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Subnanosecond transient photoconductivity in poly(3-hexylthiophene)

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We present the results of comprehensive measurements of photoconductivity in films of poly(3-hexylthiophene-2,5-yl), a soluble alkyl derivative of polythiophene. Transient measurements in the subnanosecond-time regime reveal a fast, temperature-independent photoconductive response which decays within about 100 ps after photoexcitation. Information on the anisotropy of the transient photocurrent is obtained from nonoriented films by using polarized light and varying the direction of the polarization with respect to the biasing electric field; the results imply that intrachain photoexcitation of polarons is the dominant process. Measurements of the spectral response of both transient and steady-state photoconductivity demonstrate that the magnitude of the photocurrent follows the absorption profile, consistent with the photogeneration of free carriers via an interband transition in a system with relatively weak effective electron-electron interactions.

INTRODUCTION

Subnanosecond transient-photoconductivity measurements have proven to be important in the study of conjugated polymers.[1-5] By determining whether the onset of photoconductivity coincides with that of the principal absorption band (as in polyacetylene[1,2] and in the emeraldine-base form of polyaniline[4]) or whether the onset of photoconductivity occurs at a higher energy (as in the polydiacetylenes[5]), one can learn whether an interband transition (with the generation of free electron-hole pairs) or an exciton (with the electron and hole bound by their Coulomb attraction) is involved. Moreover, such measurements offer the possibility of probing the intrinsic charge transport at times before the sample morphology and/or defects become dominant. Information on the generation and transport of the photoexcited charge carriers can be obtained through measurements of the anisotropy of the transient photocurrent[1(b),3] and by comparison of the data with the results of transient photoinduced-absorption measurements.

For conjugated polymers in which the ground state is nondegenerate, charged photoexcitations with long lifetimes have been studied previously through infrared photoinduced absorption.[6] The observation of infrared-active vibrational modes and the characteristic pair of subgap electronic absorption bands indicated the photogeneration of bipolarons (confined soliton pairs) in polythiophene,[7] poly(3-alkylthiophene-2,5-yl) derivatives,[8] and poly(phenylenevinylene) (PPV).[9] However, since bipolarons cannot be directly photogenerated, the photoexcitation process must involve at least the following steps: (1) direct photogeneration of free carriers (electrons and holes), (2) chain relaxation to form charged polarons, and (3) bipolaron formation through $2P^{\pm} \rightarrow B^{2\pm}$; with relaxation back to the ground state occurring in parallel at all time scales. Since both steps (1) and (2) occur at times less than 10^{-13} s,[10] transient photoconductivity in the picosecond regime is likely to be dominated by polaron transport, whereas the bipolarons are formed at later times and can contribute to the steady-state photoconductivity.

Polythiophene (PT) and the poly(3-alkylthiophene-2,5-yl) (P3AT) derivatives are of interest as a series of conjugated polymers with nondegenerate ground states.[6] As an initial approximation, the backbond and π-electronic structure of this series of polymers can be viewed as similar to that of *cis*-polyacetelene, but stabilized in that structure through the sulfur heteroatom which forms an aromatic ring.[7(c)] The addition of the alkyl chain[11] has little effect on the intrachain π-electronic structure; for example, the absorption spectra of the various P3AT's are essentially identical.[12] The alkly chains serve to spatially separate the backbones of different chains and, thereby, to lower the melting point[13] and to reduce the interchain electronic interaction. For sufficiently long alkyl chains, the P3AT's can be melt-processed,[13] and they are soluble in common organic solvents.[14]

Because of their solubility, the P3AT's can be prepared in the form of relatively pure films with uniform thickness. Moreover, the P3AT's can be doped in solution,[14] thereby enabling uniform doping at a well-defined and reproducible doping level. These features make the P3AT's of interest for a variety of potential technological applications. Using P3AT film cast from solution, both Schottky diodes[15] and field-effect transistors[16] have been fabricated.

