

SUBPICOSECOND PHOTOINDUCED ELECTRON TRANSFER IN
SEMICONDUCTING POLYMER - C₆₀ COMPOSITES

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Abstract We present the results of ultrafast photoinduced absorption studies of poly(3-octylthiophene), (P3OT) poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) and poly(2,5-bis(cholestanoxo)-1,4-phenylene vinylene), (BCHA-PPV) in their pure form and mixed with C₆₀. The results show a subpicosecond photoinduced electron transfer from the polymer host onto the C₆₀ molecule.

INTRODUCTION

The observation of reversible, metastable, photoinduced electron transfer has been reported¹. The time scale for electron transfer was inferred indirectly through luminescence quenching to be on the picosecond time scale, which was later confirmed². We now report the results of a comprehensive study of the ultrafast kinetics of electron transfer from polymer hosts to C₆₀, utilizing as hosts P3OT, BCHA-PPV, and MEH-PPV.

EXPERIMENTAL

The details of the experimental setup have been published elsewhere.² In the current study a 1 kHz pulsed YLF laser was used to amplify the seed pulses from the colliding pulse mode-locked laser. The amplified pulses were recompressed using a four prism arrangement. Typical pulse energies were 5 μ J, with pulse widths of 90 fs assuming a sech^2 pulse profile. A broad band (1.2 - 2.3 eV) continuum pulse was generated by focusing 50 % of the amplified pulse into a 3 mm cell of flowing ethylene

glycol.

RESULTS AND DISCUSSION

P3OT, BCHA-PPV, and MEH-PPV were studied in their pure form and mixed with C₆₀ at concentrations of 1%, 10% and 50% C₆₀ to polymer by weight. The room temperature photoinduced absorption spectra for pure P3OT, 1% C₆₀ in P3OT, and 10% C₆₀ in P3OT are shown in figure 1 at various delay times.

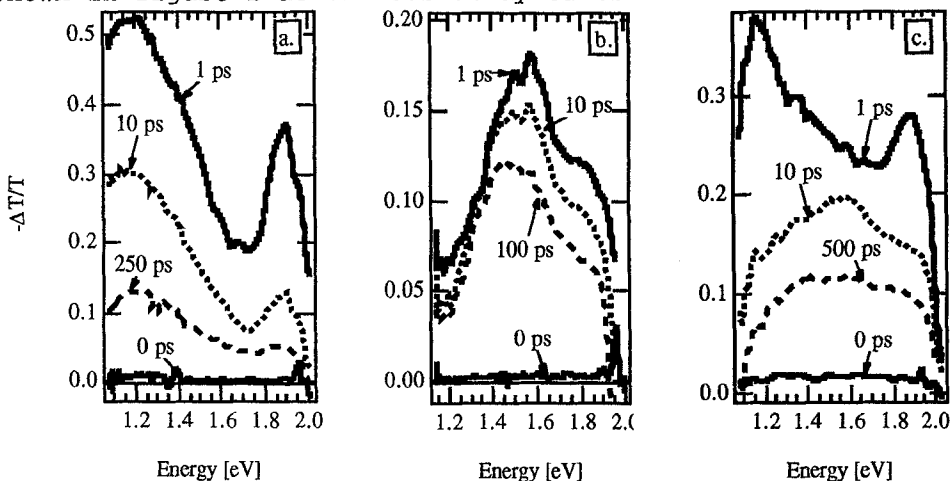


FIGURE 1 a) P3OT b) 1% P3OT/C₆₀ c) 10% P3OT/C₆₀

The pure P3OT spectrum shows a feature at 1.9 eV and one at 1.2 eV, with the rise time of both being resolution limited (< 250 fs). The kinetics of the 1.9 eV feature shows a slow component which follows a stretched exponential decay $\exp(-(t/\tau)^\beta)$ with $\tau \approx 100$ ps and $\beta = 1/3$, and a fast component which is exponential with a lifetime of 800 fs (figure 2). The fast component lifetime agrees with that found earlier,³ and is attributed to the self-trapped singlet exciton. At 1 ps, the 1.9 eV feature follows a slightly sublinear intensity dependence, $I^{0.8}$, while the 1.2 eV feature goes as $I^{0.5}$. After the singlet exciton has decayed, (> 2 ps) both bands have a square root dependence on the incident intensity. This, combined with the similar

kinetics of both features, shows that these long lived bands arise from the same species. The fact that these features are not present in dilute (5×10^{-6} M) solutions of P3OT⁴ in toluene (on the ps timescale) where interchain interactions are known to be minimal,⁵ suggests that the species seen in the film is primarily the result of interchain absorption. The dichroic ratio of 1.3 seen in our samples⁴ for these bands also suggests that interchain excitations are dominant⁶.

