Photoinduced absorption of \( \pi \)-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 \( \pi \)-conjugated polymers has been successfully used to characterize the non-linear photoexcitations and their associated electronic states in the \( \pi-\pi^* \) energy gap.\(^ 1,2 \) Intrachain excitation above the \( \pi-\pi^* \) 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\(^ \pm \)). The latter requires in general an interchain mechanism to prevent geminate \( e^-h^+ \) recombination. To distinguish between intrachain and interchain mechanisms, \( \pi \)-conjugated polymers have been studied in a polymer matrix (e.g. PE).\(^ 3 \) Alternatively, isolated \( \pi \)-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'-ethyloxyvinyl)-1,4-phenylene vinylene] (MEH-PPV), poly(bis-2,5-epi-cholestanoxy-1,4-phenylene vinylene) (BCHA-PPV), and poly(bis-2,5-epi-cholestanoxy-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.

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 2.48 eV (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 \( \Delta T \sim I^{0.84} \). The monomolecular lifetime as determined from the modulation frequency (\( \omega \)) dependence of \( \Delta T \) 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.\(^ 3,5,10 \) For a charged excitation (P\(^ \pm \)),

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Triplet excitons have recently been reported for poly(2,5-dibutane-1,4-phenylene ethynylene) in films.\textsuperscript{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 ($< 50 \mu$s).\textsuperscript{4} A tentative rationalization for the fact that the $T_{1}-S_{0}$ 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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