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Photoinduced absorption of π -conjugated polymers in solution

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Abstract

Near steady state photoinduced absorption (PIA) studies on soluble poly(p-phenylene vinylene) (PPV) and poly(p-phenylene ethynylene) (PPE) derivatives in various solvents reveals that the principal metastable photoexcitation is a triplet state. In contrast to poly(3-alkylthiophene) solutions, no charged photoexcitations are found in the PPV or PPE solutions.

1. INTRODUCTION

PIA spectroscopy of π -conjugated polymers has been successfully used to characterize the non-linear photoexcitations and their associated electronic states in the π - π^* energy gap.^{1,2} *Intrachain* excitation above the π - π^* energy gap produces initially a transient singlet state which can be described by a band model (weak electron-hole correlation) or an exciton model (strong e^- - h^+ correlation) depending on the nature of the polymer. The transient singlet state can decay via various pathways, e.g.: luminescence; intersystem crossing to the triplet manifold; and via the creation of long-lived charged polarons (P^\pm) and bipolarons ($BP^{\pm 2}$). The latter requires in general an *interchain* mechanism to prevent geminate e^- - h^+ recombination. To distinguish between *intrachain* and *interchain* mechanisms, π -conjugated polymers have been studied in a polymer matrix (e.g. PE).³ Alternatively, isolated π -conjugated polymer chains can be studied in dilute solutions. Recently, we have shown that the dominant metastable photoexcitation of poly(3-alkylthiophene) (P3AT) in various solvents corresponds to a (neutral) triplet state.⁴ In a secondary process, polaronic (P^\pm) excitations of P3AT are formed via a solvent-mediated photo-oxidation reaction.⁴ The efficiency of the latter mechanism strongly depends on the nature of the solvent, which is actively involved in the stabilization of the ejected electrons.^{4,5} In this contribution we present PIA studies on poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), poly(bis-2,5-*epi*-cholestanoxo-1,4-phenylene vinylene) (BCHA-PPV), and poly(bis-2,5-*epi*-cholestanoxo-1,4-phenylene ethynylene) (BCHA-PPE) (Figure 1) in various solvents in order to elucidate the nature of long-lived photoexcitations in various solvents and to establish whether a branching between neutral and charged photoexcitations as observed in solutions of P3AT, also occurs in PPV and PPE.

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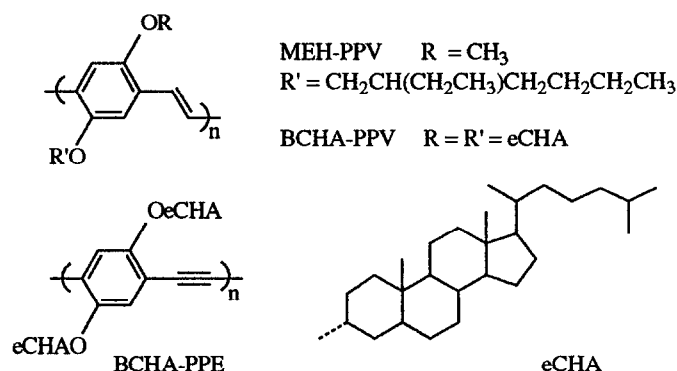


Figure 1. Structures of MEH-PPV, BCHA-PPV and BCHA-PPE.

2. EXPERIMENTAL

The synthesis and characterization of MEH-PPV, BCHA-PPV, and BCHA-PPE have been described elsewhere.⁶⁻⁸ Their linear absorption onsets are found at 2.22, 2.25 and 2.48eV (in THF), respectively. Deoxygenated solvents were used; samples (0.5 mg/mL) were prepared under argon in 1 mm cuvettes. PIA spectroscopy was performed with a mechanically modulated pump-and-probe technique.^{3,4}

3. RESULTS AND DISCUSSION

3.1. MEH-PPV

The PIA spectrum of MEH-PPV in THF exhibits a single well-defined band centered at 1.55 eV (Figure 2) and increases slightly sublinear with intensity (I) according to $\Delta T \propto I^{0.84}$. The monomolecular lifetime as determined from the modulation frequency (ω) dependence of ΔT is 0.7 ms (Figure 3). Similar PIA bands have been observed in a MEH-PPV/PE blend as well as in films of other dialkoxy-PPV derivatives, and have been assigned to triplet excitons.^{3,9,10} For a charged excitation (P^\pm),