The polymer/C₆₀ composite materials show different behavior for different concentrations of C₆₀. In the low concentration regime ($\approx 1\%$), the PIA spectrum at the earliest times is dominated by a broad band centered at 1.55 eV, characteristic of the charge transferred state^{7,2} (figure 1). This is in contrast to what is seen in the 10% composite, where the early time (1 ps) PIA spectrum shows characteristics of the polaron spectrum seen in the pure material in addition to the 1.55 eV charge transfer band. Hence charge transfer occurs on a subpicosecond time scale in both samples, but in the low concentration sample the charge transfer rate dominates the relaxation path, whereas in the high concentration sample some of the excitations that are seen in the pure material are formed and are subsequently converted to the charge transferred species. The delay in charge transfer in the 10% sample may be attributed to increased disorder and phase segregation into C₆₀ rich and deficient regions, requiring the photoexcitations in the C₆₀ deficient regions to diffuse to the nearest C₆₀ cluster before charge transfer can occur.

In addition to the spectral change caused by the charge transfer, the kinetics and the intensity dependence are also affected. The 1.55 eV band follows a linear intensity dependence at 1 ps in the 1% sample and in both the 1% and 10% samples by 10 ps, implying that the dominant recombination pathway is different than in pristine P3OT, which has a square root intensity dependence. The kinetics of the 1.55 eV band are different for the high and low concentration regimes. In the 1% sample,

a fast exponential component ($\tau = 300$ fs) is superposed on a stretched exponential ($\beta = 1/3$). These results are independent of temperature from 300 K to 21 K, and are similar to the kinetics of the pure material (see figure 2). This is in contrast to the 10% material, in which the decay is also temperature independent but follows a double exponential with time constants of approximately 500 fs and 500 ps. The fact that the lifetime of the photoexcitation is enhanced in the high concentration sample is also attributed to phase segregation of the sample. C₆₀ clusters may stabilize the electron once it is transferred, thereby increasing the lifetime of the charge separated species over that of the 1% material, in which the electron is transferred to a single C₆₀ molecule. Furthermore, the fact that the forward charge transfer is resolution limited (< 250 fs) even at cryogenic temperatures suggests a very efficient excited state transfer integral between the semiconducting polymer and C₆₀.

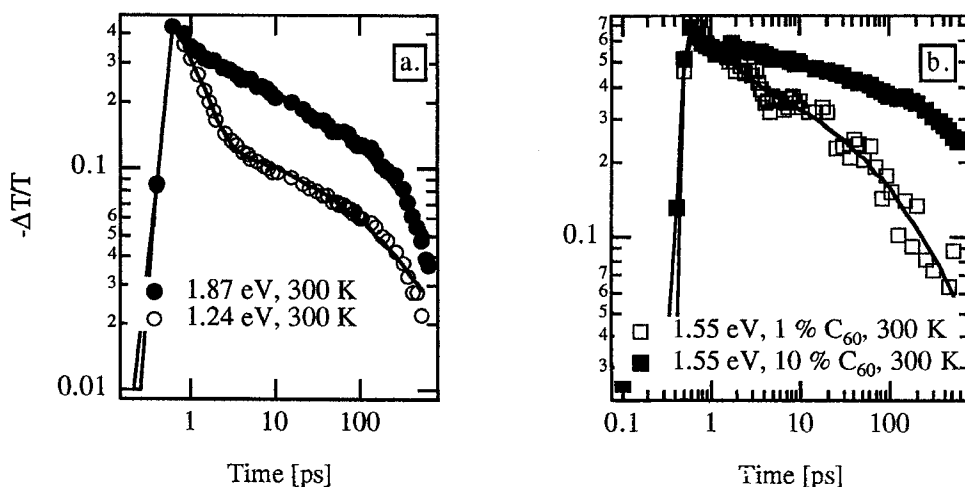


FIGURE 2 a) P3OT B) P3OT/C₆₀

The PIA spectrum for pure BCHA-PPV, and a 1% composite of BCHA-PPV/C₆₀ is shown in figure 3. The pure material shows a broad absorption peaking below 1.2 eV. However, it appears that two species exist since at 1.2 eV the decay is temperature independent and goes as $t^{-0.46}$, while at 1.46 eV it follows $t^{-0.21}$

at 21 K, and $t^{-0.46}$ at 300 K. A more detailed study is required to correctly interpret the PIA in BCHA-PPV.

