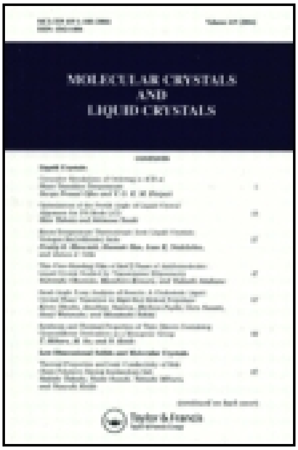

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Photoinduced Hole and Electron Transfer from Poly(phenylene Vinylene) into Molecularly Doped Polymers

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Version of record first published: 24 Sep 2006.

To cite this article: M. A. Abkowitz , H. Antoniadis , J. S. Facci , S. A. Jenekhe , B. R. Hsieh & M. Stolka (1994): Photoinduced Hole and Electron Transfer from Poly(phenylene Vinylene) into Molecularly Doped Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 252:1, 1-10

To link to this article: http://dx.doi.org/10.1080/10587259408038205

*Mol. Cryst. Liq. Cryst.* 1994, Vol. 252, pp. 1–10
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Printed in the United States of America

# PHOTOINDUCED HOLE AND ELECTRON TRANSFER FROM POLY(PHENYLENE VINYLENE) INTO MOLECULARLY DOPED POLYMERS

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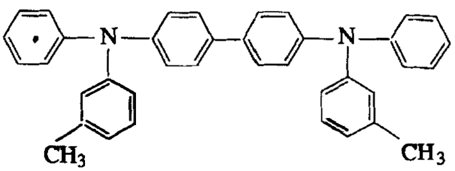
Abstract. Photoinduced *hole* transfer between photoexcited π-conjugated polymer, poly(p-phenylene vinylene) (PPV) and an adjacent trap-free hole-transport molecularly doped polymer containing TPD in a polycarbonate binder in an electric field, is analyzed. Also analyzed and described, under similar electric field conditions, is photoinduced *electron* transfer between PPV and a trap-free electron transport polymer containing BCFM and a polycarbonate binder. Transfer of carriers, both holes and electrons, to the respective transport layers is fast and coherent, without delay. The collection efficiency at an electric field of $4\times10^5$Vcm$^{-1}$ is 25% for photoinduced holes and near 0.2% for photoinduced electrons.

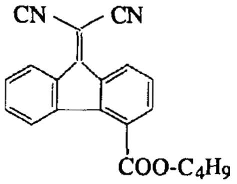
*Keywords: poly(phenylene vinylene), photoconduction, hole transport, electron transfer*

## INTRODUCTION

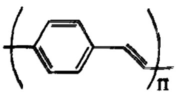
Organic polymers have been studied as active components in devices for many optoelectronic applications such as electrophotographic receptors,[1] light emitting diodes,[2] rechargeable batteries,[3] photovoltaic cells,[4] field-effect transistors,[5] and others, and also as electrodes in some of these devices.[6] In most instances, the device efficiency and the useful life are determined by the nature and stability of interfaces between the device components. Of particular importance is the ability of a polymer to inject or accept charge from, or into the adjacent layer, an electrode or another polymer. Notable examples of interface-sensitive devices are organic light emitting diodes in which the efficiency is determined by the nature of interfaces between the transparent anode and the hole transporting layer, and between the cathode and the medium which delivers electrons to the recombination zone. One of the device-active polymers considered for use in many types of electronic devices is poly(phenylene vinylene) (PPV). This polymer has been studied in detail as a conductor but little is known about the characteristics of its interfaces with other active polymers or electrodes. In a previous communication we discussed photovoltaic properties of the PPV-aluminum interface.[4] In this communication, we describe photoinduced *hole* transfer from PPV into a hole-transporting polymeric insulator comprised of molecularly dispersed TPD in polycarbonate PC, and photoinduced *electron* transfer from PPV into an electron-transporting insulator comprised of molecularly dispersed BCFM in polycarbonate PC(Z). The molecular structures of these materials are shown below. Also described is the use of bilayer devices consisting of PPV in conjunction with essentially trap-free charge transporting dielectric such as those above in obtaining estimates of charge carrier generation efficiency in PPV.



