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TRANSIENT PHOTOCONDUCTIVITY OF MEH-PPV AND ITS SENSITIZATION BY C_{60}

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Abstract We report the results of comprehensive measurements of photoconductivity (PC) in films of poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene], MEH-PPV and MEH-PPV/C_{60} composites. The peak transient PC of MEH-PPV is proportional to the light intensity and the electric field, and independent of temperature. The spectral response of the picosecond transient PC shows that the onset of the photocurrent coincides with that of photo-absorption, consistent with the photogeneration of charge carriers via an interband transition. The transient PC (lifetime and magnitude) of MEH-PPV increases substantially on increasing the concentration of C_{60} in MEH-PPV/C_{60} composite films; ultrafast photoinduced electron transfer minimizes early-time recombination and enhances the quantum yield for photogeneration of free charge carriers.

INTRODUCTION

There is a controversy over the charge carrier photogeneration mechanism in poly(*p*-phenylenevinylene), PPV: Are free carriers generated via an interband transition[1,2] or through dissociation of excitons in the context of the Onsager[3] model?[4,5] To address this issue, we present the results of comprehensive measurements of the picosecond transient PC in a soluble derivative of PPV, poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene], MEH-PPV. We have also investigated the effect of photoinduced electron transfer on the PC of MEH-PPV/C_{60} composite films by comparing the PC of MEH-PPV sensitized with C_{60} with that of pure MEH-PPV.

EXPERIMENTAL

The procedures for the synthesis of MEH-PPV[6] and MEH-PPV/C60 composites solutions[7,8] have been described in previous publications. Films of MEH-PPV and MEH-PPV/C60 composites were drop-cast from solution onto alumina substrates. The transient PC was measured using the Auston-switch technique[9] with the EG&G PAR 4400 boxcar system fitted with a Tektronix S-4 sampling head. Excitation pulses were obtained from a PRA LN105A dye laser system pumped with a PRA LN1000 N_2 laser.

The pulse width was approximately 20-30 ps, and the pulse intensity was about 1-5 μJ/pulse. The overall system temporal resolution is about 50 ps. Details regarding the transient PC measurements were summarized in earlier publications.[2,8]

RESULTS AND DISCUSSION

Figure 1 shows the time-resolved transient PC of MEH-PPV at 300 K and at 81 K for the photoexcitation at $\hbar\omega$=2.92 eV. The photon flux incident onto the sample per pulse was ~ $6x10^{15}$ photons/cm^2. The transient photocurrent decays exponentially in the subnanosecond time regime, followed by a weak slower component which becomes negligible at 81 K. Similar transient PC was observed at other photon energies as well.

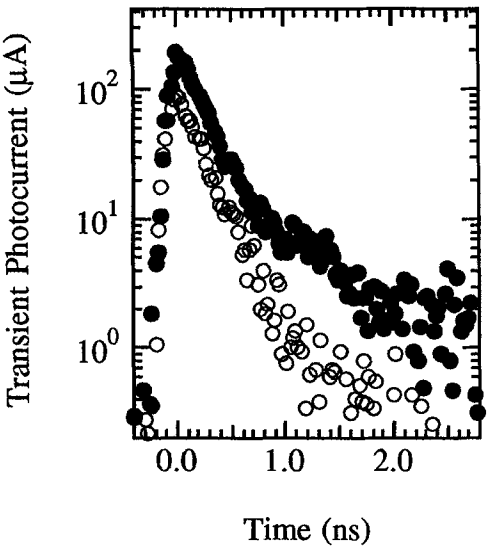

FIGURE 1 The time-resolved transient photocurrent of MEH-PPV at room temperature (●) and at 81 K (○) under an electric field of $3x10^4$ V/cm.

Figure 2 shows the temperature dependence of the peak transient PC from 80 to 300 K for photoexcitation at 2.3 eV and 2.92 eV. The data peak transient PC is nearly independent of temperature. From a detailed analysis of the transient PC in PPV,[2] we previously showed that the slight temperature dependence of the peak transient PC is due to that of the slower component; the fast response is independent of temperature.

