

PHOTOEXCITATIONS IN CARBAZOLYL SUBSTITUTED POLYDIACETYLENE (PDA) FULLERENE COMPOSITES

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Abstract

It is well known that many non-degenerate ground state conjugated polymers like PPV derivatives show an ultrafast electron transfer to fullerenes upon photoexcitation. In this work we investigate the photoexcited states of fullerene - carbazolyl substituted PDA composites and compare them to the pristine components. We report the finding of photoexcited spins as well as charges in one asymmetric carbazolyl substituted PDA, the CPDO (poly(1-N-carbazolyl-penta-1,3-diyne-5-ol)). While PIA FTIR measurements show strong IRAV bands for this material, LESR studies on the same samples reveal photoexcited spins. Although CPDO samples show a dark ESR signal, which is well known for the topochemical polymerization, photoexcitation studies clearly reveal, that the LESR does not come from photoinduced polymerization. No enhancement of LESR signal is found for mixtures of CPDO and fullerenes, in our case a special solubilized fullerene, PCBM. We conclude therefore, that even PDA which show photoexcited charges and spins, do not exhibit a photoexcited charge transfer to fullerenes.

Keywords: Electron Spin Resonance, Photoinduced Absorption Spectroscopy, Polydiacetylenes, Fullerenes and Derivatives

1. Introduction

An important result from the photophysical studies on conjugated polymer/fullerene composites is the complete absence of photoinduced interaction between fullerenes and red form polydiacetylenes [1]. Spectroscopic results from absorption - emission spectroscopy, transient and cw photoinduced absorption studies as well as photoconductivity studies show, that in contrast to the high quantum efficiency photoinduced electron transfer definitely established in the PPV as well as P3AT composites with C₆₀ [2], photoinduced electron transfer from red phase PDA to fullerenes is absent. Comparison of the ionization potentials of the PDAs (around 5.5 eV [3]) are very close to that of P3ATs and PPVs (5.1 - 5.2 eV). Even though these results seem to indicate that PDAs are not a class of conjugated polymers suitable for the study of the electron transfer process to fullerenes, recent studies on a carbazolyl substituted blue form PDAs [4] indicated the generation of photoinduced charges in PDAs.

2. Experimental

Raman, FTIR and UV/Vis absorption spectra of polyCPDO and a polyCPDO/[6,6] PCBM mixture, dropcasted from solution onto KBr pellets show that the CPDO monomer polymerizes in the composite with PCBM. The absorption spectrum of polyCPDO proves the rather strong absorbance in the full range from 200-700 nm.

Photoinduced FTIR, ESR and LESR (light induced ESR) spectra have been measured from these pellets. ESR and LESR spectra have also been taken from samples where the monomer and a

composite mixture have been poured into a 3mm ESR tube. After evaporation of the solvents samples have been polymerized. Monitoring of the polymerization in these samples was not possible.

3. Results and Discussion

The action spectrum of the photoconductivity in polyCPDO clearly shows that charges are photogenerated when photons, whatever is their energy, are absorbed [5]. This is in contrast to the typical case of PDAs where the presence of an excitonic state below the conduction band prevents the photogeneration of charges for photon energies below the interband gap which is situated around 2.5 eV (3 eV) for the blue (red) form.

An interesting feature of these materials is their PIA spectrum in the IR region. To this end we studied the PIA spectra of polyCPDO mixed with [6,6]PCBM. In Fig. 1 the PIA spectrum of polyCPDO/[6,6]PCMB is reported and compared with that of pure polyCPDO. The spectrum looks very similar to that previously reported for polyCPDO alone, even though it is more noisy due to the disorder caused by the partial phase segregation between the two components.

It was shown [4] that the band at 800 cm⁻¹ has a correlating band around 8000 cm⁻¹ which is due to photogenerated charged states (polarons or bipolarons). The presence of the IRAV modes unambiguously shows that the photexcitation process of the material generates charged excited states. It was shown that the photogeneration of charged states in PDAs is typical of their blue form [6] that is of the form achieved when the conjugated chain is fully extended and highly ordered. From the point of view of the photovoltaic applications, the PIA spectrum of polyCPDO is highly interesting because it shows only photoexcited charged

states. Indeed, in this polymer, no signal associated with triplet excitons could be detected. This characteristic seems to be typical of polycarbazolyldiacetylenes with the carbazolyl group directly bound to the conjugated skeleton.