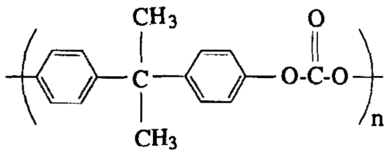
TPD



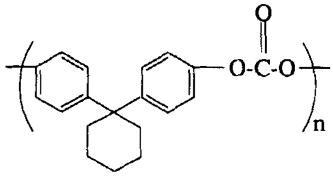
BCFM



PPV



PC



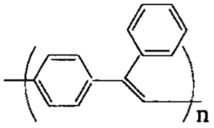
PC(Z)

## EXPERIMENTAL

*Materials*: PPV was prepared from the sulfonium precursor polymer as described in a previous publication.[7] The hole transport molecule, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) and the electron transport molecule, (4-*n*-butoxycarbonyl-9-fluorenylidene) malononitrile (BCFM), were synthesized according to the literature procedures.[8,9] The bisphenol A polycarbonate (PC) was received from Bayer and poly(4,4'-cyclohexylidene - diphenylcarbonate) (PC(Z)) was received from Mitsubishi Gas Chemical. These polymers were used as received.

*Devices*: The bilayer devices shown in Figure 1 were prepared by spin-casting the PPV-precursor polymer solution onto a substrate, aluminum or indium-tin oxide (ITO), followed by thermal conversion at 300°C in argon for 2 hrs. to form thin (~0.2 μm) films of PPV. On top of the PPV film was deposited a thicker charge transport layer, CTL, (6-22μm) of a molecularly doped polymer (50% by weight of TPD in PC or 30% by weight of BCFM in

PC(Z)). The layer was deposited by draw-bar coating from methylene chloride or chloroform solutions, respectively, each containing 15% solids. The devices were then vacuum dried for 20 hrs. at room temperature. To eliminate the occasionally observed hole injection from the aluminum substrate into the PPV layer, a thin (0.1μm) blocking layer of phenyl substituted PPV, (PPV-P),



was inserted between the aluminum electrode and the PPV charge generation layer (CGL). We suspected that the Al electrode may become hole injecting after it had been exposed to hydrochloric acid liberated during the precursor conversion to PPV. Insertion of the PPV-P blocking layer substantially reduced the dark current. Semitransparent (50%) gold or aluminum electrodes were then vacuum deposited on top of the CTLs.

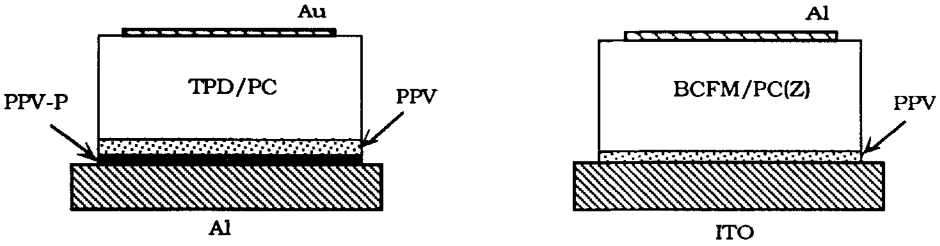


Figure 1. Schemes of layered devices.

*Measurements:* Transient photoconductivity measurements were carried out using the Time-Of-Flight (TOF) technique and recorded using a digital oscilloscope controlled by a personal computer. The excitation light source was a nitrogen pumped dye laser producing pulses of 1 ns duration, far shorter than the typical transit times which were of the order of milliseconds. The total number of incident photons was monitored by a calibrated thermopile detector. The loss of the light energy due to reflection at the surface of the film and attenuation by the semitransparent gold surface electrode was 25%, and was corrected for.

