lattice relaxation of the triplet state (${}^{3}T_{1}$) the unusual spin polarization will be transferred in the douplet states of the radical ions and often we will observe emission spectra which are independent of the magnetic field position of the observed ESR lines. (The radical system acts as a microwave emitter until the occupation of the thermal equilibrium is reached.)

A second reason for CIDEP is the so-called Radical Pair Mechanism (RPM) which effects changes between singlet and triplet states (S-T-mixing) during separation, diffusion and reencounter of radical pairs. It effects that the spin polarisation in the low-field region is different from that in the high-field region.

Some times CIDEP effects are to observe also in the usual continues wave ESR spectra if these are registered during steady state illumination with light of a Xenon lamp or a laser as published, for example, in [11, 12]. If the effect of RPM is observed it informs us that radical <u>pairs</u> are formed also if we detect only the spectrum of one radical.

The usual continues wave ESR register the spectra with modulation technique and the first derivative of the absorption spectra will be observed as seen, for example, in Fig.s 1, 2, 5...of this paper. For the TR-ESR measurements no field modulation was used but a direct detection have been applied. The transient ESR signals were digitized by a fast digital oscilloscope synchronized with the laser pulses. Photo-excitation was performed by an excimer laser Compex 205 operating at 308 nm and with a pulse repetition rate of 10 Hz. The pulse energy of the Laser was 100 – 200 mJ and the pulse duration was about 20 ns. The time resolution of our detection system is approximately 50 ns.

The effect of TM and the influence of RPM can be seen in Fig. 6 for radicals of maleic anhydride (MA) and in Fig. 7 for radicals in P3DDT/MA [10].





Fig. 6 ; TR-ESR spectra of 3 various radicals of MA radicals and the belonging splitting diagrams a) in THF solution, b) in butanol The H-containing solvents are in this contribution labelled as LH. The electrical neutral radicals R_1 and R_2 are formed by attachment of H⁻ and L⁻ via abstraction of H from the LH-molecule ($R_1 = HMA$, $R_2 = LMA$). In butanol $R_3 = MA^{-}$ is formed by the attachment of an electron from a solvent molecule.

Fig. 7; TR-ESR spectra (S_1 , S_2) of radicals in blends from P3DDTand MA solved in THF. S_1 and S_2 are measured 0.35 µs after the laser flash. For the spectrum S_2 about two times more P3DDT has been in the solution than for S_1 . S_3 is the fitted spectrum of S_2 . S_4 and S_5 are extracted spectra from S_3 belonging to the anion radical $R_3 = MA^-$ and the polaron P^+ , respectively.

In Fig. 7 the field position H_1 of the central lines of R_3 corresponds to g = 2.0037 for the anion radical. The position H_2 corresponds to g = 2.0022 which is in agreement with the isotropic g-factor of the polaron P^+ , estimated from measurements on a film of P3DDT/PCBM [5].



Fig. 8:

The measured time dependence of the polaron signal. Although the signal to noise rate is with $S/N \approx 3.5$ low the time dependence is clear and allows in a fitting process the estimation of the relaxation times T_1 and T_2 . The low spin-spin relaxation time T_2 is caused mainly by the high hole mobility of P^+ in the conjugated polymer P3DDT and is of the same order of magnitude as estimated by a saturation method in a solid PDDT layer [5].

Complete three-line TR-ESR spectra of MA⁻⁻ have been published by Honma et al, [13] and by He et al. [14], however, not with a conjugated polymer as donor but with a low molecular compound.

Results regarding ET in P3DDT/MA [10].

The simultaneous detection of both ion radicals, the polaron P^+ and the anion radical R_3^- informs us that in solutions of P3DDT/MA blends in THF the most probable version of the formation of R_3 anion radicals will be via the electron attachment from the photo-excited poly(3-dodecylthiophene). The emissive character of the spectra informs that the dominating CIDEP mechanism is the triplet mechanism (TM). That means a precursor of the photo-induced electron transfer is a triplet state generated via intersystem crossing from an excited singlet state.

Additionally the polarization by the radical pair mechanism (RPM) occurs, however, with opposite sign in comparison with the electrically neutral radical pairs R_1 and R_2 where the RPM by S-T₀ mixing effects clear E/A spectra with emissive signals in the low field region and enhanced absorption signals in the high field region of the spectra. In case of the electrically charged radical pairs the polarization is not only influenced by the exchange interaction $J \le 0$ but especially by dipole-dipole or Coulomb interaction (CI). In such ion radical pair systems a "J ≥ 0 " behaviour is possible [15], and in the above mentioned system with MA⁻⁻ radicals the S-T₋₁ mixing seems to be the most plausible polarization mechanism [13]. Also in the case of the radical pair R_3^- and P^+ a "J ≥ 0 " behaviour is probably influencing the spectra of $R_3 = MA^-$. This behaviour is caused by dipole-dipole or Coulomb interaction (CI) within the geminately generated ion radical pairs. This is in agreement with the theoretical treatment of Shkrob [15].

The CI is larger in donor/acceptor systems with smaller molecular radius of acceptors than in that with larger acceptor molecules. The CI promotes the back electron transfer, and as a result, limits the efficiency of the charge separation process. The small CI in polymer blends with the acceptor fullerene is probably the reason for the high efficiency of the photo-induced electron transfer in blends of conjugated polymers with fullerene derivates.



Additional experiments with two other conjugated polymers have been carried out with the aim to compare the resonance positions and the spin polarisation (CIDEP) of polarons in different polymers. The spectra are seen in Fig. 9. The spectrum S_3 of Fig. 9 is identical with the spectrum S_2 of Fig. 7.

