Optical probes of pristine and C_{60}-doped Silicon bridged PT polymer; a novel highly luminescent, low bandgap polymer.

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ABSTRACT

Silicon bridged PT polymer (PTSi) is a new soluble polymer with a strong luminescence in the infrared band (0-0 transition at 1.6 eV). We have applied various spectroscopies such as absorption, electroabsorption (EA), photo induced absorption (PA), electromodulated PA (EPA), photoluminescence (PL) and photo induced absorption detected magnetic resonance (PADMR) to pristine and C_{60} doped PTSi thin films in order to eluvidate the photoexcitation and electronic states this material.. The absorption spectrum consists of three bands, one in the visible with a peak at 2 eV and the others in the UV at 4.5 eV and 6.2 eV respectively. The PL band at 1.6 eV contains also three pronounced phonon replica, each 150 meV apart. An electric field reduces the luminescence due to dissociation of excitons into polarons. The PA spectrum is dominated by a broad PA band peaked at 1.1 eV which is due to triplet-triplet transitions, with a shoulder at 1.7 eV due to polaron pairs; there is also a distinctive band at 0.3 eV due to both, polarons and polaron pairs. Upon doping with C_{60} the 1.1 eV triplet band loses intensity, whereas the 0.3 eV feature dramatically increases and the typical signature of C_{60}^{-} HOMO to LUMO transition appears at 1.15 eV.

Keywords: Silicon bridged PT polymer, low bandgap p-conjugated polymer, C_{60} doping, luminescence, electric field induced exciton dissociation

1. INTRODUCTION

Recently luminescent conductive polymers (LCP) have been the focus of extensive research efforts. The drive for these efforts are the potential applications such as molecular light emitting diodes (LED), large panel display and perhaps even "plastic lasers". The bright photoluminescence (PL) of the order of 50% is the most important property of LCP. The PL band in LCPs has been reported to span the visible spectral range from red to blue. However PL in the near IR range has not been yet reported. We present in this communication a new type of LCP with the emitting PL band in the IR range. The new polymer is the Silicon bridged PT polymer (PTSi) of which repeat unit is shown in Figure 1 inset.

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The strong luminescence in PTSi and the fact that the absorption and PA bands are at least 0.4 eV away from the PL (Figure 1), reduce self absorption in PTSi. This makes PTSi promising for infrared LED and possibly also laser applications. The low bandgap of PTSi is also useful to improve understanding of theoretical models describing the visible and UV absorption bands. The photoexcitation dynamics and the electronic structure in PTSi are also interesting and have been studied using a variety of optical techniques.

Electroabsorption (EA) measures the change in absorption due to the application of an electric field. The analysis of signal is based on a $\chi^{(3)}$ process and allows to determine the excitonic levels and their strongly coupled vibrations. Experimental setup and analysis of EA spectroscopy are described elsewhere in more detail [1, 2]. Electric fields in the order of 10^5 V/cm and sample temperatures of 80K were used in this study.