## RESULTS AND DISCUSSION

Photoconductivity in PPV has been observed[10-12] but clear TOF signals have never been obtained, mainly because of a severe charge carrier range limitation. Also, the limited carrier range makes the determination of carrier photogeneration efficiency and carrier drift mobility extremely difficult. Interpretation requires many simplifying assumptions. It is estimated[13] that at E~$10^5$ $Vcm^{-1}$, photogenerated carriers (holes) can travel, on average, only about 1000Å. Electron transport has not been observed in PPV, either because electrons are much less mobile or because the density of deep traps is even higher than for holes. In some specimens of PPV, however, and specifically in those in which the conversion from the precursor polymer was not complete, we were able to obtain reasonably well defined TOF transient signals for holes even in samples about 10 μm thick[14] which showed that the hole mobility was about $10^{-5}$ $cm^2$ $V^{-1}$ $sec^{-1}$ at 295K and E ~ $10^5$ V $cm^{-1}$. In fully converted PPV specimens, the carrier range limitation is much more severe and no TOF transients could be obtained.

It is now well established that photoconductivity measurements in bilayer devices with trap-free charge transport layers schematically illustrated in Figure 1 are valuable for studies of polymers with a range limitation. In these devices, the trap-filled polymer layer is only thick enough to absorb most of the incident light which, in this case, is comparable to the mean carrier migration distance. Consequently, the photogenerated charges have a better chance to reach the interface before being trapped, and are injected into a trap-free charge transport polymer. Charge trapping in the photoconductive polymer is thus minimized and collection of photogenerated charges is facilitated.

## Photoinduced hole transfer from PPV into TPD:PC

Figure 2 shows the time-of-flight transient signals obtained on a bilayer device containing the PPV charge generation layer (CGL) and the TPD:PC (50:50) hole transport layer (CTL). The thicknesses of the layers were 0.4 and 22μm, respectively. The trace (a) shows the photocurrent of holes generated in the CGL by a 460 nm laser pulse, injected into and then migrating through the CTL under negative bias at an electric field of E = 1.4 x $10^5$$Vcm^{-1}$. The wavelength of the excitation light pulse was selected to minimize the absorption in the CTL and maximize the absorption in the CGL (see Figure 3). The light penetration depth in PPV is about 0.1μm. A control experiment confirmed that the dark current due to injection of dark carriers from PPV was very small. The trace (b) shows the photocurrent of holes photogenerated in the surface region of the TPD layer by uv flash photoexcitation at 337nm at the same electric field and positive bias. The transit time $t_{Tr}$ of 1.3 ms in the trace (b) corresponds to the mobility μ in TPD:PC of 1.3 x $10^{-5}$$cm^2$$V^{-1}$$sec^{-1}$ at E = 1.4 x $10^5$ $Vcm^{-1}$ which is the same as previously reported for 50% TPD

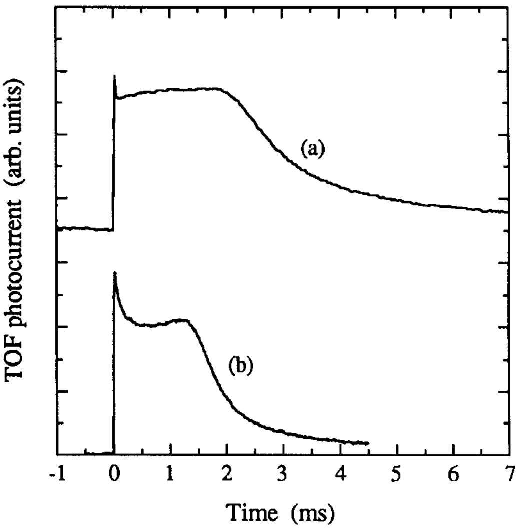


Figure 2. TOF transients in the bilayer device (a): carriers are photogenerated in PPV and injected into the TPD:PC layer, (b): photogeneration occurs near the top surface of the TPD:PC layer.

