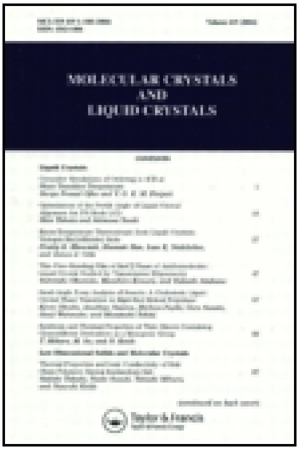

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Optical Excitations of Acceptor Substituted Poly-Thiophene Derivatives

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OPTICAL EXCITATIONS OF ACCEPTOR SUBSTITUTED POLYTHIOPHENE DERIVATIVES

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Abstract We have studied acceptor substituted polythiophene derivatives in order to examine its usefulness as an intrinsic charge-trap under laser excitation. The polymers studied are the chemically prepared poly 3 - Butylethylether Thiophene (BETh) and the copolymer 3 - (4 - nitrobenzene 1,2 - ethen) Thiophene / BETh (1:3.5). We have established that the excitations which survive at long times in these polymers are: (a) bipolarons, which are doubly charged segments of the polymer accompanied by a significant bond alternation relaxation and having spin 0, and (b) triplet excitons, with zero charge and spin 1.

When compared to unsubstituted polythiophene, it is noted that triplet excitons are much more efficiently photogenerated in these polythiophene derivatives.

INTRODUCTION

Photoexcitation has been long used as a means to study charged carriers as well as neutral defects in conjugated polymers.[1,2] Due to the strong interaction between the electrons and lattice vibrations, each defect (charged or neutral) is accompanied by local distortion of the bonds in its vicinity, creating thus charged polarons or bipolarons, or neutral excitons, in conjugated polymers having non-degenerate ground state. A polaron has a single charge ($\pm e$) and spin $1/2$ (radical cation, or radical anion) and a bipolaron has a pair of like charges of opposite spins (dication or dianion). The local geometric relaxation associated with each of these defects, induces two localized electronic states in the HOMO–LUMO gap. The occupation of these two levels is such that for positive polarons (bipolarons) the lower level is half filled (empty) and the upper level is empty, while for negative polaron (bipolaron) the lower level is fully occupied and the upper level is half filled (fully occupied). The difference in occupation affects the number optical transitions. Bipolarons are expected to show two transitions (between each of the gap states and either the

HOMO or LUMO band), whereas polarons would show a third transition between the two gap states. [3] Polarons are formed following charge separation after phtoexcitations. Bipolarons are the result of the merging together of two like charge polarons, which thus require interchain hopping. Therefore, polarons are formed almost instantaneously (within one period of a C–C vibration, $\simeq$0.1 psec), while bipolarons are formed only after several nano-seconds. [4]

The extent of bond relaxation near excitons is in general considerably less than that of polarons or bipolarons. The excitons which are formed immediately following photoexcitations prior to charge separation are spin singlet. In many conjugated polymers, however, triplet excitons are known to exist. These can be created from singlet excitons by system crossing due to spin orbit coupling, and/or, photoproduced via an excited A_g state.

In this work we have studied, photoexcited acceptor substituted polythiophene derivatives (Fig. 1), using the photoinduced absorption (PA) and photoinduced absorption detected magnetic resonance (PADMR) techniques, under nearly steady state conditions. In these derivatives we have observed bipolarons as the long time survivors of the photogenerated charges and triplet excitons.

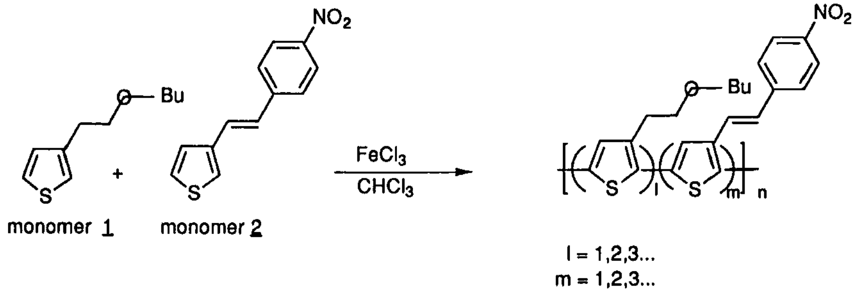

Fig. 1 Sketch of the polymerization process of BETh (monomer 1) and NBETh (monomer 2) into the copolymer NBETh/BETh with the ratio m/l.

EXPERIMENTAL

Sample Preparation

The co-polymers studied are composed basically of two units. (a) 3 - Butylethylether Thiophene, (BETh), (monomer 1 Fig. 1). The monomer as well as the homopolymer were prepared according to the procedures described by Zinger et al.[5] (b) and the copolymer 3 - (4 - nitrobenzene 1,2 - ethen) Thiophene / BETh (1:3.5), (NBETh), (monomer 2 Fig. 1). It was prepared using the common Wittig reaction for preparing stilbene derivatives as described by McDonald and Campbell[6] resulting in a yield of ≃50% yellow crystals. Chemical co-polymerization was carried out using the above procedures with different monomer ratio in the reaction solution, resulting in a co-polymer as shown in Fig. 1. The monomer ratio in the resulting co-polymer was roughly determined from NMR spectra in $CDCl_3$ solution. In this report we present results on the homopolymer Poly-BETh and the co-polymer-(NBETh/BETh) (m:l=1:3.5).