In this paper we present the results of comprehensive measurements of the photoconductivity of poly(3-hexylthiophene-2,5-yl) (P3HT) films. Transient measurements in the subnanosecond time domain reveal an extremely fast, temperature-independent photoconductive response (the risetime is resolution limited) which decays within about 100 ps after photoexcitation. Measurements of the photocurrent as a function of the angle between the polarization of the light and the direction of the biasing electric field[2] in nonoriented films were carried out; the results indicate a weak polarization dependence with a 10% larger photocurrent with light polarized parallel to the field. From analysis of these data, we conclude that the transient photoconductivity in P3HT is dominated by polarons formed via photoexcitation of electrons and holes on the same chain rather than on different chains. Rapid trapping is implied by the more rapid decay of the photocurrent in comparison with the decay of the photoinduced absorption. Spectral response measurements indicate that the excitation profiles of both the transient and the steady-state photoconductive response follow the absorption spectrum, consistent with an interband transition and the photogeneration of free carriers. The absence of a bound exciton implies relatively weak effective electron-electron interactions.

EXPERIMENTAL METHODS

The P3HT samples used in this study were prepared as films spin-cast from solution (2 mg of polymer per ml of chloroform). Details of the synthesis, purification, and film preparation have been reported.[15] For the transient-photoconductivity measurements, 0.5 in. × 0.5 in. alumina substrates (thickness 0.65 mm) were first prepared in the Auston switch configuration;[17,18] gold stripline electrodes and a gold backplane were evaporated onto the upper and back surfaces, respectively, to form a transmission line with 50 Ω impedance and with a frequency response over tens of gigahertz. The P3HT films were cast directly over the gap in the upper strip electrodes, thus completing the circuit. For steady-state photoconductivity measurements, P3HT films were cast onto alumina (or glass) substrates, and gold electrodes were subsequently evaporated on top, forming a surface cell configuration. The gaps between electrodes were 0.2 mm for both the transient and the steady-state measurements. Thicknesses of the films (0.2–0.3 μm) were measured by a Dektak surface profiler. The dark conductivity was measured with a Keithley 616 digital electrometer; typical values indicated a dark conductivity of about 3×10^{-7} S/cm at room temperature.

Details of the apparatus used for the transient-photoconductivity measurements have been published previously.[1] The excitation pulses were obtained from a PRA (Photochemical Research Associates, Inc) LN105 dye laser pumped with a PRA LN1000 N_2 laser; pulse widths were approximately 20 ps. The temporal resolution of the electronic detection system was about 40–50 ps and results from a combination of the gatewidth and trigger jitter of the boxcar (EG&G PAR 4400 system with a Tektronix S-4 sampling head) and the response of the cable transmission line between the probe and the boxcar. For experiments involving polarized light, a polarizer was used to establish the polarization and a half-wave plate was used to rotate the polarization vector of the light.

The sample was mounted onto the cold finger of a Helitran cryostat, and the system was pumped to a vacuum of less than 10^{-4} Torr during the measurement. A 650-W tungsten-halogen lamp dispersed by a grating monochromator (with relevant filters) was used for the steady-state photoconductivity measurements. Standard photomodulation techniques were employed; the light was chopped with a Stanford SR540 mechanical chopper, and the signal was processed through a Stanford SR530 lock-in amplifier. To normalize out the spectral response of the measurement system, the probe head used to obtain the photoconductivity data was replaced by a photoacoustic cell. A saturated photoacoustic spectrum of carbon-black powder was then taken under identical conditions and used as the background for normalization of the photocurrent spectrum. It is well known that the magnitude of the saturated photoacoustic signal is proportional to the intensity of the incident light (the signal is related to the thermal properties of the sample, but independent of the optical constants).[19] The source intensity was also independently calibrated at specific wavelengths by means of a standard photodiode. The absorption spectrum of P3HT was taken with a Perkin-Elmer Lambda-9 spectrometer.

RESULTS

Figure 1 displays the transient-photoconductive response of a P3HT film biased with an electric field of 2×10^4 V/cm; the excitation-laser-pump pulses were at 2.58 eV (481 nm) with a 20-ps pulse width. The photon flux incident onto the sample (per pulse) was about 10^{16} photons/cm^2 (the energy per pulse was ≈ 3 μJ, and the peak power was ≈ 100 MW/cm^2), and the cross-sectional area of the incident beam was about 0.3 mm in diameter. To obtain the necessary signal-to-noise ratio, signal averaging was necessary; the curve shown in Fig. 1 is the result of a 10-sweep accumulation.

