

Carrier Photogeneration and Mobility in Polydiacetylene: Fast Transient Photoconductivity

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Transient-photoconductivity experiments have been carried out on single crystals of polydiacetylene-(*bis p*-toluene sulfonate), PDA-TS. The low-electric-field photocurrent decay consists of a temperature-independent fast (picosecond) initial component and a longer-time (nanosecond) component with magnitude that is strongly temperature dependent. Using small spacings between electrodes, we have succeeded in achieving sweepout for the longer-lived carriers; the data yield a mobility of $\approx 5 \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature in the nanosecond regime. These results demonstrate that the Onsager geminate-recombination model, used extensively for the polydiacetylenes, is not applicable to PDA-TS.

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A prediction of remarkably high mobility,^{1,2} of the order of $2 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$, has been advanced by the analysis of transient transport experiments with the assumption that the quantum efficiency for electric-field-dependent carrier creation could be derived from the Onsager theory of geminate recombination.

In this Letter, we report fast-transient-photoconductivity measurements on polydiacetylene-(*bis p*-toluene sulfonate), PDA-TS, which enable us to address both the photogeneration mechanism—Is it limited by the geminate recombination processes usually described by the Onsager theory for localized states?—and the magnitude of the carrier mobility. We find that the photocurrent decay consists of a *temperature-independent* fast (picosecond) initial component and a longer-time (nanosecond) component with magnitude that is strongly temperature dependent. Using very small spacings between electrodes on the samples, we have succeeded in achieving sweepout of the of the longer lived carriers in relatively high electric fields ($> 3 \times 10^4 \text{ V/cm}$); the data yield a field-independent mobility of $\approx 5 \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature in the nanosecond regime, far below the previously inferred value. The temperature independence of the initial photocurrent is interpreted as evidence for “hot” carriers.

The transient photoconductivity was measured with the Auston microstrip transmission line switch technique.^{3,4} A dye-laser system was used to produce 20-ps pulses; detailed experiments were carried out at photon energies of 2.9 and 2.58 eV. The laser pulse energy was kept constant at $0.5 \mu\text{J/pulse}$. The transient signals were amplified and detected with overall time resolution limited by the preamplifier. Single-crystal samples used in these experiments were grown at Queen Mary College, cleaved to an approximate thickness of $100 \mu\text{m}$, and mounted on the alumina substrate. The crystals were oriented with the PDA chains parallel to the electric field within the gap. The gold microstrip was evaporated directly onto the single crystal with gaps of $L = 200, 10,$

and $2.5 \mu\text{m}$. The observation of carrier sweepout (see below) implies that the contacts are collecting (rather than Ohmic) at the short times relevant to this experiment. Since the transient signal amplitude is reproducible over long times, carrier injection is sufficient to eliminate any surface charging effects.

In Fig. 1, we show the transient photocurrent decay following a 2.9-eV photopulse at a series of temperatures (electric field of $2.5 \times 10^4 \text{ V/cm}$ across a gap of $200 \mu\text{m}$). Experiments at a lower field, $1.5 \times 10^3 \text{ V/cm}$, yield the same temperature dependence of the waveform. Each waveform is characterized by a fast initial response followed by a fast decay to a more slowly decreasing “tail.” The rise time is limited by the temporal resolution of the measuring system, since the initial photogeneration process is instantaneous on this time scale. For the 2.9-eV pump, as the temperature is lowered, both the peak value

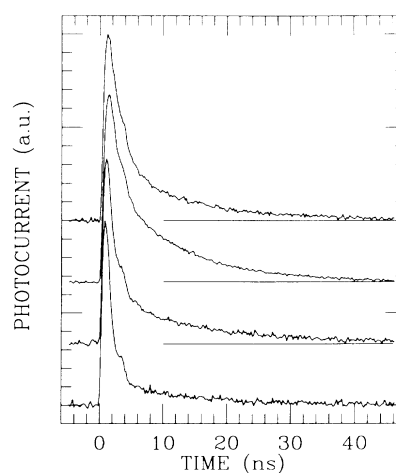


FIG. 1. Transient photocurrent wave forms (resolution 400 ps) for PDA-TS at various temperatures: from top to bottom; 300, 180, 60, and 15 K. The horizontal lines indicate the zero for the upper three wave forms.

and the magnitude of the tail initially increase reaching a gentle maximum at about 180 K; at lower temperatures, the tail decreases much more rapidly going toward zero at the lowest temperatures. With excitation at 2.58 eV (near the single-particle gap edge), both the peak value and the magnitude of the tail appear to decrease monotonically with decreasing temperature. While the peak value decreases by only a factor of 2, the tail has almost completely disappeared at 15 K. With our best time resolution (50 ps without preamplifier), an initial fall time of 300 ps was measured at 15 K. This unusually fast initial decay may be in part due to the one dimensionality (1D) of the PDA π electrons; since the photo-generated carrier transport is principally along the PDA chains,⁵ the carriers cannot efficiently escape recombination by three-dimensional delocalization. Although the tail portion of the transient photocurrent extends out to relatively long times, the initial decay of the tail can be adequately fitted by a single exponential⁶ of the form $i = i_0 \exp(-t/\tau)$, where $\tau \sim 40$ ns. As shown in Fig. 1, the amplitude (i_0) is found to be strongly temperature dependent, while τ is insensitive to the temperature.

