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Effects of bimolecular recombination and charge-trapping on the transient photoconductivity of poly(*p*-phenylene vinylene)

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Abstract

We report on fast transient photoconductivity measurements on highly oriented films of poly(*p*-phenylene vinylene) at various excitation densities and temperatures via linear (400 nm) or two-photon (800 nm) excitation. The photocurrent waveform is found to be independent of the applied electric field (up to $F \sim 3\times10^5$ V/cm) but strongly dependent on excitation density. A significant reduction of the photocurrent lifetime is observed at higher light intensities, clearly indicating carrier bimolecular recombination. A transport mechanism mediated by traps is also evident by the long-lived (up to 1 μs) photocurrent 'tail' that diminishes at low temperatures. We have fitted the transient photocurrent waveforms to a kinetic model from which the dynamics of carrier recombination, trapping and de-trapping were deduced.

Keywords: Photoconductivity, Poly(phenylene vinylene)

1. Introduction

Understanding of the charge carrier transport in conjugated polymers is essential for the realization of various polymer-based devices such as LEDs, FETs and photovoltaics. Fast transient photoconductivity (PC) measurements have provided information on the prevailing transport mechanisms promptly after photoexcitation such as the carrier mobility and lifetime. However, photoconductivity is a complex phenomenon, as it involves with various processes such as light absorption, charge photogeneration, charge transport, charge recombination, and charge trapping and de-trapping from localizing states. Some of the above processes have been unraveled by means of ultrafast spectroscopic techniques [1], however the role of traps on the early-time transport properties and their effect on the photocurrent decay mechanism have been lacking. Here we present a fast (t>100 ps) transient photoconductivity studies at a wide range of light intensities and external electric fields and a comprehensive kinetic model that describes the experimental observations. At the high intensity regime, we find a clear evidence for a dominating bimolecular carrier recombination mechanism, while at the low intensity regime, when the density of photocarriers is comparable to that of the trap states ($\geq 10^{16}$ cm^{-3}), the carrier trapping dominates the photocurrent decay, giving rise to an apparent monomolecular decay. The existence of a prevailing bimolecular carrier recombination has important implications since it signifies their delocalized nature.

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2. Experimental

The poly(*p*-phenylene vinylene) (PPV) samples are free-standing films (with thickness of about 17 μm), highly oriented by tensile drawing (draw ratio of l/l_0=4). These samples show a high degree of crystallinity [2], anisotropic optical features [3], and enhanced transport properties [4]. Transient photoconductivity measurements were performed in the Auston switch configuration [5] where planar Au contacts were evaporated on top of the PPV film surface, with a gap between the electrodes ranging between 10 and 20 μm. The contacts were deposited in such a way that the applied electric field (F) was parallel to the polymer chains axis. The pulsed excitation was generated by an amplified Ti:Sapphire laser system, yielding laser pulses of 100 fs duration at 1 KHz repetition rate. For the two-photon excitation we used the 800 nm output of the laser while for the linear excitation we utilized its second harmonic (400 nm). In order to improve the uniformity of the excitation across the photoconductive switch, the laser was collimated to a relatively wide beam, where only the central part of it was used to illuminate the sample. The PC was recorded by

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a fast integrating boxcar system (EG&G PARC 4400) with an overall time resolution of about 100 ps. The zero-field background signal was subtracted from each PC waveform. Measurements were performed while the sample was kept in vacuum (pressure of ~10^{-4} Torr). We verified that the contribution due to electron photoemission was negligible in our measurements by checking the reproducibility of the experimental results while the sample chamber was filled with an electron quenching gas mixture [6]. Low temperatures, down to 80 K, were obtained by a Helitran cryogenic system.

3. Results and Discussion

3.1 Experimental Results.

Low densities of charge carriers can be achieved either by using linear excitation (at energy above the π-π^* transition) with polarization perpendicular to the polymer chains direction, or alternatively by exciting the polymer via two-photon absorption [7]. Due to the longer optical penetration depth in the above cases with respect to the linear excitation with polarization parallel to the chain axis, carriers are photoexcited across a greater volume, resulting in low densities of carriers but yet in a large, detectable photocurrent [8]. A logarithmic plot of the intensity dependence of the peak transient PC for linear (perpendicular polarization) and two-photon excitation at various F is shown in Fig. 1. As expected, the data can be fitted by a power law with exponent n~1 and n~2 for linear and two-photon excitation, respectively.