Experimental Techniques

The PA measurements were performed using the pump (Ar^+ and dye lasers) and probe (incandescent source) technique, in which the pump beam was chopped at audio frequencies. Both the transmission (T) and the photomodulated transmission (ΔT) were recorded using a phase sensitive lock-in technique. ΔT was corrected for photoluminescence, and the results then are presented as $-\Delta T/T$, which is the net change in the absorption due to the pump.

For the PADMR measurements, the pump and probe beams continuously illuminate the sample, which is mounted in a high-Q microwave (μ-wave) cavity at ≃3 GHz, equipped with optical windows and a superconducting magnet.[7] Microwave resonant absorption, modulated at frequencies in the range 0.5–3 kHz, leads to small changes (δT) in the transmission proportional to δn, the change in photoexcitation density n produced by the pump beam. δn is induced by transitions in the μ-wave range that change spin-dependent recombination rates. Each experiment is done in one of the two following modes. One is an H-scan, in which the probe is fixed at one of the PA bands and the magnetic field is scanned. The other is an E-scan, in which the magnetic field is fixed at one of the lines found in the H-scan and the probe energy is scanned. Using these two modes we were able to relate the different PA bands with their spin.

RESULTS AND DISCUSSION

The PA spectra of both the homopolymer P-BETh and the co-polymer (NBETh/BETh) (1:3.5) are shown in Fig. 2. The two spectra feature strong PA band centered at ≃1.7 eV (HE), a smaller PA band centered at ≃0.64 eV (LE), and a set of much weaker lines at the molecular vibrations range 0.1–0.2 eV (IRAV lines). Above 2.26 eV, the PA turns into photo-bleaching (PB). Although the spectra are similar to those found previously in polythiophene[8] and poly(3-methylthiophene),[9] in that they show two main electronic bands (HE and LE) and a set of IRAV lines, the much stronger HE band in the present case signifies that the main photogenerated long lived species are chargeless. This conclusion is based on previous studies, where it was found that the strength of the IRAV lines is associated with the charge of the defect.

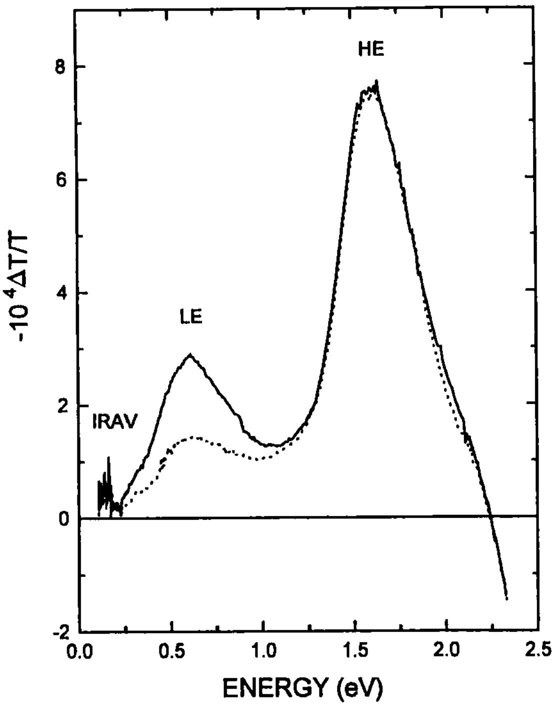

Fig. 2 The photoinduced absorption (PA) spectra of P-BETh (solid line) and the copolymer BETh/NBETh (1/3.5), using as a pump the 4579 Å Ar^+ laser line. The spectra were taken at 80 K.

The H-scan PADMR of P-BETH is presented in Fig. 3a as $-\delta T$ *vs.* the external magnetic field while the probe is fixed at the peak of the HE band, 1.7 eV. The HE H-scan spectrum (Fig. 3a) shows three main features. (i) A strong line centered at $\simeq$400 G ("g=4" line). (ii) A broad band in the field range of 600-1200 G. (iii) A narrow line centered at $\simeq$1069 G ("g=2" line). The g=4 line is an evidence that there is considerable contribution to the HE band from triplet species (S=1) in the photoexcited state. Moreover, the broad band (ii), which is associated with the g=4 line, is the powder pattern of the S=1 spectrum. Line (iii) originates from $S={}_{1/2}$ species.

Fig. 3b shows the H-scan PADMR of the whole LE band. Only a g=2 line is observed without any traces of either g=4 line or the broad band observed in the

HE H-scan. The position of the LE g=2 line is different from that of the HE g=2 line by about 1.5 G ($\Delta g=0.003$), and it, therefore, originates from different $S=1/2$ species. We believe that the HE $g=2$ line is due to extrinsic radicals.

