

Infrared Ultrafast Optical Probes of Photoexcitations in π -Conjugated Organic Semiconductors

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Abstract: We measured the ultrafast dynamics of photoexcitations in a variety of semiconductor π -conjugated polymer films and solutions, in the spectral range from 0.13 eV to 1.05 eV and time domain from 100 fs to 800 ps. The measurements were made in the low signal regime, where the relative changes in transmission, $\Delta T/T < 10^{-5}$. In pristine poly [2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene] (MEH-PPV) solution we found that the primary photoexcitations are excitons with a photoinduced absorption (PA) band PA₁ at 1.0 eV. In pristine MEH-PPV film, however we found two PA bands, PA₁ at 1.0eV and P₁ at 0.3eV. We consider P₁ to be due to a polarons that are photogenerated intrinsically via defects and/or impurities. When following the transient dynamics of PA₁ in C₆₀-doped PPV-based films we could easily measure the dynamics of exciton dissociation from the polymer chains onto the C₆₀ molecules. We found the charge transfer time to range from about 100 fs to 100 ps, depending on the concentration of C₆₀ molecules in the films.

INTRODUCTION

Photoexcitations in π -conjugated polymers have been extensively investigated both theoretically and experimentally because of the surge of potential optoelectronic applications for these materials [1,2]. In addition, films of polymers/C₆₀ mixtures, and especially MEH-PPV/C₆₀ composites have been also extensively studied, driven by their possible use in photovoltaic devices [3,4]. This interest calls for detailed ps transient spectroscopy measurements, especially in the mid-IR spectral range, to study the role of excitons and polarons in the earliest events following photon absorption.

Here we report on the fs time-resolved transient spectroscopy in the mid IR range from 0.13 to 1.05 eV, in pristine and C₆₀-doped semiconductor polymer films and solutions that include MEH-PPV and MEH-PPV/C₆₀ composites. We found that excitons are the primary photoexcitations. However polarons can also be generated at early times due to imperfections. In C₆₀-doped films we measured the charge transfer time from the polymer chains onto the C₆₀ molecules, which we found to depend on the concentration of the C₆₀ molecules in the polymer/C₆₀ mixture.

EXPERIMENTAL

For our transient photomodulation (PM) measurements we used the fs two-color pump-probe correlation technique with linearly polarized light beams. The ultrafast laser system used was a 100 fs titanium-sapphire oscillator operating at a repetition rate of about 80 MHz, which pumped an optical parametric oscillator (OPO). The OPO generates signal and idler beams that were used as probes at photon energy ω_s and ω_i ranging between 0.55 and 1.05 eV. These two beams were mixed in a nonlinear crystal (AgGaS₂) to generate probes at $\omega = \omega_s - \omega_i$ in the spectral range of 0.13 to 0.43 eV. The pump beam was the second harmonic of the fundamental at 3.2eV with energy/pulse of about 0.1 nJ.

The semiconductor polymer films were obtained by dissolving the polymers in toluene solution and subsequently drop casting onto CaF₂ substrates. MEH-PPV/C₆₀ composites were obtained by dissolving the polymer and C₆₀ powders (1:1 by weight) in toluene.

RESULTS AND DISCUSSION

The transient PM spectra of pristine MEH-PPV

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The PM
the film
polarons

cannot be generated in solution, where the polymer chains are isolated, we thus conclude that the primary excitations in semiconductor polymers are excitons, with PA_1 at 1.0 eV. It is noteworthy that excitons in MEH-PPV have another PA band in the near ir range (ca. 1.6 eV), which, however cannot be reached with our present set-up. In solution, all probe wavelengths share the same dynamics that are longer than in films. In films, however there is a new PA band at 0.3eV that does not have the same dynamics as PA_1 , which according to steady state PA measurements [4] can be attributed to the lower polaron PA band, P_1 . Since the optical properties of MEH-PPV film are extremely sensitive to imperfections such as impurities and defects[4], we attribute the difference in the early-time photoexcitations between solution and film to a defect-and/or impurity- induced charge transfer in the film.

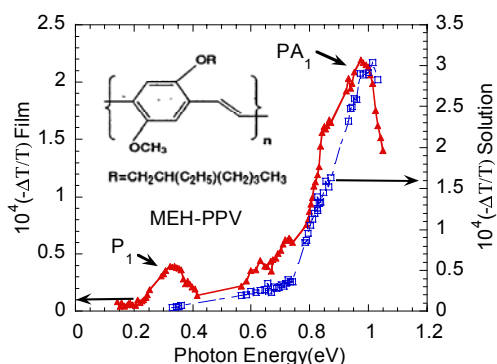


FIGURE 1. Transient PM spectrum of pristine MEH-PPV film (triangles) and solution (squares) at $t = 0$. MEH-PPV repeat unit is shown in the inset.

In Fig. 2 we show that in 50% C_{60} -doped MEH-PPV film we can measure the dissociation time of excitons from the polymer chains onto C_{60} molecules

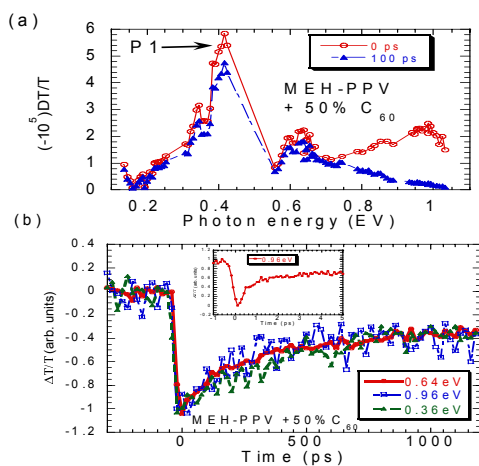


FIGURE 2. (a) Transient PM spectra of C_{60} /MEH-PPV film at $t = 0$ (squares) and $t = 100$ ps (triangles). (b) PA decay dynamics at various probe energies. The inset to (b) is the ultrafast PA_1 decay measured at 0.96 eV.

by following the transient dynamics of PA_1 . This band disappears in about 1 ps (Fig. 2(b) inset) when the charge transfer process is completed. In C_{60} -doped MEH-PPV the lower polaron band P_1 is at ca. 0.4 eV [4], and its lifetime is much longer (Fig. 2(a)) compared with PA_1 of excitons in pristine MEH-PPV (Fig. 1). We also note that in 10% C_{60} -doped film (not shown here) the charge transfer time is longer than in 50% C_{60} doped film, and occurs within 10 ps [5]. The other noticeable spectral feature in Fig. 2(a) is the dip at ca. 0.15 eV that is due to infrared active vibrational (IRAV) modes [1,4] that are a unique signature of charges induced on the polymer chains; this also support the ultrafast charge transfer in MEH-PPV/ C_{60} composites.

CONCLUSIONS

We report the ultrafast spectroscopy of photoexcitations in pristine MEH-PPV film and

solution, and in MEH-PPV/ C_{60} composites, in the spectral range from 0.13 to 1.05 eV. We found that excitons are the primary photoexcitations in single polymer chain. However polarons can also be photogenerated at early time in films, but we consider this process to be extrinsic in nature. In C_{60} -doped PPV-based films we found that the charge transfer dynamics depends on the concentration of the C_{60} molecules in the composite.

ACKNOWLEDGMENTS

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