

Temperature-Independent Photoconductivity in Thin Films of Semiconducting Polymers: Photocurrent Sweep-Out Prior to Deep Trapping

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(Received 20 October 1997)

In thin films, the steady-state photoconductivity is temperature (T) independent in agreement with transient photoconductivity in the subnanosecond regime. As thickness is increased, an activated T dependence emerges. The T independence of the product of the carrier density (n) times the mobility (μ) for thin films results from carrier sweep-out prior to trapping; the crossover from T -independent μ to activated μ occurs when the transit time across the film is comparable to the time required for deep trapping. Thus, steady-state photoconductivity confirms that, in semiconducting polymers, the carrier generation mechanism is T independent, inconsistent with the Onsager model of photocurrent generation. [S0031-9007(98)05607-5]

PACS numbers: 73.50.Pz

The “traditional” theoretical approach to the problem of carrier generation in low mobility materials (e.g., conducting polymers, amorphous semiconductors, and molecular crystals) has favored the exciton model. According to the exciton model, the probability of the geminate electron-hole ($e-h$) pair remaining bound (an “exciton”) during thermalization is high. Therefore, models of carrier photogeneration [1–3], including the Onsager model [4], have emphasized the importance of the Coulomb interaction in binding the pair and the role of external field (E) and temperature (T) in processes which dissociate the pair into “free” carriers. Thus, generally, the exciton model predicts a strong dependence of the quantum yield ϕ on T and E [1–4].

Although strong T dependence is typically observed in steady-state photoconductivity [5], fast time-resolved photoconductivity measurements in semiconducting polymers have shown that the carrier generation process is T independent [6–9]. Time-resolved photoconductivity offers the possibility of studying carrier transport prior to trapping. Such measurements can separate thermally activated mobility (μ) due to trapping from thermally activated carrier density (n) due to phonon assisted dissociation of Coulomb bound geminate $e-h$ pairs. The facts derived from the time-resolved photoconductivity of conjugated polymers include the following [6–9]: (i) The fast transient photocurrent is T independent; (ii) the fast transient photocurrent is linear in E in the low to moderate field regime, but increases nonlinearity with E at high fields, as does the mobility; (iii) the nonlinear dependence of the photocurrent on E does not correlate linearly with the luminescence quenching; (iv) the fast transient photocurrent is linearly proportional to the light intensity. Note that (i) and (ii) imply that the quantum efficiency of carrier generation is independent of T and E ; (iii) implies that the field-induced luminescence quenching does not originate from exciton dissociation, and (iv) implies that the carriers are generated by a first order

process that cannot be attributed to interactions between excitations.

Nevertheless, the nature of photoexcitations in poly(phenylenevinylene) (PPV) and its soluble derivatives has remained controversial [10,11]. In part, the controversy arises from the conflict between the results obtained with fast time-resolved photoconductivity and those obtained by the more familiar steady-state photoconductivity; the latter indicate a strong T dependence for the $n\mu$ product. Here, we resolve the apparent conflict. The idea is rather simple: If the sample is sufficiently thin that the photocarriers can be swept out before a significant fraction fall into traps, the steady-state photocurrent will provide information similar to that obtained at short times by transient photoconductivity (in the latter, sample thickness is not important since pretrapping and trap dominated transport are separated in the time domain).

Using this approach, we show that, in thin samples (thickness $d \leq 120$ nm), the $n\mu$ product obtained from steady-state photoconductivity exhibits a temperature dependence in agreement with fast transient photoconductivity data obtained in the subnanosecond time regime. As the film thickness is increased, an activated temperature dependence emerges. We conclude that the T independence of the $n\mu$ product for thin films results from carrier sweep-out prior to trapping and that the crossover from T -independent μ to activated μ occurs when the transit time across the film is comparable to the time required for deep trapping. At longer times (thicker films), the mobility becomes trap dominated with an activated T dependence. Consequently, the steady-state photoconductivity data indicate that the carrier generation mechanism in semiconducting polymers is independent of temperature. Thus, using thin film samples, information regarding the transport prior to trapping can be obtained from steady-state photoconductivity (an experimental approach that is both simple and broadly available), while similar experiments on thicker samples yield information on

trap-limited transport. This straightforward experimental approach enables the identification of the origin of the temperature dependence of the $n\mu$ product as thermally activated mobility rather than thermally activated carrier generation. Moreover, from the combined results of steady-state and transient photoconductivity measurements, we obtain values for the quantum yield ($\phi \approx 3 \times 10^{-3}$) and the pretrapping mobility ($\mu \approx 0.2 \text{ cm}^2/\text{Vs}$).