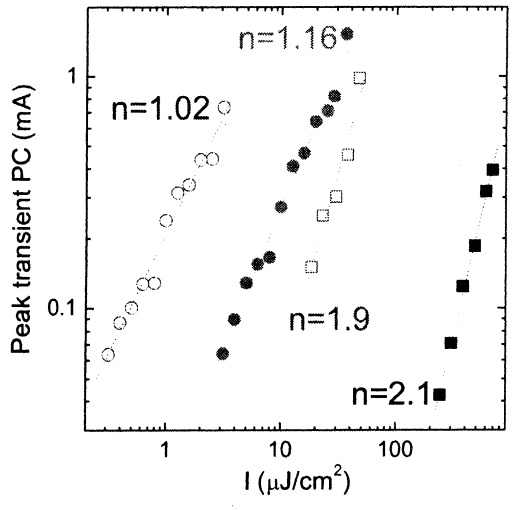

Figure 1: The dependence of the peak transient PC on excitation intensity (I): open and solid circled are for linear excitation at F=2.7 x 10^5 V/cm and F=6.7 x 10^4 V/cm, respectively; open and solid squares are for two-photon excitation at F=3.3 x 10^5 V/cm and F=2 x 10^4 V/cm, respectively. The dotted lines represent a fitting of the data with a power law of exponent n, whose value is indicated in the figure.

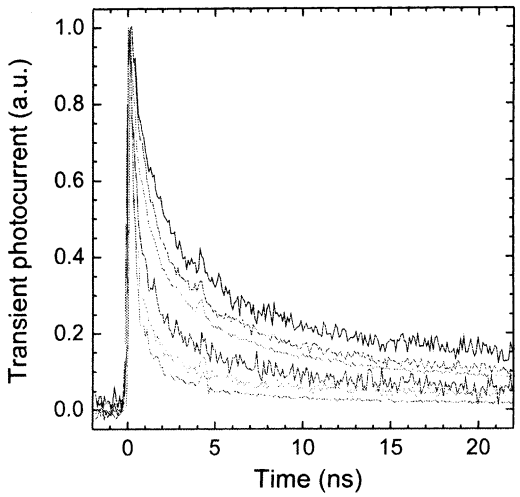

Figure 2. Intensity dependence of the transient PC waveforms obtained by linear excitation, with polarization perpendicular to the polymer chains; the displayed normalized curves, from top to bottom, are obtained for the following photon fluxes: 2.1 x 10^{12} cm^{-3}, 5.4 x 10^{12} cm^{-3}, 1.1 x 10^{13} cm^{-3}, 1.7 x 10^{13} cm^{-3}, 4.2 x 10^{13} cm^{-3} and 1.2 x 10^{14} cm^{-3}.

For similar carrier densities, generated either by linear or two photon absorption, we have obtained similar PC waveforms, indicating that the carrier recombination dynamics is independent of the carrier generation route. The PC waveform is also found to be independent of F (up to F~3×10^5 V/cm), but strongly dependent on the excitation intensity, as reported in Fig. 2. These data clearly show that the higher is the intensity the faster is the PC decay rate, as expected from a bimolecular recombination process.

One can estimate the extent of the carrier wavefunction from the charge-carrier density onset for bimolecular recombination. The lowest carrier density (n=6x10^{15} cm^{-3}) used in our experiments sets a lower limit for the average inter-carrier distance of $r=(n)^{-1/3}$~ 55 nm.

At the lowest excitation intensities, the data of Fig. 2 indicate a long lived photocurrent 'tail' that may persist up to $t > 1$ μs. This latter behavior suggests the effect of trapping and de-trapping that significantly extend the carrier life time. This interpretation is indeed corroborated by its dependence on temperature (T). As depicted in Fig. 3, as T reduces the PC 'tail' diminishes, and below 100 K it is completely suppressed. The effect of traps is manifested also at short time scales as indicated by the variation of the PC peak with T (Fig. 4). The T dependence of the PC peak exhibits a weak thermally activated behavior that originates from the phonon assisted carrier release from traps during a time span comparable to the temporal resolution of our measuring system (~100 ps). The small activation energy (ΔE=45 meV) deduced from the data in Fig. 4 indicates that shallow traps dominate the initial transport after the photoexcitation.