The initial photoresponse is extremely fast; the risetime

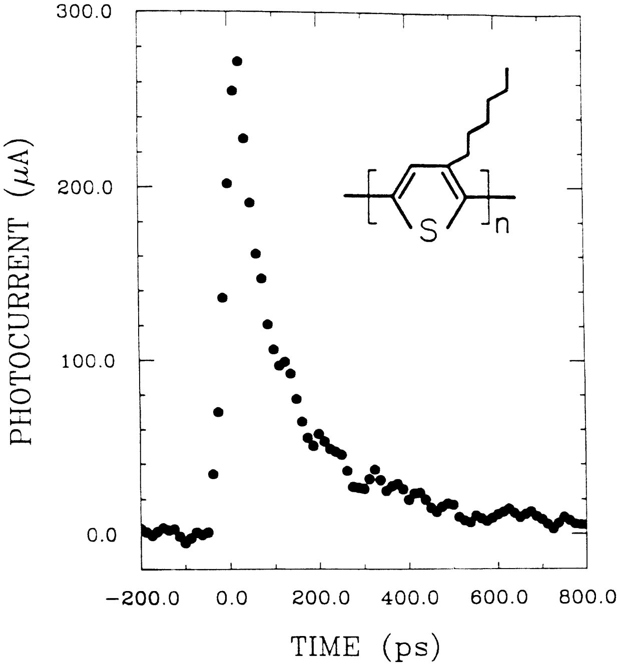

FIG. 1. Transient-photoconductive response of a P3HT film. The data were taken at room temperature; 20 ps pulse width at 2.58 eV with a photon flux of 10^{16} photons/cm^2. The bias field is 2×10^4 V/cm. The inset shows the chemical structure of poly(3-hexylthiophene-2,5-yl).

of the asymmetric peak results form the pulse width of the pump beam broadened by the temporal resolution of the detection system. The peak is followed by a rapid decay; the photocurrent decays to e^{-1} of its initial value in about 80 ps. The initial decay is consistent with an exponential; however, as shown in the log-log plot of Fig. 2, after about 100 ps the decay is a power law, $I_{\mathrm{ph}} \sim t^{-\alpha}$, where $\alpha \approx 1$. The coefficient of the $1/t$ decay is somewhat greater than that reported for polyacetylene.[1-3]

As demonstrated by Sinclair *et al.*,[1(b)] information on the anisotropy of the transient photocurrent can be obtained from nonoriented films by using polarized light and varying the direction of the polarization with respect to the biasing electric field. We found that the time profile of the transient photocurrent pumped with light polarized parallel to the biasing field is essentially identical to that with light polarized perpendicular to the biasing field; the latter is about 10% smaller than the former. The larger value of the photocurrent for light polarized parallel to the biasing field is a genuine effect: (1) the error in the relative measurement (as a function of the polarization) is much less than the observed variation, and (2) transmission measurements through thin films prepared in this manner show that they are isotropic in the plane.

In Fig. 3 the transient photocurrent obtained at 300 K is compared with that obtained at 25 K. The peak photocurrent and the subsequent decay are essentially temperature independent, as found in polyacetylene.[1-3] The inset shows the dependence of the peak photocurrent on temperature. The magnitude decreased by only 20% upon cooling from 300 to 25 K, perhaps indicative of more rapid trapping at low temperatures.

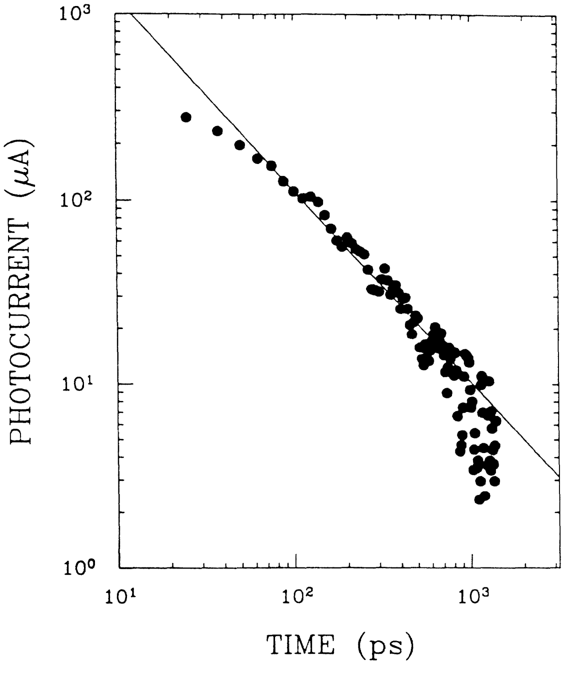

FIG. 2. Time dependence of the transient photocurrent in P3HT plotted on a log-log scale. The solid line represents a T^{-1} dependence.