PPV and its derivatives are excellent systems for studying carrier sweep-out: They can be easily formed into thin films, they have sufficient dielectric strength to enable high field measurements, and they are sufficiently pure that the dark current is small. Photoconductivity was measured in the “sandwich” configuration. Thin films ($d < 500 \text{ nm}$) of poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV) were prepared by spin-casting from solution onto glass substrates coated with indium/tin oxide (ITO). The top electrode was Ca, vapor deposited in vacuum ($< 2 \times 10^{-6}$ torr). Thicker films (4100 and 5700 nm) were drop-cast onto ITO substrates; again Ca was vapor deposited as the top electrode. All samples were prepared and handled in inert atmosphere. For measurements, the samples were mounted onto the cold finger of a cryostat and kept under vacuum.

The Ca/MEH-PPV/ITO diode has been studied in detail in the context of light emission from and photodetection by semiconducting polymers [12,14]. Current vs voltage (I - V) curves were typical of ITO/MEH-PPV/Ca diodes. The asymmetric contacts of the Ca/MEH-PPV/ITO diode give rise to a built-in potential and a built-in electric field $E_{\text{bi}} = 1.8/d \text{ V/cm}$, where d is the thickness of the polymer layer. In reverse bias (Ca positive and ITO negative), both electrodes are blocking with negligible injection. Thus, the Ca/MEH-PPV/ITO sandwich cell, operated in reverse bias, is ideal for steady-state photoconductivity measurements. The action spectrum of Ca/MEH-PPV/ITO sandwich cell devices has been studied previously. The onset of photoconductivity (in reverse bias) and the onset of photovoltaic response (at zero bias and in forward bias) coincides with the onset of absorption at $\hbar\omega \sim 2.08 \text{ eV}$ [12]. For these experiments, samples were dc biased and illuminated through the ITO electrode using 2.708 eV photons from an Ar laser. Photocurrents were measured with a Keithley 236 source/measure unit.

The steady-state photocurrent (i_{SS}) increased linearly with the light intensity in all samples except for the thickest ($d = 5700 \text{ nm}$). For the latter, where the response was strongly activated and trap dominated, the intensity dependence was sublinear, $i_{\text{SS}} \sim I^{0.86}$. Note that, in the thick samples, $d \gg 1/\alpha$, where α is the absorption coefficient.

Figure 1 compares the field dependence of i_{SS} at a few temperatures for the thinnest sample, $d = 120 \text{ nm}$, under negative bias (i_{SS} is plotted vs total field, $E = E_o + E_{\text{bi}}$, where E_o is the external field). The photocurrent is