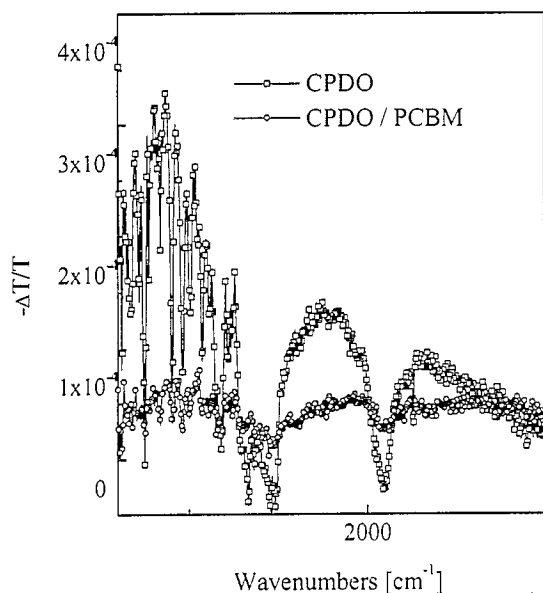


Figure 1: PIA spectrum of CPDO and CPDO/PCBM KBr pellet polymerized under identical conditions.

These results stimulated us to further study the photogeneration process of the charged excited states in PDAs and in particular the spin signature of the photoexcited charges. LESR studies, i.e. the differential ESR spectra obtained by subtracting the ESR spectra with light on and off, which are able to distinguish between spinless (bipolarons) and spin 1/2 (polarons) photoexcitations have been performed on the same CPDO KBr pellets that have been investigated before by PIA FTIR measurements. CPDO shows a strong dark signal, which gains intensity under illumination. Both, the dark and light induced signal have similar microwave saturation behavior. The LESR signal shows a bimolecular dependence on the light intensity. At lower temperatures (below 200 K), two different time domains are detected for the photoinduced radicals, i.e., a prompt contribution which comes immediately with switching on/off the light, and a persistent contribution, which generates metastable spins that can only be annealed by heating the sample up to elevated temperatures. CPDO is well known to polymerize under heat or intense light. We therefore checked the temperature dependence of the photoinduced radicals and found Curie behavior. Moreover, it was found that the photoinduced generation of radicals is reversible. Photoinduced polymerization can therefore be excluded as the origin for the photoinduced spins.

Since the addition of PCBM does not alter the spin signature of CPDO, and no signal is found from PCBM, which is easy to detect due to its g value lower than two and its unusual saturation behavior. This is in accordance with the PIA studies. We conclude, that we do not see photoinduced electron transfer between CPDO and PCBM in our samples. The nature and the influence of the morphology on the spectroscopic studies of this compound is not known. Strong phase separation between polyCPDO and PCBM seems to be very probable.

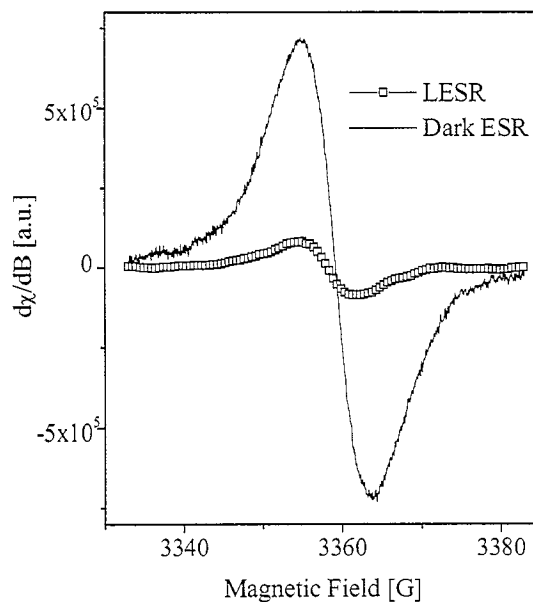


Figure 2: Dark and LESR spectrum of CPDO. LESR signal is the difference between the light on and light off signal.

4. Conclusion

Spectroscopic studies of CPDO proved the presence of photoexcited states with charges and radical character. Dark and persistent LESR signals indicate the presence of traps. No photoinduced charge transfer to PCBM is observed. The effect of phase separation which occurs between CPDO and PCBM during polymerization can not be ruled out for the inhibition of the photoinduced electron transfer.

5. References

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