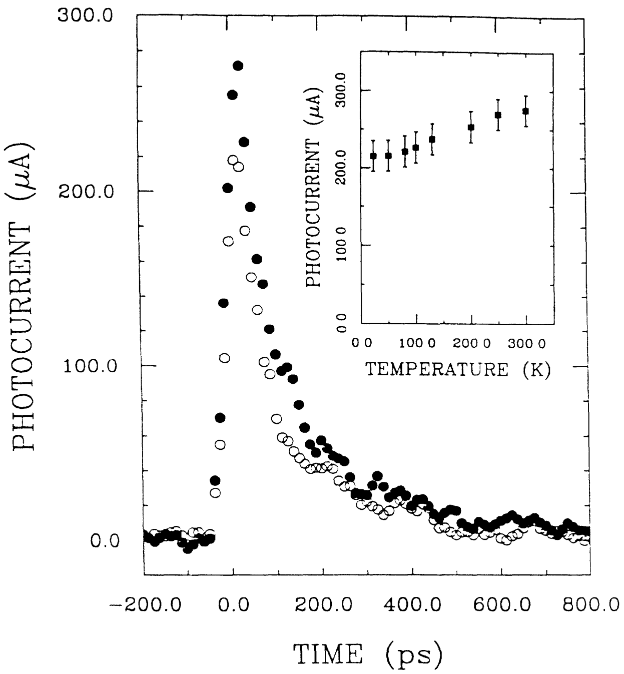

FIG. 3. Time dependences of the transient photocurrents in a P3HT film are plotted at 300 K (solid dots) and 25 K (open circles). The inset shows the peak photocurrent vs temperature.

Figure 4 compares the photoconductive response (as a function of photon energy) to the absorption spectrum; photocurrent results from transient experiments and from steady-state experiments are included. Both sets of data come from samples cast from the same batch of solution. Moreover, the samples for the steady-state photoconductivity experiment and the optical-absorption experiment were taken from the same polymer film (on a glass substrate) with thickness corresponding to an optical density of 1.2 at 500 nm.

The data in Fig. 4 demonstrate that both the transient and the steady-state photoconductivity follow the absorption spectrum to within the experimental accuracy; there is no significant shift of the onset of photoconductivity with respect to the onset of absorption.

The temperature dependences of the fast and slow components of the photoconductive response are quite different. As shown in Fig. 3, the fast component is essentially temperature independent. Under steady-state conditions, however, the photocurrent is strongly temperature dependent with an activation energy of 0.11 eV. Although activated steady-state photoconductivity can arise from many mechanisms (e.g., hopping of polarons or bipolarons, or activation near a band edge), the small activation energy, together with the t^{-1} time dependence of the transient decay, suggests trap-dominated transport (with multiple release and retrapping) at long times. In this context the temperature independence of the subnanosecond photocurrent response implies pretrapping transport; thus, the fast decay probably results from the initial trapping. Although there is a long tail (with an ac-