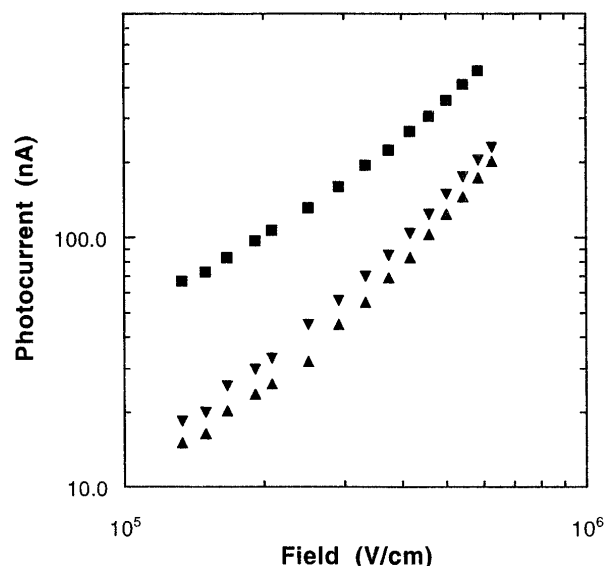


FIG. 1. Steady state photocurrent in spin-cast MEH-PPV vs the electric field at various temperatures in a thin sample ($d = 120 \text{ nm}$, area = $4.4 \times 10^{-2} \text{ cm}^2$) illuminated by 10^{-2} W/cm^2 ; (■) 297 K, (▼) 140 K, (▲) 100 K; the field data were modified due to an internal field of $1.33 \times 10^5 \text{ V/cm}$ in this sample.

superlinearly dependent on E and weakly T dependent. Figure 1 shows that, in the high field regime, i_{SS} is even less sensitive to the sample temperature. In similar experiments at 300 K, monochromatic light (generated by dispersing the light from a tungsten lamp through a monochromator) was used as the excitation source, and the I vs V dependence was examined at different wavelengths from 400 to 600 nm. I - V curves similar in shape to that shown in Fig. 1 were observed [13,14].

The T dependences of i_{SS} at $E = 1.33 \times 10^5 \text{ V/cm}$ in four samples with thicknesses from 120 to 5700 nm (a range of nearly 50) are compared in Fig. 2. The thinnest sample (120 nm) exhibits the weakest T dependence; i_{SS} initially decreases but remains nearly constant below about 80 K, behavior which is similar to that obtained from transient experiments in the subnanosecond regime. When thicker films are used, the dependence of i_{SS} on T increases. By fitting the low temperature data to a thermally activated form $\exp(-\Delta/k_B T)$, the activation energy can be obtained for samples with various thicknesses. As summarized in Table I, Δ increases with the thickness of the semiconducting polymer film.

The similarity of the temperature dependence of steady-state photocurrent in thin films to that of the transient photoconductivity in the subnanosecond regime implies that, in thin films, carrier sweep-out occurs prior to deep trapping. The weak residual T dependence above 80 K in the thinnest sample is again similar to that observed in subnanosecond time-resolved experiments. In the time domain, this corresponds to the temperature dependent “tail” characteristic of the transient photocurrent [6]. This weak T dependence arises from the effect of shallow traps with

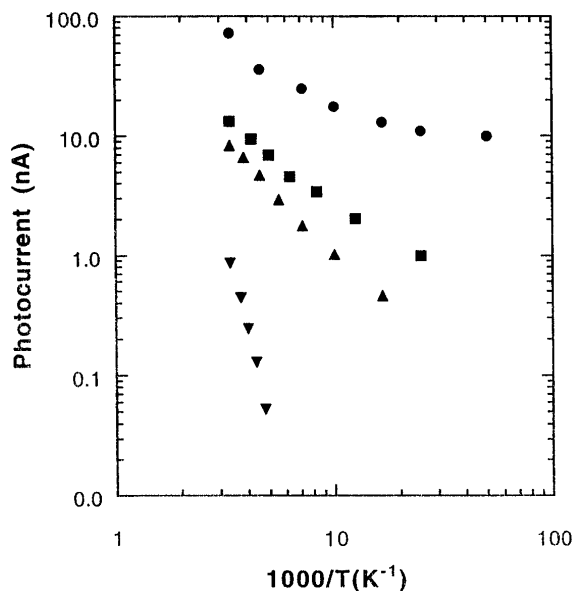


FIG. 2. Steady-state photocurrent in spin-cast MEH-PPV vs $10^3/T$ for samples of various thicknesses at $E = 1.33 \times 10^5$ V/cm under illumination by 10^{-2} W/cm 2 : (●) 120 nm, (■) 500 nm, (▲) 4100 nm, (▼) 5700 nm.

multiple release and retrapping during carrier sweep-out. Note that the change from the linear dependence of the photocurrent on light intensity in the thinner samples to the sublinear dependence in the thickest sample is consistent with the intensity dependences observed in the time-resolved response for the peak photocurrent and the tail, respectively (i.e., the change from a linear dependence of the prompt transient photocurrent to a sublinear dependence of the transient photocurrent tail). The weaker T dependence of the photocurrent at high fields (see Fig. 2) is consistent with faster sweep-out at higher fields.