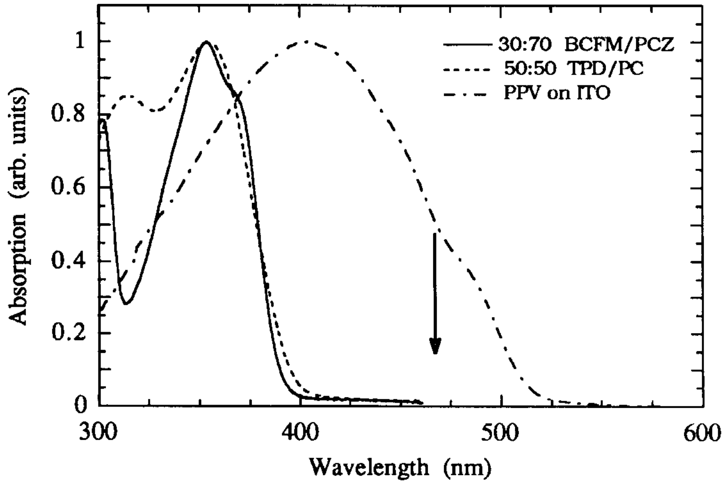


Figure 3. UV - vis spectra of TPD, BCFM and PPV. The arrow shows the position of the laser pulse.

in PC.[8] Somewhat longer transit time $t_{Tr}$ (2 ms, corresponding to the drift mobility $\mu = 8.1 \times 10^{-6}$ cm$^2$ V$^{-1}$ sec$^{-1}$) was observed in the case when charges were photogenerated in PPV under negative bias. We suspect that some charge accumulation may have occurred, presumably at the PPV/TPD:PC interface, which could alter the externally applied electric field and thus could be responsible for the difference in drift mobilities. Delayed injection from PPV to the CTL can be ruled out as the cause of the difference because the shape of the recorded TOF signals is characteristic of quick and coherent injection. The overall carrier supply efficiency $\eta_s$ is determined from the integrated TOF signal:

$$\eta_s = \frac{\int_0^\infty I_{TOF}(t)dt}{eAN_{ph}}$$

where $AN_{ph}$ is the number of photons absorbed in PPV and $I_{TOF}(t)$ is the time-of-flight photocurrentdue to migrating holes. The efficiency $\eta_s$ is a product of four factors, the quantum efficiency of photogeneration $\eta_g$, (the number of charges produced per incident photon), the probability to escape trapping in PPV $\eta_{tg}$, the injection efficiency $\eta_i$ and the probability to escape trapping in the CTL $\eta_{tT}$:

$$\eta_s = \eta_g \, \eta_{tg} \, \eta_i \, \eta_{tT}.$$

Hole transport in the TPD:PC layer is known to be trap-free[8,15,16] and therefore $\eta_{tT}$ is unity. The energy diagram presented in Fig. 6 suggest that there is a very small energy barrier associated with the PPV/TPD interface. An evidence of that also comes from the near-perfect shape of the TOF transient with a flat plateau of constant current and a short tail. Therefore, $\eta_i$ should also approach unity, at least at high electric fields. Consequently, $\eta_s$, reaching 25% at $E \sim 4\text{x}10^5$ Vcm$^{-1}$, is considered to be the lower bound for the *intrinsic* generation efficiency $\eta_g$.[13] If trapping in PPV indeed occurs and the photogeneration is intrinsic, the actual photogeneration efficiency in PPV is higher and can approach unity. However, this study does not attempt to distinguish between *intrinsic* and *extrinsic* photogeneration (dissociation of $\pi \rightarrow \pi^*$ excitons at the PPV/TPD:PC interface in the presence of the electron donating TPD). Experiments to determine the role of the adjacent CTL in the charge carrier generation process (fluorescence quenching etc.) are underway.