Once C₆₀ is added the spectrum changes. The spectrum for 1% C₆₀ in BCHA-PPV is shown in figure 3, and consists of a single broad band peaking at 1.45 eV, similar to that seen in P3OT/C₆₀, and MEH-PPV/C₆₀⁷. The risetime is again resolution limited. Since this band is associated with the charge transferred state in MEH-PPV⁷ we conclude that the 1.45 eV band in BCHA-PPV/C₆₀ is the result of an ultrafast electron transfer from the polymer chain to a C₆₀ molecule.

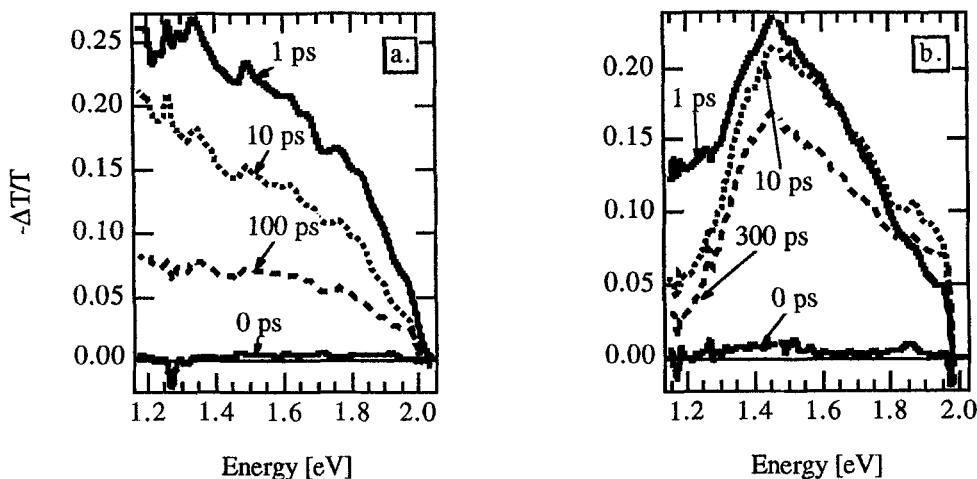


FIGURE 3 a) BCHA-PPV, 300 K b) BCHA-PPV/C₆₀, (1) 300 K

The kinetics of the 1% samples of BCHA-PPV/C₆₀ and MEH-PPV/C₆₀ show a longer lifetime at 1.45 eV as compared to the pure material than is the case for P3OT. In BCHA-PPV/C₆₀ the decay is temperature independent and can be fit to a power law ($t^{-0.09}$) plus a fast exponential component with a time constant of 400 fs. Although the initial decay is faster than in pristine BCHA-PPV, the power law tail is slower than the $t^{-0.46}$ seen in BCHA-PPV, implying the charge transfer state is metastable. For 1% by weight C₆₀ in MEH-PPV a power law decay with an exponent of -0.19 is observed, which is also slower than $t^{-0.26}$

seen in pure MEH-PPV. Addition of more C₆₀ in MEH-PPV converted the power law decay to a double exponential, with time constants similar to those given above for P3OT/C₆₀.

Finally, it should be noted that 1% C₆₀ corresponds to approximately one C₆₀ molecule per 100 PPV repeat units. The ultrafast charge transfer hence implies significant delocalization of the primary photoexcitation on the PPV derivatives.

In conclusion we have demonstrated that photoinduced electron transfer from semiconducting polymers to C₆₀ occurs on a subpicosecond time scale in P3OT, MEH-PPV, and BCHA-PPV hosts. The long lived component of the PIA implies the charge transferred state is metastable upon addition of > 1% C₆₀ in P3OT, and 1% C₆₀ in the PPV derivatives.

ACKNOWLEDGEMENTS

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