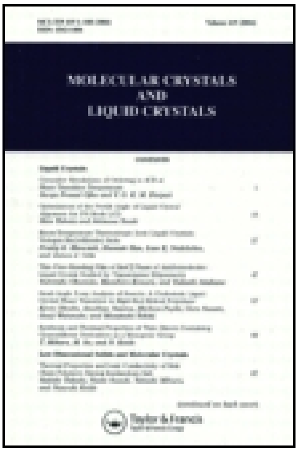

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Subpicosecond Photoinduced Electron Transfer in Semiconducting Polymer - C_{60} Composites

Brett Kraabel [a], Duncan McBranch [a], N. Serdar Sariciftci [a], Daniel Moses [a] & Alan J. Heeger [a]

[a] Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA, 93106

To cite this article: Brett Kraabel, Duncan McBranch, N. Serdar Sariciftci, Daniel Moses & Alan J. Heeger (1994): Subpicosecond Photoinduced Electron Transfer in Semiconducting Polymer - C_{60} Composites, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 733-738

To link to this article: http://dx.doi.org/10.1080/10587259408039317

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 733–738
Reprints available directly from the publisher
Photocopying permitted by license only

SUBPICOSECOND PHOTOINDUCED ELECTRON TRANSFER IN SEMICONDUCTING POLYMER - C_{60} COMPOSITES

Brett Kraabel, Duncan McBranch, N. Serdar Sariciftci,
Daniel Moses, and Alan J. Heeger
Institute for Polymers and Organic Solids, University of
California, Santa Barbara, CA 93106

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(cholestanoxy)-1,4-phenylene vinylene), (BCHA-PPV) in their pure form and mixed with C_{60}. The results show a subpicosecond photoinduced electron transfer from the polymer host onto the C_{60} molecule.

INTRODUCTION

The observation of reversible, metastable, photoinduced electron transfer has been reported[1]. The time scale for electron transfer was inferred indirectly through luminescence quenching to be on the picosecond time scale, which was later confirmed[2]. We now report the results of a comprehensive study of the ultrafast kinetics of electron transfer from polymer hosts to C_{60}, 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 µJ, 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 C_{60} at concentrations of 1%, 10% and 50% C_{60} to polymer by weight. The room temperature photoinduced absorption spectra for pure P3OT, 1% C_{60} in P3OT, and 10% C_{60} in P3OT are shown in figure 1 at various delay times.

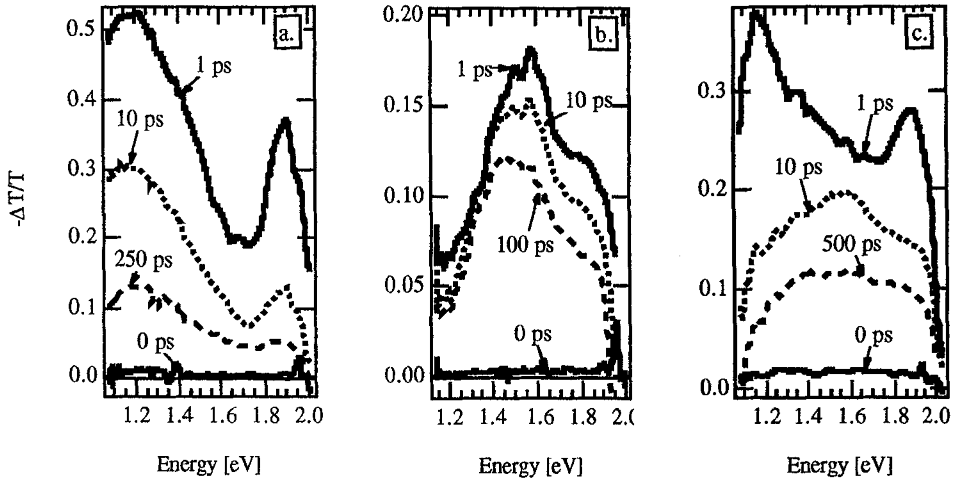

FIGURE 1 a) P3OT b) 1% P3OT/C_{60} c) 10% P3OT/C_{60}

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 X 10^{-6} M) solutions of P3OT [4] 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 samples[4] for these bands also suggests that interchain excitations are dominant[6].

The polymer/C60 composite materials show different behavior for different concentrations of C60. In the low concentration regime (≈ 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 (τ = 300 fs) is superposed on a stretched exponential (β = 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 photoexcitiation is enhanced in the high concentration sample is also attributed to phase segregation of the sample. C_{60} 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 C_{60} 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 C_{60}.