Photoinduced absorption (PA) spectroscopy measures the change in absorption of a infrared probe beam due to pumping of the material with a strong light beam of photon energies above the absorption edge. In this study, the 0.1 mW of the UV lines of an Ar$^+$ laser were mechanically chopped at 400 Hz to periodically pump the material. The pump induces excitation which are detected with the probe beam. A more complete description of the experimental technique and the analysis of the spectra is given by Vardeny et al. [3]. As probe a tungsten lamp was used and the signal was spectrally resolved using a monochromator and infrared filters. Spectra were taken at 80 and 300 K.
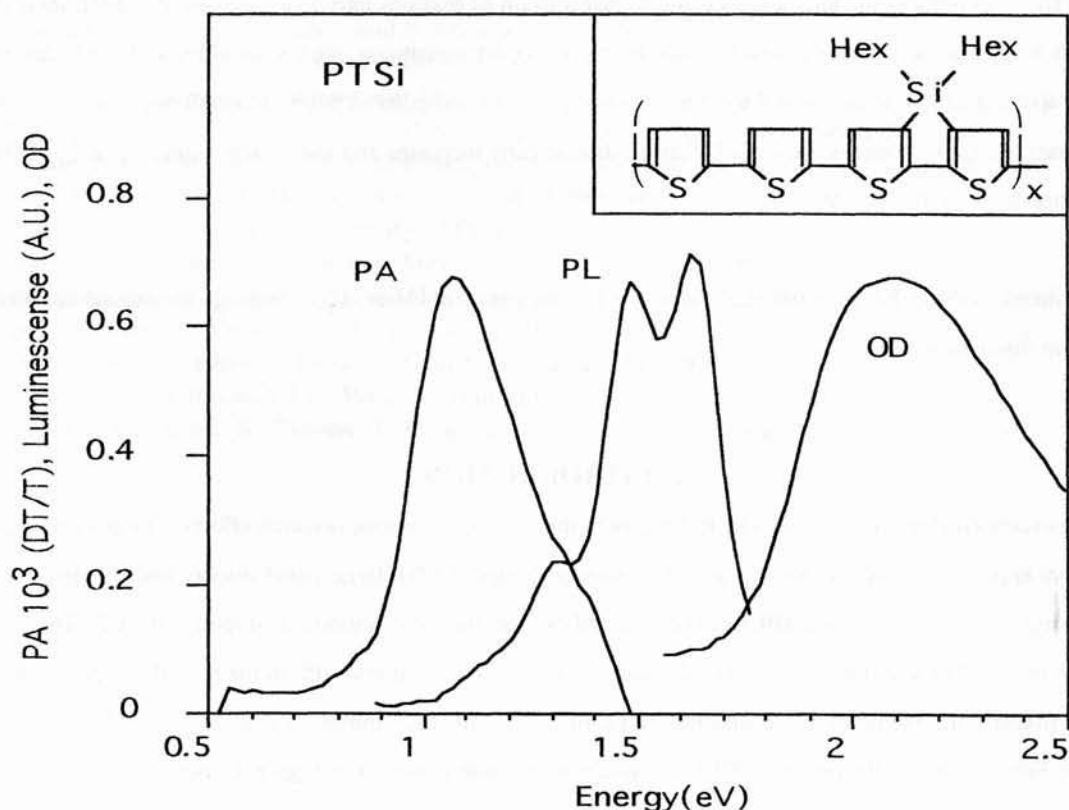

Figure 1: Spectra of PA, PL, and optical density of PTSi

Photoinduced absorption detected magnetic resonance (PADMR) measures the change in PA due to magnetic resonance. The spectra were taken at 10K using a microwave frequency of 3 GHz and magnetic fields at around 500 G and at around 1000 G. The experimental setup is described elsewhere [3-5] . The measurements allow to characterize the spin quantum number of PA and active excitations.

2. EXPERIMENTAL TECHNIQUES

EPA and EPL measures the change in PA and PL respectively due to exposure of the material to an electric field. The effects can have many different origins as discussed elsewhere in this volume [6] . In PTSi an electric field leads to an enhanced dissociation of excitons into polarons. Thus the EPA shows the field related generation of polarons, while EPL indicated the field related reduction of 1Bu excitons. To measure EPA, PA active photoexcitation were generated using 100 mW of the 514 nm line of an Ar^+laser, distributed over $1/2$ cm^2 area of the sample. The sample was exposed to an electric fields in the order of 10^5 V/cm. The electric field induced change in IR transmission of the sample indicates a modulation of the PA. EPL measurements were done similarly by spectrally detecting the field induced changes of photoluminescence. A temperatures of 80K was used for these measurements.