## Photoinduced Electron Transfer From PPV Into BCFM:PC(Z)

Figure 4 shows two TOF transient signals obtained on a bilayer device as in Figure 1. The charge transport layer was BCFM molecularly dispersed in polycarbonate PC(Z) at 30 wt% loading. The transient current signal (a) was obtained after photoexcitation of the PPV layer (0.4μm thick) with a pulse of 460 nm light from the nitrogen pumped dye laser, under positive bias on Al. Figure 3 shows that the absorption of incident light in the BCFM:PC(Z) layer is negligible. The signal (b) was produced by uv photoexcitation (337nm) of the surface region of the BCFM:PC(Z) layer under negative bias. In a control experiment, with a single layer BCFM:PC(Z) device of the same thickness as above, no TOF signal was detected upon exposure to the 460 nm light pulse at negative bias. This, in addition to the demonstrated absence of hole transport in BCFM-containing layers (no photocurrent was detected upon exposure to uv light at positive bias) proves that the transient signals in Figure 4 are due to the migration of electrons photogenerated in PPV or at its interface with BCFM:PC(Z). The transit times determined from the two TOF signals are practically identical, and the mobilities calculated from these transit times ($\mu = 1.8\text{x}10^{-7}$ cm$^2$V$^{-1}$sec$^{-1}$ at 8x10$^5$ Vcm$^{-1}$) are in a good agreement with the previously published values for BCFM.[17] The form of the TOF signals which show flat regions of constant transient current and relatively short tails again indicate that transport of electrons through the 6 μm thick BCFM layer is essentially trap-free. The supply efficiency of electrons $\eta_s$ exhibits a stronger

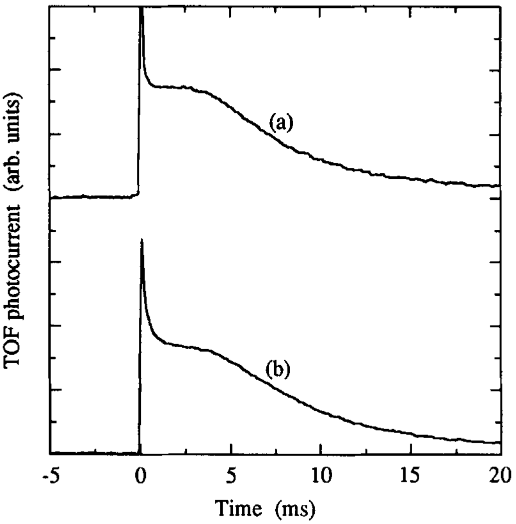


Figure 4. TOF transients in the bilayer device (a): carriers are photogenerated in PPV and injected into the BCFM:PC(Z) layer, (b): photogeneration occurs at the top surface of BCFM:PC(Z)

electric field dependence than that of holes ($\eta_s \sim E^{2.4}$) and approaches 7% at the electric field of E= 1.6x10$^6$ Vcm$^{-1}$. If we assume that photogeneration is *intrinsic* within PPV - in which case the photogeneration efficiency $\eta_g$ of electrons and holes is the same, the stronger electric field dependence of $\eta_s$ in PPV/BCFM:PC(Z) (cf. Fig. 5) is either due to the field dependence of electron range (trapping) in PPV, or to the difficulty to overcome the interfacial barrier between PPV and BCFM:PC(Z). The energetic consideration (see Fig.

6), however, seems to argue against the latter. The large difference between the reduction potentials of PPV and BCFM suggests that the lower supply efficiency for electrons is not caused by the interfacial barrier but is rather due to trapping in PPV. If, on the other hand, photogeneration is *extrinsic*, i.e. with the assistance of the charge transport molecules at the interface, one can attribute the difference in $\eta_s$ to the effects of the respective small molecules. As the scheme in Figure 6 indicates, injection of holes into TPD and electrons into BCFM is energetically favored. The oxidation and reduction potentials, $E^{ox}$ and $E^{red}$, (vs Ag/AgCl) of fully converted PPV are 0.76V, and -1.74 V, respectively, and its bandgap is 2.5 eV.[18] The value of $E^{ox}$ is dependent on the