The data of Fig. 1 indicate two decay mechanisms with different decay rates. In order to separate the two more quantitatively, we have integrated the respective areas. The functional form of the tail was fitted at times well beyond the initial decay (> 5 ns), the form extrapolated back to $t=0$, and the tail current integrated to obtain Q_{tail} . The integrated charge associated with the fast decay was obtained by subtraction of Q_{tail} from the area under the whole transient curve to obtain Q_{initial} . The resulting values for Q_{tail} and Q_{initial} are plotted as functions of temperature in Fig. 2. Within our experimental accuracy, Q_{initial} is independent of temperature, while Q_{tail} is

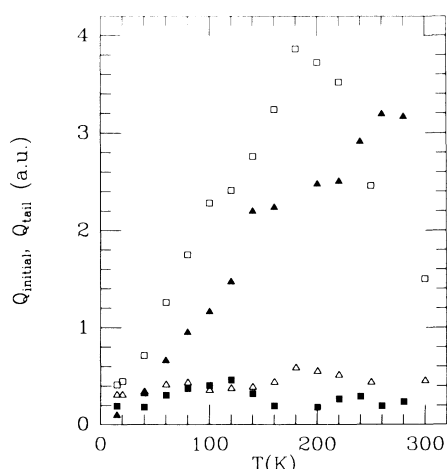


FIG. 2. Temperature dependence of Q_{initial} and Q_{tail} following excitation at two energies (2.9 and 2.58 eV); open triangles, Q_{initial} for 2.9-eV excitation; open squares, Q_{tail} for 2.9-eV excitation; closed squares, Q_{initial} for 2.58-eV excitation; and closed triangles, Q_{tail} for 2.58-eV excitation.

temperature dependent, extrapolating to zero at $T=0$ K. The temperature independence of Q_{initial} implies that the product $\eta\phi$ of the photocarrier quantum yield η and the probability of escaping early-time recombination, ϕ , is independent of temperature.

We were able to measure successfully the transport mobility at room temperature in the nanosecond regime by achieving carrier sweepout using a narrow gap (≤ 10 μm). Photocurrent wave forms at various electric fields (E) are shown in Fig. 3. In these experiments, the light intensity was reduced as E was increased so as to keep the peak signal approximately constant. The tail gradually decreases in relative magnitude as E is increased until at $E=3 \times 10^4$ V/cm, it completely disappears.

The data imply an increase in average drift velocity with increasing E to the point where the carriers are swept out to the contacts. The tail will completely disappear when all the carriers leave the sample during a time interval equal to the integration time of the measuring system. This time is set by the particular choice of the signal amplifier that is used and is determined by the measured rise time (3 ns in Fig. 3) of the initial photocurrent. For a sample length of 10 μm and approximately uniform illumination, the typical carrier must drift 5 μm to the contact, implying a drift velocity of $\sim 2 \times 10^5$ cm/s for $E=3 \times 10^4$ V/cm and a mobility of about 5 $\text{cm}^2/\text{V}\cdot\text{s}$ (at room temperature). The same value (within experimental error) was inferred from experiments with $L=2.5$ μm where the sweepout field is correspondingly lower. In these high-field experiments both electrons and holes are swept out (the tail current is reduced to the base line). The fact that the sweepout has a sharp cutoff suggests that one species of carrier has a substantially higher mobility than the other. The value

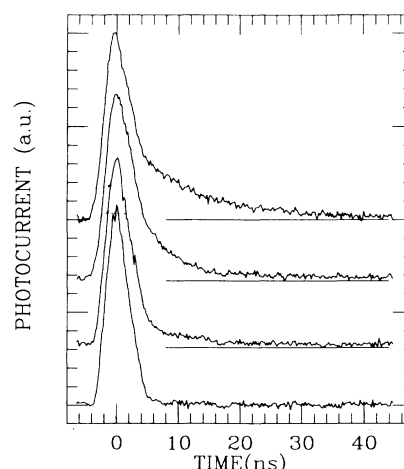


FIG. 3. Electric-field dependence of the transient photocurrent wave forms (resolution 3 ns) for $L=10$ μm , where complete carrier sweepout is achieved. The applied electric fields are (from top to bottom) 10^3 , 3×10^3 , 10^4 , and 3×10^4 V/cm, respectively.

determined from the sweepout is in agreement with that inferred in the 200–400-ns time scale by Reimer and Bassler in their attempt to carry out time-of-flight measurements from contact injected carriers.⁷

Because of the sweepout, Q_{tail} saturates at fields above 3×10^4 V/cm; Q_{initial} , however, continues to increase even at the highest fields. Since the unresolved initial peak decays in less than 300 ps, there is not sufficient time to sweep out the charge before it is thermalized and trapped, etc., into the tail.