3. EXPERIMENTAL RESULTS

3.1 LUMINESCENSE AND SUBGAP PHOTO EXCITATIONS

The PL band at 1.6 eV contains three pronounced phonon replica, each 150 meV apart (Figure 2). Electromodulated photoluminescence (EPL) spectroscopy shows that an electric field of 10^5 V/cm applied to the film reduces the PL by a factor of $1 + 1/2000$ (Figure 2). The PA spectrum of the pristine PTSi films (Figure 3 (a)) is dominated by a broad PA band which peaks at 1.1 eV with a shoulder at 1.65 eV; there is also a distinctive band at 0.3 eV. An applied electric field enhances the bands at 0.3 eV and above 1.2 eV, while it reduces the PA bands at 1.1 eV as shown elsewhere in this proceedings [6] . Also upon doping with C_{60} , the 1.1 eV band loses relative intensity, whereas the 0.3 eV and 1.65 eV bands dramatically increase, and the typical signature of C_{60}^- HOMO to LUMO transition appears at 1.15 eV (Figure 3(b)). It is important to note that the PA between 0.7 eV and 0.9 eV is clearly above zero in the pristine sample due to the long tail of the broad absorption band at 1.1 eV. Upon C_{60} doping the PA goes down to zero at 0.8 eV. This is an indication that the excitation which causes the broad feature at 1.1 eV gets reduced by C_{60} doping while another excitation with a much sharper absorption signature appears at the same energy. This excitation consists of three correlated bands at 0.3 eV 1.15 (C_{60}^- -ion HOMO-LUMO transition) and 1.65 eV due to polaron pair complexes ($P^+ C_{60}^-$). Additional evidence for this interpretation is given by ADMR spectroscopy. The ADMR spectrum (Figure 4) of the undoped material shows a reduction of the PA due to magnetic resonance. For spin-1/2 excitations (g=2), this reduction peaks at 1.1 eV (polarons) and 1.65 eV (bipolarons). For g=4 the PADMR shows only one broad band due to triplet excitons that peaks at 1.1 eV. The fact that in PTSi three
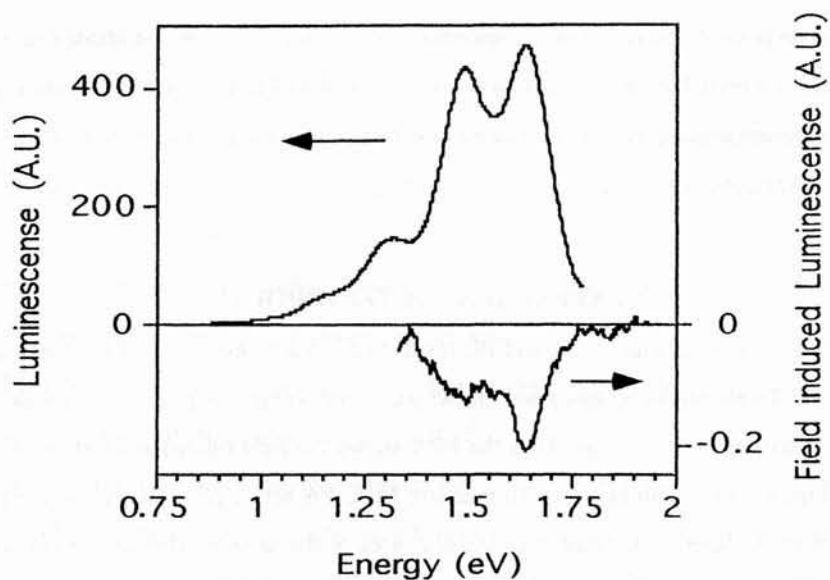
Figure 2: PL and electro-modulated change in PL (EPL) in pristine PTSi: An electric field reduces the luminescence slightly.
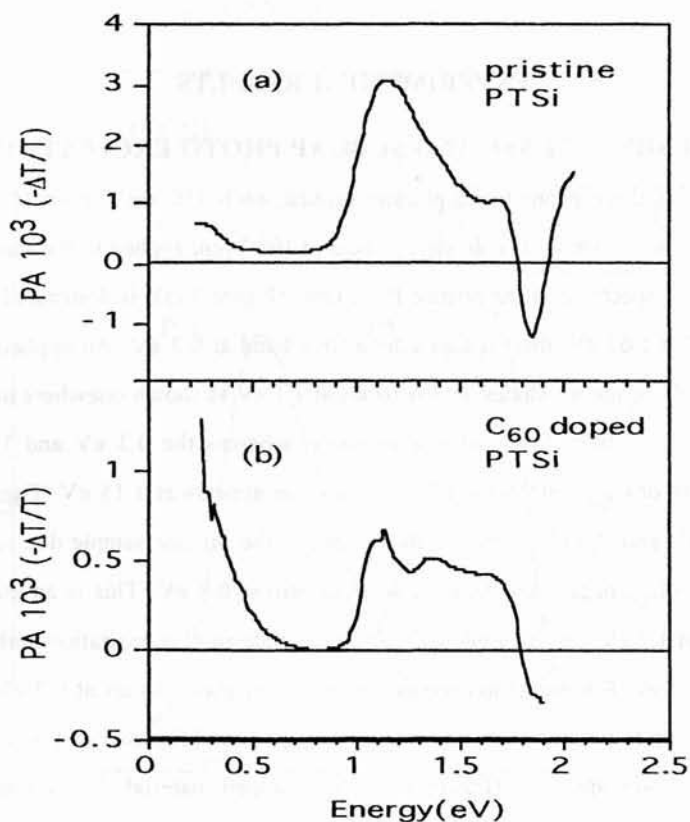