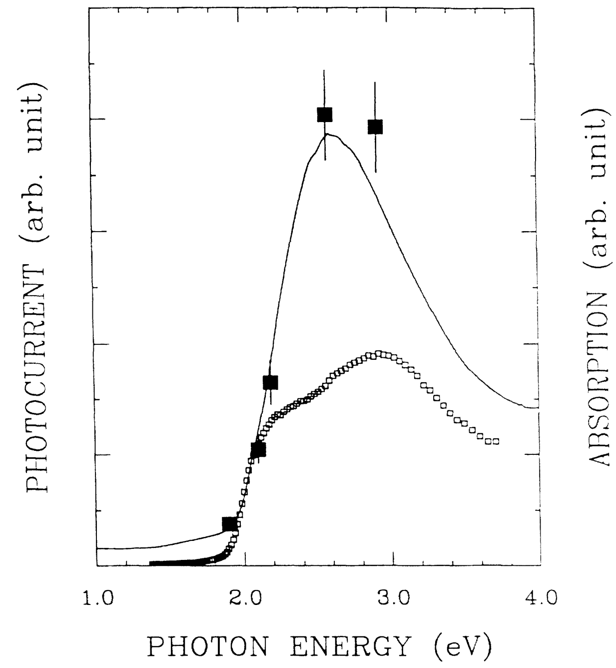

FIG. 4. Spectral response of the peak photocurrent (solid squares), the steady-state photocurrent (open circles), and absorption coefficient (solid line) measured in a P3HT film are compared (all data were acquired at room temperature). The photocurrent-response curves are plotted at constant photon density.

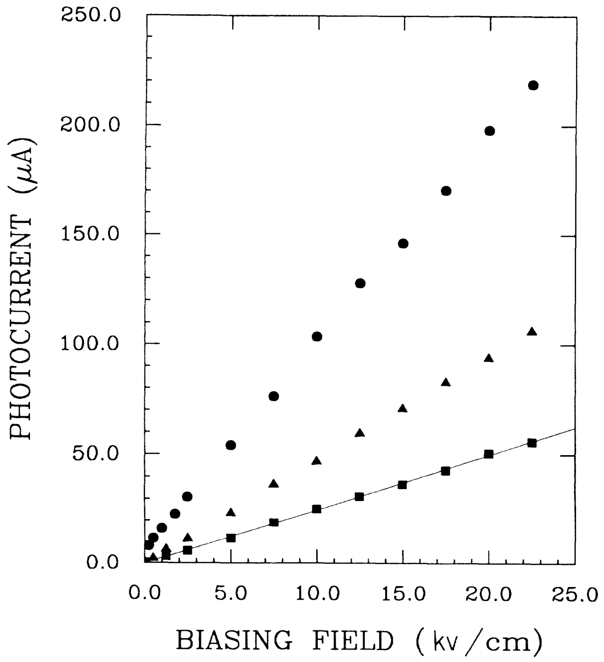

FIG. 5. Dependence of the peak transient photocurrent as function of bias field at three different light intensities: 8×10^{15} photons/cm^2 (solid dots), 4×10^{15} photons/cm^2 (solid triangles), and 2×10^{15} photons/cm^2 (solid squares).

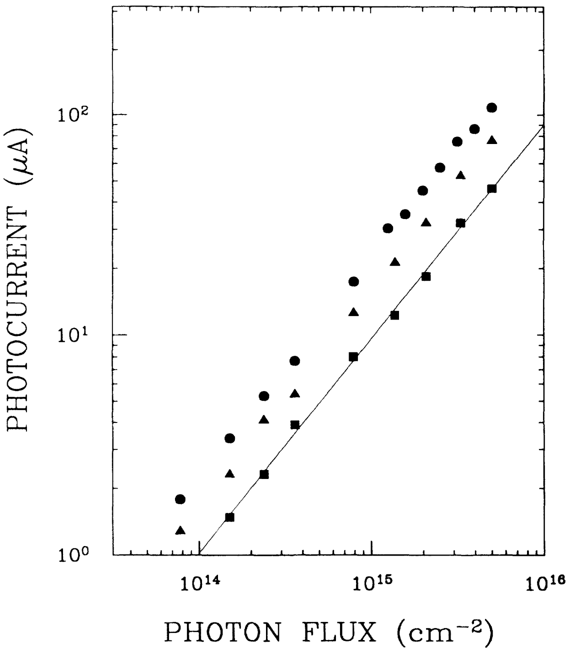

FIG. 6. Dependence of the peak transient photocurrent as function of light intensity in three different biasing fields: 20 kV/cm (solid dots), 14 kV/cm (solid triangles), and 8 kV/cm (solid squares).

tivated temperature dependence) in the transient data which produces the steady-state photocurrent, the magnitude of the current tail is too weak at long times to give an observable signal across the 50-Ω impedance in the Auston switch configuration.[17]

Figure 5 shows the peak values of transient photocurrent as a function of voltage bias at three different light intensities (photo energy of 2.58 eV, or 481 nm). At low light intensities, the current is strictly linear in the applied field (Ohmic behavior). At high light levels, however, the current versus voltage is nonlinear at low fields, reminiscent of similar effects observed in polyaniline.[4] As in polyaniline, this may arise from a combination of charging and imperfect contacts. This effect was also found by pumping with other wavelengths (566 and 425 nm).