Quantitative comparison of the magnitude of the steady-state and fast transient photocurrent densities confirms the proposed carrier sweep-out prior to trapping. The steady-state photocurrent density j_{SS} is given by the following expression [15]:

$$j_{SS} = (I_{SS}/\hbar\omega)\alpha\tau_t e\phi\mu E \{1 - (w/d) \times [1 - \exp(-d/w)]\} \quad (1)$$

where $w = \mu E\tau_t$ is the average distance a carrier travels in the time (τ_t) available prior to trapping and recombination, I_{SS} is the light intensity absorbed by the sample ($\hbar\omega$ is the energy per photon), and e is

TABLE I. Activation energy for samples with various thicknesses.

Sample length (nm)	Activation energy (K)
120	...
500	385
4100	475
5700	2060

the electronic charge. In the limit of $w \ll d$, $j_{SS} = (I_{SS}/\hbar\omega)\alpha\tau_t e\phi\mu E$ (proportional to τ_t and E), while in the sweep-out limit where $w \gg d$, $j_{SS} = ed\alpha(I_{SS}/\hbar\omega)\phi/2$ (independent of τ_t and E). The peak transient photocurrent, on the other hand, is given by

$$j_p = n_p e \mu_p E_p, \quad (2)$$

where $n_p = \phi\alpha(I_p/\hbar\omega)\Delta t_p$, and Δt_p is the pulse width of the pulse laser ($I_p\Delta t_p$ is the energy per laser pulse, and n_p is the total number of carriers produced per pulse per unit volume).

If $w \approx d$, then the carriers are continuously photogenerated and continuously swept out prior to deep trapping. Under these conditions, the steady-state mobility and the transient mobility are the same and equal to the pretrapping temperature independent mobility. Thus,

$$(j_{SS}I_pE_p)/(j_pI_{SS}E_{SS}) \approx \tau_t/\Delta t_p. \quad (3)$$

At room temperature and for $E_p = E_{SS} = 1.3 \times 10^5$ V/cm, $j_{SS} = 1.66 \times 10^{-6}$ A/cm 2 , $I_{SS} = 8.9 \times 10^{-3}$ W/cm 2 , $j_p = 1.02 \times 10^3$ A/cm 2 (extrapolated back to $t = 0$), and $I_p = 1.44 \times 10^7$ W/cm 2 (see Ref. [16]). Thus, $(j_{SS}I_pE_p)/(j_pI_{SS}E_{SS}) \approx 2.63$. The trapping time indicated by the transient response is approximately 0.3 ns and $\Delta t_p = 25$ ps; i.e., $\tau_t/\Delta t_p \approx 12$. Thus, Eq. (3) implies sweep-out of a significant fraction of the photogenerated carriers prior to deep trapping under steady-state conditions for thin samples. The validity of Eq. (3) implies a high collection efficiency for photocarriers. This, too, has been confirmed by direct measurements [12].

These conclusions are confirmed by a direct numerical solution of Eqs. (1) and (2) using the experimental values for j_{SS} , I_{SS} , j_p , I_p , τ_t and Δt_p given above. Since the superlinear dependence of the steady-state photocurrent on E indicates that the mobility is field dependent (see Fig. 1) [9,17], we solve Eqs. (1) and (2) at a particular value of E in the range used in the experiments. For $E_p = E_{SS} = 1.33 \times 10^5$ V/cm, one obtains $\mu = 0.23$ cm 2 /V s and $\phi = 1.2 \times 10^{-3}$. The mobility $\mu = 0.23$ cm 2 /V s implies that $w = \mu E\tau_t = 91.8$ nm $\approx 0.76d$. The analysis is fully consistent; a significant fraction of the photocarriers are swept out prior to deep trapping.