Figure 3: PA of (a) pristine and (b) C_{60} doped PTSi at 80 K, excited with 0.1 W of 514 nm laser light.
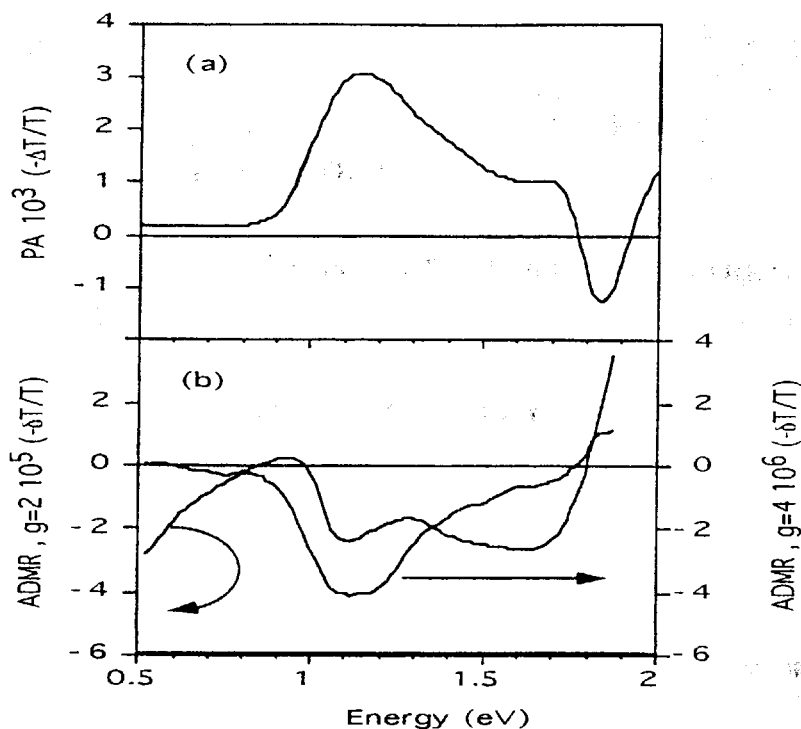
Figure 4: PA and PADMR spectra of pristine PTSi at 10K. At g=2, the PADMR spectrum shows s=1/2 (doublet) excitations and at g=4 it shows s=1 (triplet) excitations.

different excitations (polarons, C_{60}^- , and the triplet exciton) have a transition at the sampe energy ($\approx$ 1.1 eV) has to be taken into account for the interpretation of the spectra.

3.2. THE EXCITONIC BANDS IN PTSI

PT polymers show three major absorption bands. Figure 5 compares the absorption spectra of PTSi, Poly(3-butyl thiophene) P3BT and Poly (3-Octyl thiophene) P3OT. (The spectrum of P3OT was taken with permission from Jeglinski [2].) In the low gap polymer PTSi, the absorption bands peak at 2 eV, 4.5 eV and 6.3 eV. The comparison with the absorption bands of other polymers shows that the first band at 2 eV due to the 1Bu exciton occurs at a different energies in different PT polymers, while the other bands at 4.5 eV and 6.2 eV appear consistently at the same energy in all PT polymers (Figure 5).