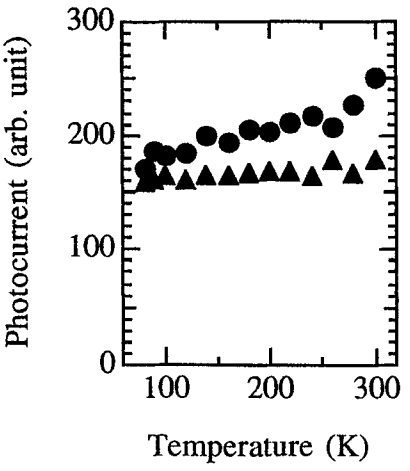

FIGURE 2 The temperature dependence of the peak transient PC at 2.92 eV (●) and 2.3 eV (▲).

The peak transient PC shows a linear dependence on the light intensity and the electric field at all photon energies as shown in Figure 3.

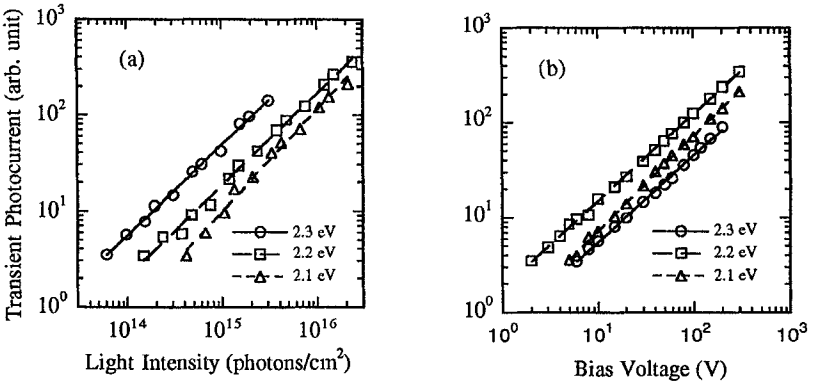

FIGURE 3 (a) The light-intensity dependence of the peak transient PC. (b) The electric-field dependence of the peak transient PC. The data are taken at room temperature at various photon energies.

In the exciton picture, the photogeneration of charge carriers is proposed to result from dissociation of excitons in the presence of the external electric field in the context of

the Onsager model.[3-5] Since the transient PC results from the transport of photoexcited charge carriers (rather than from a displacement current generated by the electric-field induced polarization of bound excitons)[2], the observed temperature-independent transient PC (see Fig. 2) is in sharp contradiction to the predictions of the Onsager model.[3] The temperature-independent transient PC can be readily understood as resulting from direct photogeneration of free charge carriers in the π and π^* bands with subsequent charge carrier transport prior to initial trapping. Furthermore, the linear field dependence of the transient PC (see Fig. 3 (b)) is also inconsistent with the Onsager model.[3]

The magnitude of the peak transient PC excited at different photon energies are presented on a semilogarithmic scale in Figure 4. The transient PC was measured at 0.1 eV intervals from 1.9 to 2.3 eV, near the onset of the π-π^* absorption. The steady-state PC and optical absorption spectra are included for comparison. Both the transient PC and steady-state PC are normalized to equal incident photon flux.

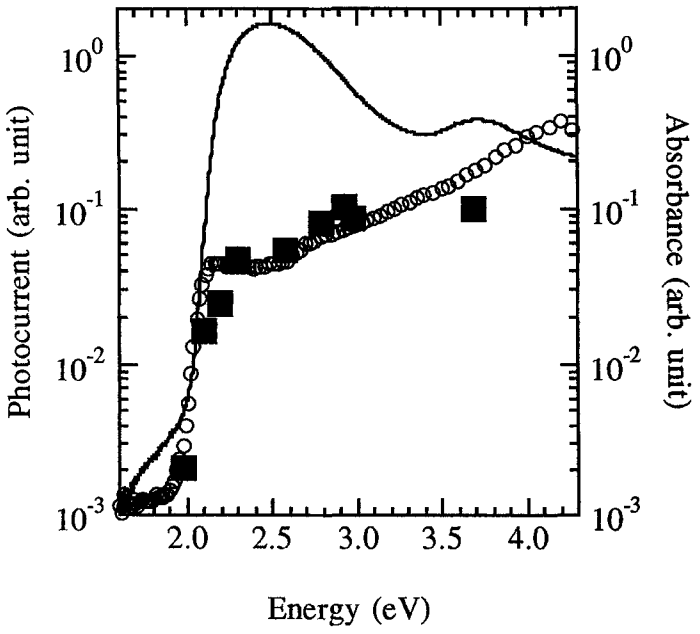

FIGURE 4 The spectral response of the magnitude of the peak transient PC (■) and the steady-state PC (○), together with optical absorption spectrum (solid line).