Nearly identical spectra, including the g values and the triplet powder pattern shape, were observed for the copolymer NBETh/BETh.

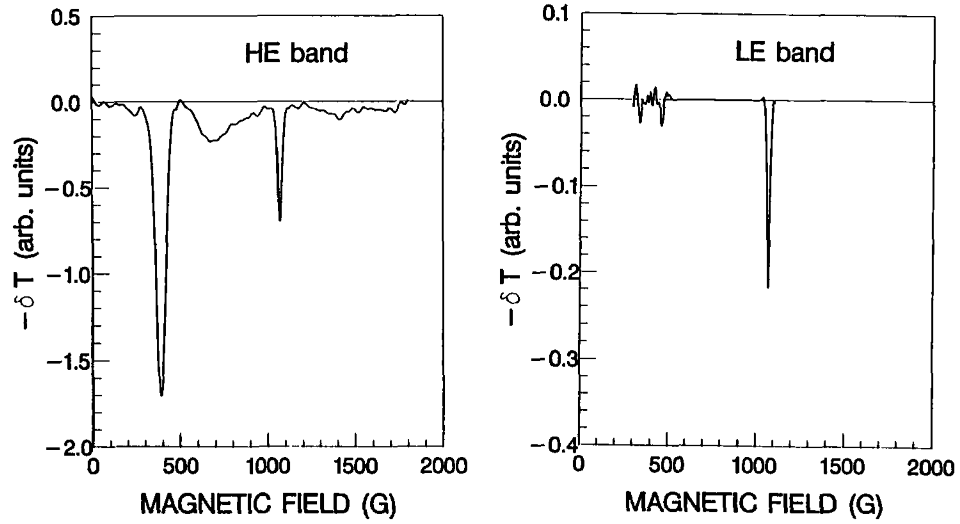

Fig. 3 (a) The H-ADMR spectrum of BETh at the HE band (1.6 eV). (b) Same as (a) but for the LE band.

H-scans were also performed at different probe energies within the width of the HE band. We have observed, that the HE band is not homogeneous and contains contributions from different sources. In particular, at $\simeq$1.24 eV, the $S=1/2$ line appears at the same position as the $S=1/2$ LE line. The main contribution to the HE band is due, however, to optical transitions within the triplet manifold, associated with photogenerated triplet excitons in both BETh and NBETh. The $S=1/2$ contribution to the HE at the vicinity of 1.24 eV, is hidden under the wide triplet band. Since the g value of the LE band and the $S=1/2$ contribution at 1.24 eV is identical, we identify these bands (i.e. LE and $\simeq$1.24 eV) as due to optical transitions associated with photogenerated bipolarons ($BP^{\pm 2}$), similar to the $BP^{\pm 2}$ bands found in PPV,[10, 11] PTO and polythiophene.[8]

The presence of both S=1 and $S=1/2$ PADMR on the triplet PA band peaked at 1.7 eV, shows that its recombination is influenced by two main channels:
Channel 1. Triplet decay with different decay rates for different sublevels.

Channel 2. Spin $1/2$ radicals in the sample. Spin-flip of these radicals may affect triplets ($S = 1$) trapped at those centers.

We envision two competing processes which give rise to the presence of both bipolarons (LE band) and triplet excitons (HE band) upon interband excitation.[11] The ^1B_u state reached upon photoexcitation can decay into spin $1/2$ polarons ($P^{\pm}$), which are relatively mobile in the sample, since they are not topological defects. Although we cannot identify a PA band in the photoinduced absorption spectrum, which is associated with $P^{\pm}$, their $BP^{\pm 2}$ byproducts are observable in the photoinduced absorption spectrum. The enhanced $P^{\pm}$ recombination, which in turn causes smaller $P^{\pm}$ steady state density under μ-wave resonance conditions, explains the negative PADMR signal for $BP^{\pm 2}$ (Fig. 3b). Alternatively, the ^1B_u state can decay, via intersystem crossing for instance, to a $2A_g$ state (or equivalently, from the singlet to the triplet manifold), forming triplet excitons with a strong transition at $\simeq$1.7 eV. These excitons become spin polarized due to different recombination dynamics of each of the triplet sublevels.[12] Under μ-wave absorption, transitions among the triplet sublevels enhance recombination. The PADMR signal resulting from this process is negative, due to the decrease in the steady state triplet population, as indeed observed (Fig. 3a).

CONCLUSIONS

Using PA and PADMR techniques, we have established that the predominant steady state excitations, in both the homopolymer BETh and its acceptor substituted copolymer NBETh/BETh, are bipolarons and triplet excitons. There is essentially no difference in the steady state behavior of the excited state of these two polymers. We thus conclude that the acceptor group (nitrobenzene) in the copolymer, does not play a significant role in the long time behavior of the photoexcitations. Any electron that is initially trapped upon photoexcitation, is released by the time which is relevant for the photomodulation experiments at modulation frequency of $\simeq$1 kHz.

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