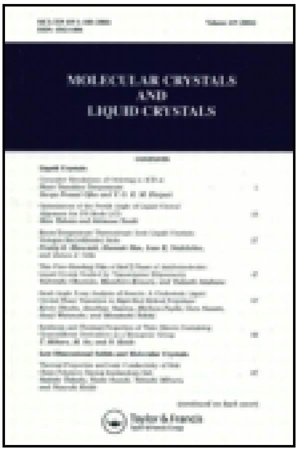

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

ESR and EDMR Applied to PPV Related Compounds

George Barbosa Da Silva [a], Lucas Fugikawa Santos [b], Rodrigo Bianchi [b], Roberto Mendonça Faria [b] & Carlos Frederico De Oliveira Graeff [a]

[a] DFM - FFCLRP, USP, Av. Bandeirantes 3900, Ribeirão Preto, 14040-901, Brazil

[b] IFSC, USP, CF 369, São Carlos, 13560-970, Brazil

Version of record first published: 29 Oct 2010

To cite this article: George Barbosa Da Silva, Lucas Fugikawa Santos, Rodrigo Bianchi, Roberto Mendonça Faria & Carlos Frederico De Oliveira Graeff (2002): ESR and EDMR Applied to PPV Related Compounds, Molecular Crystals and Liquid Crystals, 374:1, 135-140

To link to this article: http://dx.doi.org/10.1080/713738239

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 135-140

1058-725X/02 $12.00 + .00

ESR and EDMR Applied to PPV Related Compounds

GEORGE BARBOSA DA SILVA[1],
LUCAS FUGIKAWA SANTOS[2], RODRIGO BIANCHI[2],
ROBERTO MENDONÇA FARIA[2] and
CARLOS FREDERICO DE OLIVEIRA GRAEFF[1]

[1]*DFM - FFCLRP - USP, Av. Bandeirantes 3900, 14040-901 Ribeirão Preto, Brazil and*
[2]*IFSC-USP, CP 369, 13560-970 São Carlos, Brazil*

In this work the electron spin resonance (ESR) and electron detected magnetic resonance (EDMR) are applied in MH-PPV and MEH-PPV, respectively. The ESR measurements revealed that there is a change of lineshape and a clear reduction of spin density on MH-PPV degraded by light and air. This result is in agreement with the fact that the spin density resides predominantly on vinylic carbon. The EDMR measurements in MEH-PPV LEDs provided evidences that there is a spin-dependent fusion of two polarons to spinless bipolaron.

Keywords: ESR; EDMR; PPV; polaron; bipolaron.

INTRODUCTION

Among the various techniques of investigation, electron spin resonance (ESR) has been used intensively, since it enables one directly to “see” the polaron that plays a major hole in the physics of conducting polymers. In the other hand, electric detected magnetic resonance (EDMR) has been used to study the recombination process in a wide array of semiconductors. In this work, a comparison between ESR and EDMR signals from different functionality PPV materials will be present, as well as their dependency on different degradation processes.

PROCEDURES

The poly (2-metoxy-5-(2'-etil-hexiloxy)-1,4-phenylene vinylene) (MEH-PPV) and poly(2-metoxy-5-hexiloxy)-1,4-phenilene vinylene)) (MH-PPV) samples were obtained through standard procedures. The MH-PPV was measured by ESR X-band (9.4 GHz) and by K-Band (24GHz) as freestanding films. A quartz halogen illuminator with a fiber optic was used for LESR experiments. The MEH-PPV was measured by EDMR in a light-emitting diode ITO/MEH-PPV/Al. Measurements were done using a X-Band spectrometer in the temperature range of 145 K to 300 K. The spin-dependent changes of conductivity were measured by modulating the static magnetic field (H_0) and by using lock-in detection of the resonant current changes.

RESULTS AND DISCUSSION

Typical normalized signals in K-Band of MH-PPV are shown in figure 1. In figure 1 as grown and a sample exposed to light and air for 300 hours are presented. In both cases the line shape is clearly anisotropic. As can be seen in figure 1 the anisotropy is intensified when the sample is degraded by light in presence of air. Notice also a small shift in g-value as function of degradation process: g = 2.0027 for non-degraded sample and g = 2.0030 for degraded sample.