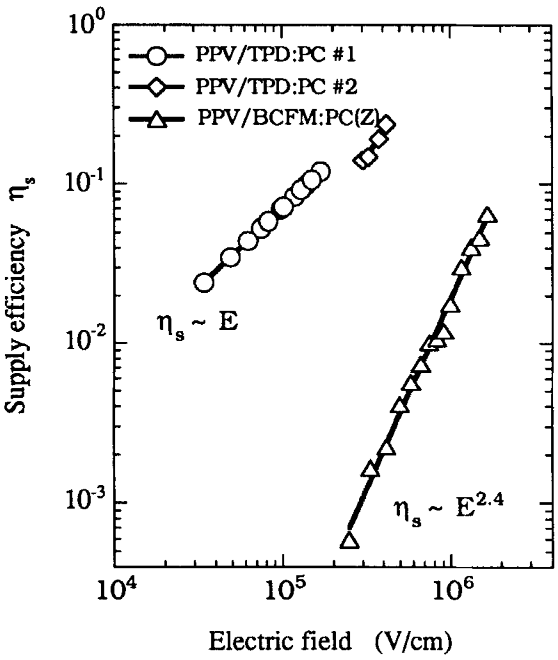


Figure 5. Electric field dependence of hole supply efficiency for two PPV/TPD:PC devices with 22μm (#1) and 10 μm (#2) thick transport layers, and of electron supply efficiency for PPV/BCFM:PC(Z).

degree of conversion as the study of oxidation of PPV oligomers indicates.[19] The extrapolation of $E^{ox}$ values of PPV oligomers also yields a value near 0.8V. The $E^{ox}$ of TPD is 0.76 V (vs SCE) which sets its HOMO level at, or slightly above the valence band of PPV which favors hole injection from photoexcited PPV into TPD, especially in the presence of an electric field. The reduction potential $E^{red}$ of BCFM is -0.65V (vs SCE) which places its

LUMO level well below the conduction band of PPV (by more than 1eV) which favors electron injection from photoexcited PPV into BCFM. It can be argued that PPV, even though it is a wide bandgap material, has states in the bandgap which can participate in the electron exchanges. On the other hand, carefully purified acid-free PPV is a good insulator which suggests that the gap states are due to impurities and their density can be substantially decreased by purification. Since the specimens were carefully purified and essentially nonconducting and the injection characteristics do not change from sample to sample, we concluded that the intragap (impurity) states are not involved in the electron transfer. Even though the illustration in Figure 6 is oversimplified, the difference between the reduction potentials of PPV and BCFM shows that transfer of photogenerated electrons into BCFM may be possible even in the absence of an electric field.

Studies elucidating the photogeneration mechanism and the role of the adjacent electron-donating or electron-accepting materials at the interface with PPV are currently in progress.

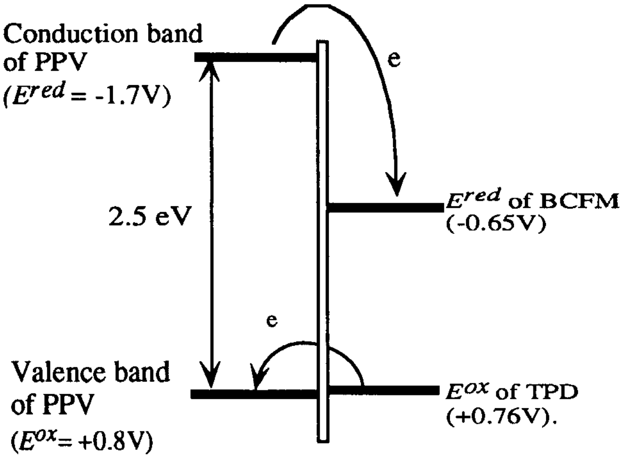


Figure 6. Energy scheme for injection of charges from PPV to TPD and BCFM.

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