We have ruled out the possibility that this effect is due to a field-induced increase in the decay rate.⁸ In that case, the decrease in relative photocurrent arises since at high fields the carriers reach recombination centers more rapidly, an effect which is particularly effective in 1D. In PDA-TS, however, the sweepout time (or equivalently, the sweepout field) depends on L as noted above. Moreover, the sweepout phenomenon is found *only* when the length of the sample is comparable to the distance that a carrier can travel during its average lifetime. Studies at the same electric field strengths on longer samples with $L = 200 \mu\text{m}$ do not indicate any change in shape of the waveforms (see Fig. 1).

Having determined the mobility in the tail, we can obtain the $\eta\phi$ product. The photocurrent measured at the beginning of the tail is 1.3×10^{-5} A, resulting from an absorbed photon density of $N = 3 \times 10^{20} \text{ cm}^{-3}$. This leads to a value for the photoconductivity of 3×10^{-3} S/cm at ≈ 4 ns. Using $\sigma = (\eta\phi)\mu eN$, we find $\eta\phi \approx 10^{-3}$ at the beginning of the tail. The sweepout experiments with $L = 10$ and $2.5 \mu\text{m}$ indicate a field-independent mobility (within our experimental accuracy). This result and the linear dependence of the photocurrent on E for $L = 200 \mu\text{m}$ (in the field range of the sweepout measurements) imply a field-independent $\eta\phi$.

The field and temperature independence of $\eta\phi$ are in sharp disagreement with the Onsager theory of geminate recombination. The theory would predict that the quantum yield, which determines the initial photoconductive response, should be limited by the probability to escape geminate recombination: $\eta\phi$ should increase linearly in the applied electric field strength and should decrease exponentially as the temperature is lowered.^{1,9} In addition, the carriers which undergo geminate recombination would produce zero net photocurrent (contributions from the geminate electron and hole would cancel). Thus, the rapid decay of the initial peak into the longer-lived tail is not due to geminate recombination. We conclude that, although early-time recombination is clearly important ($\eta\phi = 10^{-3}$ at 4 ns), this is not properly described by the Onsager theory of geminate recombination.

Traditionally, the dominant mechanism for recombination (e.g., bimolecular versus monomolecular) has been studied by the measuring of the dependence of the photoconductive response on the illumination intensity. We have measured the intensity dependence of the peak

photocurrent as well as Q_{initial} and Q_{tail} . At relatively high intensity ($> 10^5 \text{ W/cm}^2$), the exponents for the peak photocurrent, Q_{initial} and Q_{tail} , are 1.0, 1.1, and 0.74, respectively.¹⁰ In PDA-TS, the precise determination of the recombination mechanisms is made difficult by the known existence of trap levels (significant photoconductivity has been observed for photon energies well below the single-particle energy gap²) which can drastically affect the illumination intensity dependence of the photocurrent.¹¹

We suggest that the initial fast peak in the photocurrent is due to hot carriers in extended band states that have acquired excess energy due either to the difference in photon excitation energy and the minimum band-state energy at the bottom of the conduction band or to ballistic acceleration of the carriers by the external field prior to the first trapping (or scattering) event. Calculations of the latter effect for traditional semiconductors demonstrate¹² overshoot of the drift velocity in the subpicosecond regime. The larger initial photocurrent would, therefore, be due to a greater drift velocity than that inferred from μE (with $\mu \sim 5 \text{ cm}^2/\text{V}\cdot\text{s}$) at longer times. If this excess energy is much greater than $k_B T$, then the lattice temperature is not important to the initial decay rate; rather, the decay comes from a decrease in drift velocity as the hot carriers thermalize. As the carriers thermalize (and recombine), a significant fraction fall into traps that govern their transport at longer times. It is this trap-dominated transport which we associate with the longer-time "tail" photoconductivity. At low temperatures, the probability of emission from traps is drastically reduced and, consequently, the tail should go to zero, in agreement with the experimental observations.

We note that since the sweepout drift velocity in the tail is $\sim 2 \times 10^5 \text{ cm/s}$, the much higher conductivity in the peak may result from a drift velocity greater than the sound velocity (consistent with hot carriers). This would imply that the time for thermalization to a polaron configuration is in the picosecond regime and may be resolvable with improved experimental techniques.

The inapplicability of Onsager geminate-recombination theory to PDA-TS is perhaps not surprising, since one expects such concepts to be accurate only when the photoexcited carriers are localized. Although localization is to be expected in amorphous materials or in very narrow-band molecular crystals, the broad π bands of conjugated polymers tend toward extensive delocalization.¹³ Although a geminate pair can be self-localized by the Coulomb interaction, this effect can play no role if there are no bound excitons (as appears to be the case in polyacetylene¹⁴). Since bound excitons are known² to exist in PDA-TS, geminate recombination may be involved in the initial decay of photoexcitations. Our results on PDA-TS imply, however, that the role of geminate recombination as developed within the Onsager formulation^{1,9} (which has been often invoked but seldom

proven) must be reexamined more generally.

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