Direct measurements of the spectral response of both picosecond-transient and steady-state PC clearly demonstrate that the onset of the PC coincides with that of photo-absorption. Therefore, the exciton binding energy must be less than the experimental

resolution (E_{exc} < 0.1 eV). This observation together with the linear intensity dependence of the temperature-independent transient PC indicate the direct photogeneration of free charge carriers via the π-π^* interband transition.

All aspects of the transient PC in MEH-PPV are similar to those observed in PPV.[2] The magnitude of the peak transient PC in MEH-PPV is, however, an order of magnitude smaller than that found in similar thin films of PPV.[2] Thus, in MEH-PPV, where the large side-groups decrease the interchain coupling and thereby decrease the probability of separated charge carriers (polarons) on different chains, early-time recombination is enhanced over that in PPV.

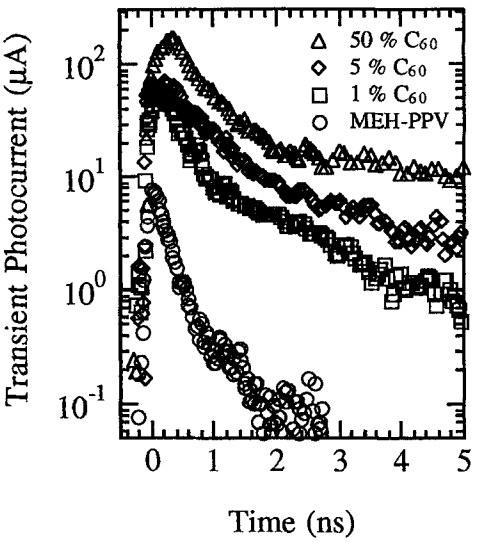

FIGURE 5 The transient PC of MEH-PPV and MEH-PPV/C_{60} at 300 K.

Because early-time recombination is significant in MEH-PPV, the magnitude and decay time of the transient PC in MEH-PPV are significantly enhanced when sensitized by as little as 1% C_{60} even though MEH-PPV dominates the optical absorption, as shown in Figure 5.[8] The transient PC data of MEH-PPV/C_{60} were taken at 300 K under an electric field of 10^4 V/cm, and normalized to an incident photon flux of 7.5×10^{14} photons/cm^2 at $\hbar\omega$=2.92 eV. The results are qualitatively consistent with ultrafast (< 1 ps) photoinduced electron transfer[10]: recombination is inhibited by the spatial separation of the electron (on the C_{60}) and the hole (on the conducting polymer).[8]

CONCLUSION

We have presented the results of comprehensive measurements of PC in films of MEH-PPV. The agreement of the onset of both transient and steady-state PC with that of absorption in MEH-PPV, in conjunction with the linearity on the intensity of the temperature-independent transient PC, imply the direct photogeneration of free carriers via an interband transition and rule out the direct photogeneration of excitons as the primary excitations in MEH-PPV.

The large side-groups in MEH-PPV decrease the interchain coupling and suppress the photogeneration of electrons and holes separated on different chains, thereby resulting in larger early-time recombination compared to PPV. Both the magnitude and lifetime of the transient PC increase substantially on increasing the concentration of C_{60} in MEH-PPV/C_{60} due to ultrafast (< 1 ps) photoinduced electron transfer which thereby minimizes early-time recombination and enhances the quantum yield for photogeneration of free charge carriers. These ultrafast photoinduced electron transfer results can be readily understood within a band model of the electronic structure of the PPV derivative.

ACKNOWLEDGMENTS

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