Concerning the spectra S_1 and S_2 of Fig. 9 it should be pointed out that the TR ESR spectra have been recorded in the presence of a small concentration (c ≈ 0.001 M) of C₆₀- and C₇₀-PCBM, respectively, especially because in pure MA/M3EH-PPV solution the signal/noise rate was too low to register polaron spectra of sufficient intensity. The resonance positions of polarons P₂⁺ (in M3EH-PPV) is shifted to the low field direction by 0.12 mT in respect to P_1^+ (in P3AT). Different g-factors of polarons in P3AT and in M3EH-PPV are the reason for the displacement.

P3OT (Poly-3-octylthiophene) and P3DDT have the same polymer backbone and the polarons have about the same isotropic g_0 -factor of around 2.0021. However, the polarons P_2^+ in M3EH-PPV have a g_0 -factor value $g_0 = 2.0029$. (In Fig. 9 signals of the anion radicals of C₆₀- and C₇₀-PCBM are de-facto not to see because of the small concentration. Its g-factors are about 2.000 and 2.0028, respectively.)

For the spectrum S_5 an about 10-times higher C_{60} -PCBM concentration (c ≈ 0.01 M) have been applied in the blend with MA-P3OT. The strong absorption signal is caused by excited triplet states of C_{60} -PCBM. It should be pointed out that the ${}^3(C_{60}$ -PCBM)* spectrum has been certainly registered by us also in THF solution without MA and polymer, and for example, by Scharber et al. [16]. For the spectrum S_5 the blend with MA has applied mainly because of the opportunity of precise line position determination relative to the spectral lines of R_1 and R_2 of maleic anhy-dride. The CIDEP signals of ${}^3(C_{60}$ -PCBM)* and of the observed polarons have opposite signs. Therefore on the field position labelled with P_2^+ in the spectra S_1 and S_2 are really the resonance signals of P_2^+ and can not be attributed to signals of anion radicals of PCBM .

Concluding remarks

With this contribution it has been shown that ESR spectroscopy allows a deeper insight in the physical processes of the electron transfer and in chemical reactions of radical ions and neutral radicals. By means of ESR spectroscopy relatively fast can be proofed

- whether in a new donor/acceptor material combination photo-induced electron transfer occurs or not
- how various additives influence the electron transfer and the electron back-transfer
- whether in the selected material combination electron back-transfer happens and how fast it is
- how special material treatments like, for example, annealing, solving and re-crystallization influences that process

By means of TR- ESR spectroscopy one can study

- excited triplet state properties of donors:
 - electron transfer rate
 - excited triplet / singlet ground state kinetics,
 - estimation of relative sublevels triplet state populations

• transient precursor states and kinetics of ion radical formation in donor-acceptor organic composites under the light excitation

Without doubt, ESR spectroscopy contributes not only to the fundamental research but it is also of practical worth for developers of solar cell materials and for related subjects of development.

References

- [1] a) Roth, H.-K., Krinichnyi, V. I.; Synth. Met. 137 (2003) 1431-1432
 b) Krinichnyi, V. I., Roth, H.-K.; Appl. Magn. Reson. 26 (2004) 395-415
- [2] Konkin, A., Roth, H.-K., Krinichnyi, V. I., Schroedner, M., Aganov, A., Nazmutdinova, G., Sensfuss, S.; Proceedings TPE 04 (2004) 167-170
- [3] Konkin, A., Roth, H.-K., Scharff, P., Aganov, A., Ambacher, O., Sensfuss, S.; Solid State Communications 149 (2009) 893-897
- [4] Konkin, A. L., Sensfuss, S., Roth, H.-K., Nazmutdinova, G., Schroedner, M., Al-Ibrahim, M. Egbe, D. A. M.; Synth. Met. 148 (2005) 199-204
- [5] Krinichnyi, V. I., Roth, H.-K., Sensfuss, S.; Schroedner, M., Al-Ibrahim, M.; Physica E 36 (2007) 98-101
- [6] Schultz, N. A., Scharber, M. C., Brabec, C. J., Sariciftci, N. S.; Phys. Rev. B. 64 (2001) 245210
- [7] Konkin, A., Ritter, U., Scharff, P., Roth, H.-K., Aganov, A., Saricftci, N. S., Egbe, D.A.M.; Synth. Met. 160 (2010) 485-489
- [8] Balch, A. L., Costa, D. A., Fawcett, W.R., Winkler, K.; J. Phys. Chem. 100 (1996) 4823-4827
- [9] Mizoguchi, K., Kuroda, S. in: Nalwa, H. S. (Ed), Handbook of Organic Conductive Molecules and Polymers, Vol. 3, John Wiley & Sons, New York 1997, pp. 251-317
- [10] Konkin, A., Sensfuss, S., Roth, H.-K., Scharff, P., Ambacher, O. Aganov, A., Schroedner, M.; J. Molecular Liquids 141 (2008) 54-61
- [11] Roth, H.-K., Keller, F., Schneider, H.; Hochfrequenzspektroskopie in der
 - Polymerenforschung, Akademie-Verlag, Berlin 1984
- [12] Roth, H.-K., Wünsche, P.; Acta Polymerica 32 (1981) 491-511
- [13] Honma, H., Murai, H. Kuwata, K.; Chem. Phys. Letters 195 (1992) 239-242
- [14] He, G., Li, X., Chen, C., Xu, G.; J. Photochemistry and Photobiology 108 (1997) 155-158
- [15] Shkrob, I. A.; Chem. Phys. Letters 264 (1997) 417-423
- [16] Scharber, M. C., Brabec, C. J., Dyakonov, V., Sariciftci, N. S.; Synth. Met. 101 (1999) 356