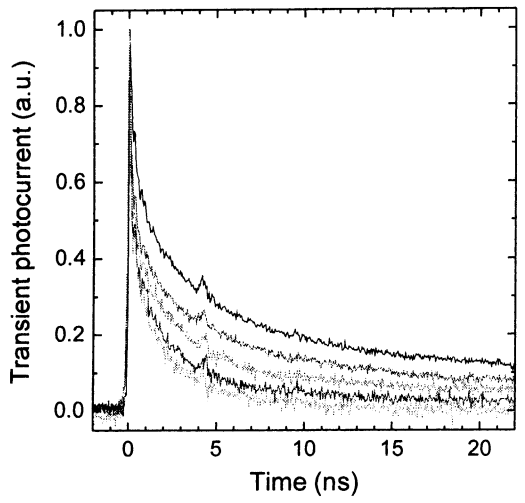

Figure 3. Temperature dependence of the transient PC waveform generated by two-photon excitation (800 nm) at F=3.3 x 10^5 V/cm and I=120 μJ/cm^2 per pulse. From top to bottom the curves are obtained at the following temperatures: 297 K, 240 K, 215 K, 165 K, and 125 K.

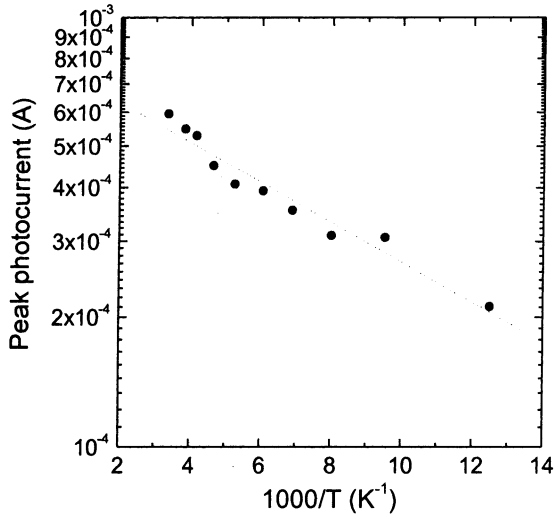

Figure 4. Arrhenius plot of the peak transient photocurrent (dots). The dotted line is a linear fit of the data.

3.2 Modeling the Charge Carrier Dynamics.

The picture of the evolution of the transport can be envisaged in the following way: initially upon photoexcitation, the charge carriers occupy extended states and are delocalized over the conjugation length of the chains. During this time the 'free' carriers contribute to transport (in the following model we neglect the contributions via hopping between localized states). As time progresses, the density of free carriers is reduced by: i) carriers annihilation via bimolecular (non-geminate) recombination; ii) localization of the carriers at trap sites. After trapping, carrier-phonon scattering may release the trapped carriers into extended states (de-trapping process) and thus enable them to contribute to the photocurrent. Once trapped, the carriers could also act as recombination centers; for example, a trapped negatively charged carrier (negatively charged polaron) could recombine with a mobile positively charged polaron. A general description of the above processes can be formulated by the following system of differential equations [9]:

$$\begin{cases} \frac{d}{dt}n(t) = -\gamma\, n(t)p(t) - \beta_n[N_n - n_t(t)]n(t) + \frac{n_t(t)}{\tau_n} - \beta_{np_t}p_t(t)n(t) \\ \frac{d}{dt}n_t(t) = \beta_n[N_n - n_t(t)]n(t) - \frac{n_t(t)}{\tau_n} - \beta_{pn_t}n_t(t)p(t) \\ \frac{d}{dt}p(t) = -\gamma\, n(t)p(t) - \beta_p[N_p - p_t(t)]p(t) + \frac{p_t(t)}{\tau_p} - \beta_{pn_t}n_t(t)p(t) \\ \frac{d}{dt}p_t(t) = \beta_p[N_p - p_t(t)]p(t) - \frac{p_t(t)}{\tau_p} - \beta_{np_t}p_t(t)n(t) \end{cases} \quad (1)$$