Only at higher fields or for thinner films would one expect to reach the saturation value of $j_{SS} = ed\alpha(I_{SS}/\hbar\omega)\phi/2$, although demonstrating this limit experimentally in MEH-PPV is complicated by the superlinear field dependence of the mobility [9,17].

The increase in ϕ by more than 2 orders of magnitude [5] for MEH-PPV: C $_{60}$ when sensitized by a few percent C $_{60}$ is consistent with the rather low quantum yield in pure MEH-PPV. The estimated value for the quantum yield, $\phi \approx 1.2 \times 10^{-3}$, is comparable to that deduced for single crystal polydiacetylene from transient photoconductivity studies when excited into the extended band states (e.g., using photon energy of 2.94 eV which is

0.94 eV above the exciton absorption line [7]. The question, therefore, is: Why do semiconducting polymers exhibit relatively small ϕ ? A plausible explanation may be related to the quasi-one-dimensional (quasi-1D) nature of the transport in conjugated polymers; on a quasi-1D chain, there is a high probability for early time recombination of a photogenerated electron and hole (in 1D backscattering by structural imperfections or impurities enhances the probability of geminate carrier recombination). Thus, free carriers result mostly from interchain hopping. The quantum yield in these systems is, therefore, governed by interchain hopping/tunneling and by direct excitation of electrons and holes on different chains. Note that, in 3D systems, the more isotropic nature of the carrier scattering provides a greater leeway for carriers to escape geminate recombination.

The fact that the transient and steady-state photoconductivity are consistent reconfirms that the transient photocurrent results from photogenerated mobile carriers rather than from a displacement current arising from exciton polarization by the external field [18].

These conclusions have two practical consequences: First, information on carrier transport prior to deep trapping can be obtained from relatively simple steady-state photoconductivity measurements, provided the sample is sufficiently thin. Second, data obtained from traditional steady-state photoconductivity experiments when conducted on relatively thick samples are considerably more difficult to interpret; the steady-state photoconductivity, which is proportional to the $n\mu$ product, is incapable of distinguishing activated mobility from activated carrier generation. In samples too thick to enable sweep-out, carriers occupy progressively deeper traps as they traverse the sample. Since the trapped carriers have smaller (and T dependent) mobility, transport after trapping limits the current and dominates the photoconductive response [5,11].

An additional benefit of steady-state photoconductivity measurements in thin films is that such measurements can be carried out at extremely low light intensities compared with those employed in transient photoconductivity and other pump/probe experiments [6–9,19,20]. Recently, photoinduced absorption and luminescence studies have indicated that exciton-exciton interactions become important at high intensities [19,20]. For example, Walser *et al.* found that, in Alq₃, the luminescence varies linearly with light intensity ($I^{1.0}$) at relatively low intensities, but becomes sublinear ($I^{0.5}$) at high intensities [21]. They suggested that the intensity dependence of the photocurrent is a by-product of exciton-exciton interaction; the photocurrent would be proportional to the square of the singlet exciton density and, thus, to $(I^{0.5})^2 = I$, consistent with the linear dependence observed at high light intensity. For low light intensities, however, this model predicts that the photocurrent should vary as I^2 . The data from MEH-PPV indicate that the linear intensity dependence of the

photocurrent persists to extremely low light intensities (1 mW/cm² as compared 10⁸ W/cm² typically used in transient photoconductivity measurements); the linear dependence at such low light intensities is inconsistent with carrier generation via exciton-exciton interactions.

In conclusion, steady-state photoconductivity has been used to study the carrier dynamics prior to trapping in semiconducting polymers. The photocurrent characteristics obtained from the steady-state photoresponse of MEH-PPV at low carrier densities in thin samples are in agreement with those obtained from time-resolved photoconductivity measurements in the subnanosecond time regime (carried out with a carrier density larger by a factor of 10¹¹). The results confirm that the carrier quantum yield in semiconducting polymers is independent of temperature and, therefore, inconsistent with the Onsager model of photocarrier generation.

The authors are grateful to J. Gao for useful discussions. This research was supported by a grant from the National Science Foundation (DMR95-10387).

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