There is strong evidence that the spin density resides predominantly on vinylic sites [1]. The degradation process has been assigned to a substitution of C=C by a C=O at the vynilic site [2]. Thus in agreement with this simple model we should expect a decrease in spin density in degraded samples of MH-PPV. The spin density was estimated by standard procedures [3] and compared as function of light exposure time. It was found 7×10^{17} spins/g in non-degraded samples and 2×10^{17} spins/g in samples that were exposure to light for 150 hours or more. The results are in good agreement with the mentioned simple model. Our results indicate that there are approximately 10^{-4} spin/monomer in our samples. This value is higher than those found by Murata *et al.* [4] which found 10^{-5} spins/monomer in PPV. LESR has been observed in our samples at room temperature as seen in figure 2.

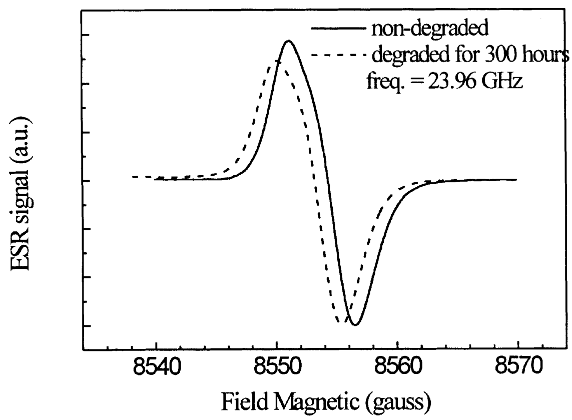

FIGURE 1 Typical K band ESR signals coming from a degraded MH-PPV (dashed line) and a non-degraded sample (solid line).

For these measurements the sample is kept at constant temperature, and at constant magnetic field and light is irradiated for a certain period of time. The magnetic field is chosen so that we are in the maximum peak of the first derivative of the ESR signal. As can be seen the ESR signal increase after illumination by about 10%. As the sample is left again in the dark, the signal starts to decrease to its initial value. According to reference [4] the LESR signal comes from the increase in the number of polarons released by light from traps. However in the case of reference [4] the LESR could only be observed below T=140 K. We believe that the fact the we are observing such a signal at room temperature comes from the interaction of polarons with water or oxygen present in our samples, this would also explain the higher spin density observed in our samples. More work is underway.

A typical EDMR signal from MEH-PPV LED is shown in figure 3. The EDMR signal amplitude is typically 10^{-5}, and only observed at forward bias, for V >10 volts. It is a quenching signal, or in other words, the conductivity of the device decreases in resonance. This signal is very similar to what is found in the literature for PPV based LEDs, and it is assigned to the spin-dependent fusion of two polarons to a spinless bipolarons [5].

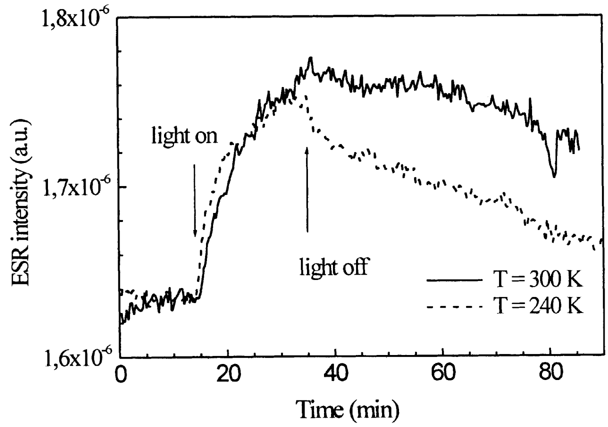

FIGURE 2 Time response of LESR taken from the upper-field peak position of the first derivative ESR signal.