where n and p indicate the density of mobile electrons and holes, n_t the density of trapped electrons, p_t the density of trapped holes, N_n the density of trapping sites for electrons and N_p the density of trapping sites for holes; γ is the bimolecular recombination coefficient, β_n and β_p are the cross sections times the carrier velocity for free electrons/holes trapping, β_{np} and β_{pn} are the cross sections times the carrier velocity for recombination of free electrons/holes with trapped holes/electrons; τ_n and τ_p are the electrons/holes de-trapping times. The carrier de-trapping time is expected to exhibit a thermally activated behavior: $\tau = \nu^{-1}\exp(E_a / kT)$, where ν is the attempt-to-escape frequency and E_a the activation energy for the de-trapping process.

The photocurrent is given by:

$$J_{PC}(t) = eF[\mu_n n(t) + \mu_p p(t)] \quad (2)$$

where e is the electron charge, μ_n and μ_p the electron/hole mobility in the extended states, and n and p are solutions of Eqs. 1 for the electron/hole densities. The theoretical electronic structure of PPV suggests that μ_n=μ_p, [10], a behavior that is compatible with the experimental results of the spatially resolved electroluminescence from oriented PPV in a planar metal-polymer-metal structure [11].

A quantum yield for carrier photogeneration of ϕ>10% has been previously determined in PPV by ultrafast carrier density measurements using transient photoinduced absorption probed at the IRAV modes [1]. In the following, we assume γ=1 x 10^{-8} cm^3/s, which is a typical value for large band gap semiconductors [9] as well as the one found for the exciton bimolecular recombination in conjugated polymers [12].

Eq. 2 can be solved numerically and the optimal parameters can be deduced from the minimal least squares distance from the experimental data. We have used the following initial conditions: n(t=0)=p(t=0) equal to the value derived from the experimental excitation intensity, taking into

account reflectivity, light penetration depth, and quantum yield for carrier photogeneration (ϕ=10%), as well as initial trap densities of $n_t(t=0)=p_t(t=0)=0$.

We find that satisfactory agreement with the experimental data can be achieved only if the de-trapping time for one of the two types of charge carrier is much greater that 25 ns, indicating the presence of two types of traps, namely deep and shallow traps. Considering that pristine conjugated polymers typically show a p-type character, we assume that electron-traps are the deep ones, while the hole-traps are the shallow ones. With these assumptions all the other fitting parameters are uniquely determined by the optimization procedure.

From the fitting we find the following parameter values: total densities of traps of N_n = 0.6 x 10^{16} cm^{-3} and N_p = 4.6 x 10^{16} cm^{-3} (in agreement with the results of the thermally stimulated currents) [13], β_n = 8.1 x 10^{-8} cm^3 s^{-1}, β_p = 23.1 x 10^{-8} cm^3 s^{-1}, β_{npt} = 2.6 x 10^{-8} cm^3 s^{-1}, β_{pnt} = 0.5 x 10^{-8} cm^3 s^{-1}. The initial trapping times, for electrons and holes ($[\beta_{n,p} \times N_{n,p}]^{-1}$) are ~2 ns and 100 ps, respectively. The product of the cross section and the drift velocity for capturing free electrons is higher than that for capturing free holes, compatibly with the assumption of shallower hole-traps. De-trapping of holes from shallow traps extends the overall carrier lifetime. We find ν = 1.28 x 10^{11} Hz and E_a = 67 meV, which is comparable to the small activation energy of the measured transient PC peak (Fig. 4). The energy of shallow traps is therefore 2-3 k_BT, (where T is the room temperature). The corresponding hole de-trapping time at room temperature is τ_p = 8 ps, while at 80 K τ_p = 18 ps.

4. Conclusions

In summary, we have demonstrated that fast transient photoconductivity measurements at various excitation densities and temperatures reveal the role of bimolecular recombination and charge trapping on the carrier transport in conjugated polymers. We find that, although traps reduce the 'effective' carriers mobility, they significantly extend the carrier life time (and thus the transport), an important feature for the operation of polymer-based devices such as LEDs and photovoltaic.

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