The EA spectrum of PTSi shows a feature at 1.95 eV that resembles the first derivative of the linear absorption (Figure 6). As an effect of the conjugation length distribution, this signature appears in the EA at lower photon energies as the corresponding band in the absorption [1]. At higher energies, however a field induced absorption band appears at 2.55 eV, which has no correspondent band in the linear absorption. This band can therefore be assigned to the optically forbidden mA_g state which gains oscillator strength in EA due to the symmetry breaking interaction of the high electric field. At higher
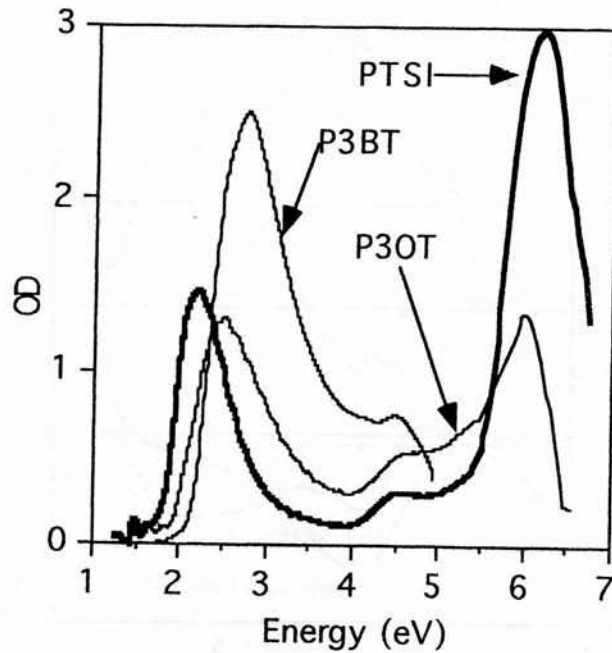
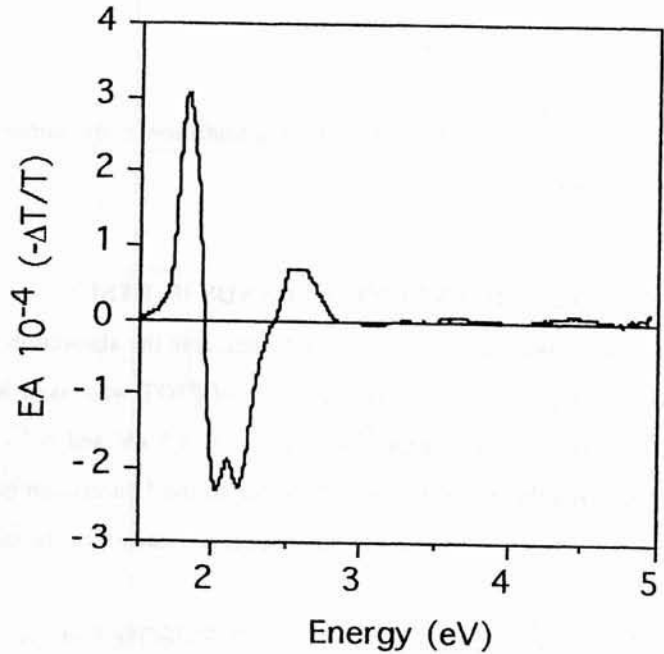Figure 5: Optical absorption of different PT polymers from 1.5 to 6.5 eV.

Figure 6: Electroabsorption of PTSi, measured at 80K with 10^5 V/cm

photon energies only at 4.5 eV a small derivative shaped feature appears where an band can be seen in the linear absorption. The fact, that the EA signature is extremely weak indicates the relatively low polarizability of the corresponding exciton.

4. DISCUSSION

4.1. PHOTOEXCITATIONS WITH SIGNATURES BELOW THE GAP:

The broad PA band between 0.9 and 1.8 eV (Figure 4 (a)) is composed of optical transitions of triplet excitons (1.1 eV), polaron pairs (1.65 eV), and free polarons (1.1 eV). The following evidence supports this interpretation:

1) A strong electric field reduces the luminescence of the pristine material (Figure 2). This might be due to field-induced dissociation of singlet excitons into polarons and polaron pairs, which in turn also reduces the percentage of the singlet excitons that may decay into the triplet manifold. EPA shows a bleaching close to the maximum of the triplet absorption band and an increase of the polaron and polaron-pair absorption bands at the low and high energy end of the spectrum due to an electric field, as discussed elsewhere in this proceedings [6] . This supports the hypothesis of field-induced dissociation of singlet excitons. Obviously, the band which is to be assigned to the triplet state behaves in a complementary fashion to the polaron bands in EPA.

2) C_{60} -doping is known to quench singlet excitons and to form polaron pairs. Therefore this path indirectly decreases the triplet density. C_{60} -doping decreases the main broad triplet-triplet absorption at 1.1 eV. At the same time it increases features due to polaron pairs at 1.6 eV and the C_{60}^- absorption at 1.15 eV. This indicates reduction of the singlet to triplet intersystem crossing due to enhancement of a competing decay route. An additional electric field increases due to singlet exciton separation the effect further. The fact that the signatures of polarons, C_{60}^- and polaron pairs partially overlap with the triplet band obscures thie process of exciton dissociation.