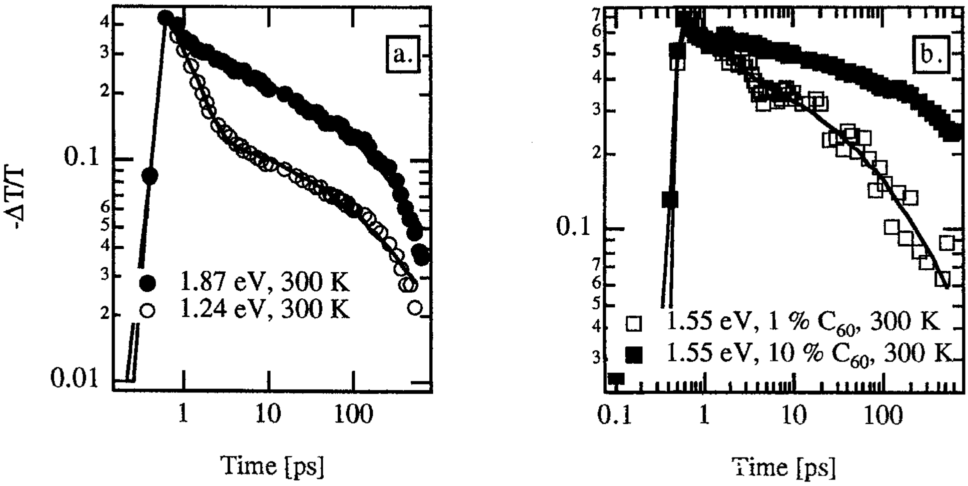

FIGURE 2 a) P3OT B) P3OT/C_{60}

The PIA spectrum for pure BCHA-PPV, and a 1% composite of BCHA-PPV/C_{60} 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/C60[7]. The risetime is again resolution limited. Since this band is associated with the charge transferred state in MEH-PPV[7] 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.

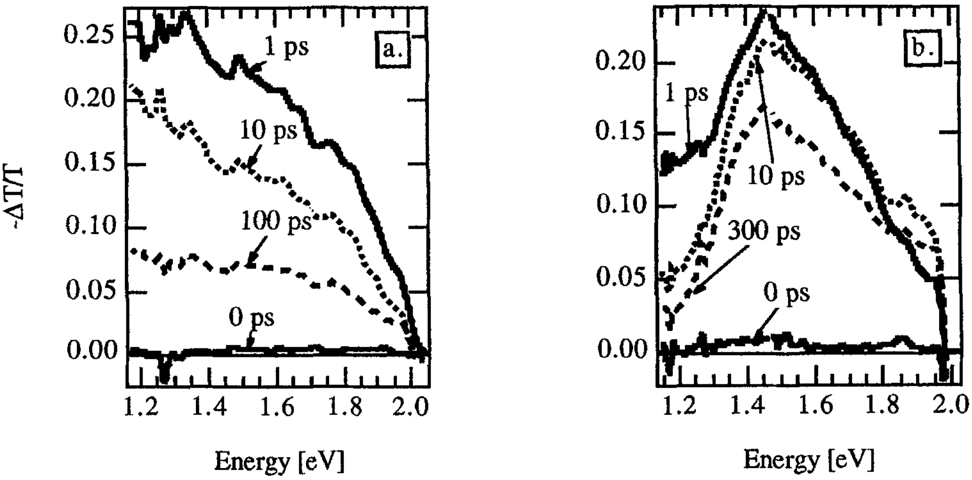

FIGURE 3 a) BCHA-PPV, 300 K b)BCHA-PPV/C60, (1) 300 K

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 BHCA-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 C_{60} in MEH-PPV converted the power law decay to a double exponential, with time constants similar to those given above for P3OT/C_{60}.

Finally, it should be noted that 1% C_{60} corresponds to aproximately one C_{60} 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 C_{60} occurs on a subpicosecond time scale in P3OT, MEH-PPV, and BCHA-PPV hosts. The long lived component of the PIA implies the charge transfered state is metastable upon addition of > 1% C_{60} in P3OT, and 1% C_{60} in the PPV derivatives.

ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation under NSF-DMR90-12808. Funding for the femtosecond laser facility was obtained through an NSF Instrumentation grant, NSF-DMR90-05866.

1. N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, Science, 258, 1474 (1992)
2. B. Kraabel, C. H. Lee, D. McBranch, D. Moses, N. S. Sariciftci and A. J. Heeger, Chemical Physics Letters, 213(3,4), 389 (1993)
3. T. Kobayashi, M. Yoshizawa, U. Stamm, M. Taiji and M. Hasegawa, Journal of the Optical Society of America, B, 7(8), 1558 (1990)
4. B. Kraabel, et. al., to be published, (1994)
5. M. Nowak, S. Hotta, S. D. D. V. Rughooputh and A. J. Heeger, Macromolecules, 20, 965 (1987)
6. D. McBranch, A. Hays, M. Sinclair, D. Moses, and A. J. Heeger, Phsical Review, B 42, 3 011 (1990)
7. L. Smilowitz, N. S. Sariciftci, R. Wu, C. Gettinger, A. J. Heeger and F. Wudl, Physical Review, B 47, 13835 (1993)