Notice that two lines (solid and dashed) shown in figure 1 are the signals with different phase setting of the lock-in amplifier φ and φ + 90°. Using appropriate φ, as can be seen in figure 3, the signal is clearly seen as composed of two components, both with a g factor of approximately 2.003, but different line widths (ΔH_{pp}). The first dominant component has a ΔH_{pp} of 7 gauss, while the second component has 3 gauss. In this case there are two paramagnetic levels involved with different spin relaxation time T_1 that can be associated with different structural properties. According to the literature [6] the microwave-induced transitions can be basically of two types: anomalously spin dependent and normally spin dependent. The normally spin-dependent was the first model developed for EDMR and it predicts that the EDMR signal has dependence with temperature of $1/T^2$ [7]. In the anomalously spin independent on temperature and for T > 220 K, it follows $1/T^2$. These show us that this MEH-PPV may be an interesting system to study the models of EDMR.

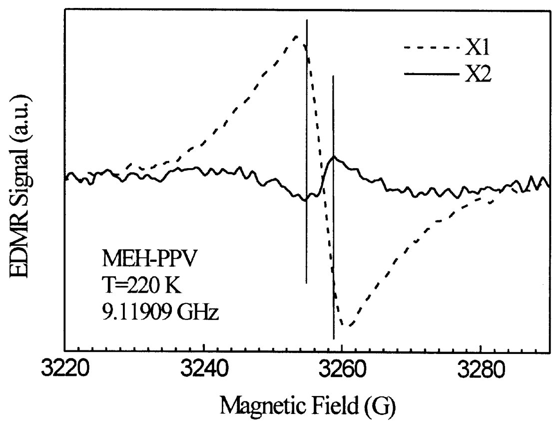

FIGURE 3 A typical EDMR spectra for MEH-PPV LEDs. The signal represented by the continuous line has been multiplied by 2.

CONCLUSIONS

In this work the photogeneration and recombination of polarons in PPV based materials and devices have been studied using LESR and EDMR. The degradation of MH-PPV has also been studied using ESR. Our results indicate a decrease in ESR signal after exposing the sample to light and air. This decrease gives support to the model of degradation of these polymers assigned to a substitution of C=C by a C=O at the vynilic site. A LESR signal has been observed even at room temperatures in MH-PPV. This result, which is partially in contradiction with previous studies in the literature, indicates that water or oxygen may have an important role in the LESR phenomena. EDMR has been observed in MEH-PPV LEDs. From the temperature dependence of the EDMR signal we observed an indication of a transition from anomalously to normally spin dependence. Thus MEH-PPV LEDs could be model systems to study spin dependent transport.

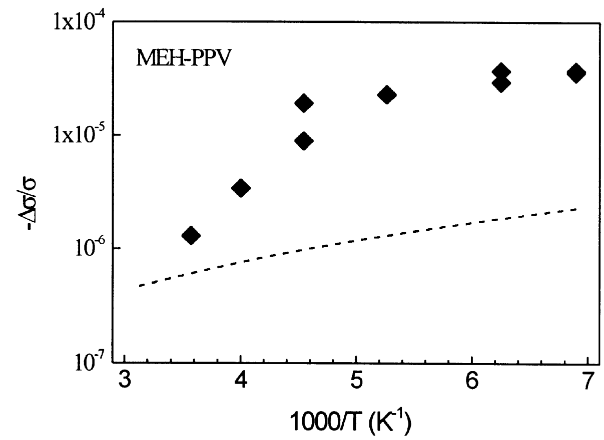

FIGURA 4 EDMR signal vs. the 1/T. The dashed line is the calculated upper limit for the EDMR in the normally spin-dependent model.

AKNOWLEDGMENTS

This work was carried out with support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

REFERENCES

[1] S. Kuroda *et al.*, Chem. Phys. Let. **325** 183 (2000).
[2] H. Cumpston and K. F. Jensen, J. Appl. Pol. Science **69** 2451 (1998).
[3] C. P. Poole, Jr., Electron Spin Resonance, A Willey-Interscience Publication, 2nd ed. (1983).
[4] K. Murata *et al.*, Chem. Phys. **227** 191 (1998).
[5] L. S. Swanson. *et al.,* Phys. Rev. B **46** 15072 (1992).
[6] B. Movaghar *et al.*, Phil. Mag. B **41** 141 (1980).
[7] C. F. O. Graeff *et al.*, Phys. Rev. B **49** 11028(1994).