3.) The PADMR spectrum of pristine PTSi (Figure 4.22) measured at g=4 clearly indicates the presence of a very broad triplet excitation peaking at 1.15 eV. The g=2 PADMR spectrum indicates that the photoexcitations with transitions below 0.5 eV and at 1.1 eV and 1.65 eV are sensitive to a spin-1/2 resonance. These photoexcitations are therefore polarons with bands at below ≈ 0.5 eV and 1.1 eV, which are spin-1/2 excitations and polaron pairs at 1.65 eV. Even though polaron pairs are spinless, their signature shows up in the spectrum due to the modulation of polarons.

4.2. EXCITON BANDS IN PTSI

The linear optically active $1B_u$ exciton lies at 1.95 eV as determined by EA. The maximum of the absorption is at approximately 2.2 eV, while the maximum of the luminescence can be found at 1.8 eV. The reason for this shift in energy is the conjugation length related distribution of the states in energy, as well as phonon sidebands which merge in the absorption spectrum to one big blue shifted absorption band. The PL however is emitted from excitons, which diffused to the $1B_u$ states which have the longest conjugation length and are thus low lying in energy.

The EA data indicates that the polarizability of the exciton at 4.5 eV is much lower than the polarizability of the $1B_u$ exciton. The energy of the delocalized $1B_u$ exciton depends highly on its substituents. This is discussed in more detail by Hotta [7]. The other two bands in the UV appear in all polythiopenes at the same energy. From this we can conclude that the bands in the UV are intrinsic to the thiophene ring and thus not largely influenced by different substituents.

5. CONCLUSIONS

Using various optical techniques, the photoexcitations in PTSi and C_{60} doped PTSi have been determined (Table 1). C_{60} doping induces the dissociation of singlet excitons into charge transfer complexes. Four singlet excitonic levels were found in PTSi: the $1B_u$ exciton and two higher energy optically allowed excitons with a low polarizability, probably intrinsic excitations of the thiophene ring; the optically forbidden mA_g state was found at about 2.6 eV.

We found than in PTSi an electric field can enhance the dissociation of of the $1B_u$ singlet excitons into polarons and polaron pairs. Because of high exciton binding energies, this effect most likely takes place at defects and impurities.

Table 1: Energy levels of excitons and photoexcitations and their transitions assembled from EA, PA, EPA, EPL and PADMR spectra of PTSi.

Excitons	
Optical gap ($1B_u$ - exciton)	1.95 eV
Luminescense (relaxed $1B_u$ - exciton)	1.65 eV
mA_g exciton	2.55 eV
mA_g^3 - exciton	~ 2.5 eV
$1B_u^3$ - exciton	~ 1.4 eV
Triplet-Triplet transition	1.1 eV
Localized B_u - states	4.5 eV , 6.3 eV
Signatures of polarons and related photoexcitations	
P_1 - transition	0.4 eV
P_2 - transition	1.1 eV
Polaron pairs: PP_2 - transition	1.65 eV
C_{60}^- (HOMO -> LUMO)	1.15 eV

REFERENCES

[1]   M. Liess, P. A. Lane, S. Jeglinski, Z. V. Vardeny, A three essential states model for electroabsorption in nonluminescent conjugated polymers, *Synthetic Metals*, **84** (1996)

[2]   S. Jeglinski, Electroabsorption spectroscopy of conjugated polymers and carbon fullerenes and conjugated polymer light emitting devices, (PhD Thesis, University of Utah, 1996).

[3]   Z. V. Vardeny, X. Wei, Optical Porbes of Photoexcitations in Conducting Polymers in *Handbook of conducting polymers* A. Skotheim , R. Elsenbaumer (eds.) (to be published in 1997).

[4]   X. Wei, (PhD Thesis, University of Utah, Salt Lake City, 1994).

[5]   X. Wei, Z. V. Vardeny, N. S. Saricifti, A. J. Heeger, Absorption-detected magnetic-resonance studies of photoexcitations in conjugated-polymer/C60 composits, *Phys. Rev. B*, **53** (1996) 2187.

[6]   Liess, P. A. Lane, Z. H. Kafafi, M. Hamaguchi, M. Ozaki, K. Yoshino, Z. V. Vardeny, Electromodulated photoinduced absorption: a new spectroscopy in p-conjugated polymer/C60 blends, (SPIE proceedings, San Diego, 1997).

[7]   S. Hottea, S. Rughooputh, A. J. Heeger, A. J. Wudl, *Macromolecules*, **20** (1987) 212.