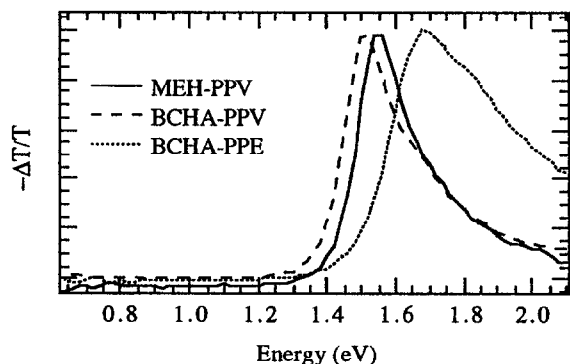


Figure 2. PIA spectra in THF at 295 K

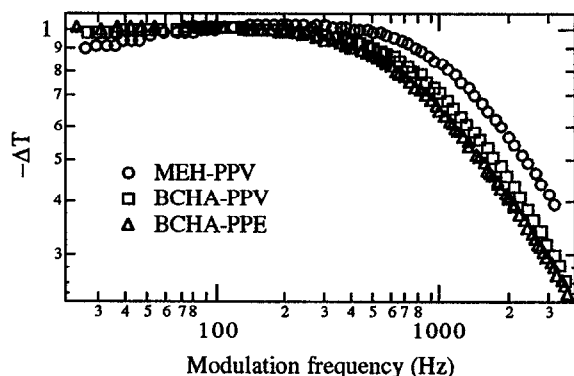


Figure 3. Relaxation behavior of PIA spectra shown in Fig. 2

at least two subgap absorptions are to be expected. Accordingly, we attribute the 1.55 eV band of MEH-PPV in THF to a transition within the triplet manifold. This assignment is further supported by the monomolecular decay and the observation that the molecular oxygen quenches the PIA band. The PIA spectrum of MEH-PPV in solution is only slightly dependent on the nature of the solvent (p-xylene 1.52 eV; CHCl_3 1.53 eV; CH_2Cl_2 1.56 eV). In neither solvent PIA bands are observed that can be attributed to polarons and/or bipolarons.

3.2. BCHA-PPV

The PIA spectrum of BCHA-PPV in THF (Figure 2) shows a single band at 1.51 eV, which is assigned to a triplet state photoexcitation. The spectrum increases almost linear with pump intensity ($\Delta T \propto I^{0.92}$) and decays with increasing ω following a monomolecular decay with a lifetime of 1.0 ms (Figure 3). In p-xylene (1.50 eV) and CHCl_3 (1.50 eV) spectra are almost identical.

3.3. BCHA-PPE

Excitation at 488 nm of BCHA-PPE in THF gives the PIA spectrum shown in Figure 2 exhibiting one band at 1.69 eV. ΔT follows $I^{0.93}$ behavior indicating monomolecular decay. The lifetime is 1.2 ms (Figure 3). In CHCl_3 , the PIA band is centered at 1.68 eV. The single subgap absorption, the monomolecular relaxation, and the result that the 1.69 eV band is quenched by air are signatures of a triplet state photoexcitation in BCHA-PPE.

Triplet excitons have recently been reported for poly(2,5-dibutane-1,4-phenylene ethynylene) in films.¹¹

4. CONCLUSION

PIA studies on MEH-PPV, BCHA-PPV and BCHA-PPE in various solvents reveal single subgap absorptions centered at ~1.55, ~1.51 and ~1.69 eV which are attributed to a triplet photoexcitation. The lifetime of this photoexcitation in solution at ambient temperature is on the order of 1 ms, and therefore significantly enhanced as compared to the lifetime of P3AT triplet excitons in solution ($< 50 \mu\text{s}$).⁴ A tentative rationalization for the fact that the $T_1 \rightarrow S_0$ decay in P3AT is faster than in PPV and PPE is the large spin-orbit coupling constant of sulfur which enhances intersystem crossing. In contrast to P3AT, we do not observe the formation of long-lived charged polaronic excitations in solution for the present PPV and PPE derivatives.

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