The transient photocurrent is plotted as a function of the light intensity in Fig. 6; the results are shown for several different biasing fields. The photocurrent increases linearly with the light intensity at least up to a light intensity corresponding to about 5×10^{15} photons/cm^2.

DISCUSSION

The magnitude of the peak transient photocurrent in P3HT films is less than an order of magnitude smaller than that found in similar thin films of nonoriented *trans*-polyacetylene made by the Shirakawa method.[1] Measured values depend on the synthesis batch, with variations in peak photocurrent ranging from $\frac{1}{3}$ to $\frac{1}{8}$ of that of *trans*-$(\mathrm{CH})_x$. This is a somewhat surprising result considering that after photoinjection of an electron and a hole the soliton-pair confinement[6,20,21] resulting from the nondegenerate ground state will lead to rapid formation of neutral "bipolaron-like" excitons—a specific mechanism for geminate recombination. The fast decay of the photoinduced bleaching of the interband transition has been interpreted as resulting from the formation and decay (radiative plus nonradiative contributions) of the neutral intrachain bipolaron excitons.[22–26]

Such neutral intrachain bipolarons can be expected to undergo relaxation to the ground state by luminescence emission in parallel with rapid nonradiative processes; it is the latter which determine the effective lifetime of the luminescence.[27] The observation of luminescence[22–25,28] (with decay in the picosecond regime)[23,26] in polythiophene at a photon energy just below the band gap is consistent with confinement and geminate recombination of the intrachain electron-hole pairs.[23] Although the same mechanism was proposed to explain the luminescence in *cis*-polyacetylene,[21] photoconductivity measurements have not been carried out because of the difficulties in maintaining the *cis* isomer.

Because of the transverse bandwidth due to interchain coupling, some of the initial photoexcitations can be generated as electrons and holes on different chains. Structural distortions will quickly form around these single charges, as shown by Su and Schrieffer,[10] leading to polaron formation. Since electron and hole polarons on different chains are not confined, they act as mobile carriers and contribute to the photocurrent. Polaron pairs can also be formed via intrachain excitation, although they have considerably higher energy than the neutral bipolaron excitons.

As shown by Sinclair *et al.*,[1(b)] the ratio of the photocurrent for polarization parallel to the field $I_p(0°)$, to that for polarization perpendicular to the field, $I_p(90°)$, is given by the following expression:

$$R=\frac{I_p(0°)}{I_p(90°)}=\frac{3\alpha_\parallel\eta_\parallel+\alpha_\perp\eta_\perp}{\alpha_\parallel\eta_\parallel+3\alpha_\perp\eta_\perp}\;, \tag{1}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the absorption coefficients for light polarized parallel and perpendicular to the bias field, and $\eta_\parallel$ and $\eta_\perp$ are the quantum efficiencies for charge-carrier generation. If $\alpha_\parallel\eta_\parallel \gg \alpha_\perp\eta_\perp$ for a π-conjugated polymer, the initial measured ratio (i.e., at $t=0$) would be $R(0)=3$. $R(t)$ is expected to decay with time as the excitations diffuse.[29] The initial drop (at shortest times) in the magnitude of $R(t)$ will occur in the amorphous regions, where diffusion over very short distances, essentially on the monomer length scale, causes the loss (locally) of any polarization memory. After this initial drop the residual $R(t)$ will fall more slowly, since excitation diffusion over much greater distances is required to restore isotropy. In this time regime,[1(b)]

$$\frac{I_p(0°)}{I_p(90°)}=\frac{(1-f)(3\alpha_\parallel\eta_\parallel+\alpha_\perp\eta_\perp)\mu_\parallel+8f\alpha_a\eta_a\mu_a}{(1-f)(\alpha_\parallel\eta_\parallel+3\alpha_\perp\eta_\perp)\mu_\parallel+8f\alpha_a\eta_a\mu_a}\;, \tag{2}$$

where f is the amorphous (isotropic) fraction, α_a is the absorption coefficient of the amorphous material, and $\mu_\parallel$ and μ_a are the transport mobilities along the chain and in the amorphous regions, respectively. This equation explains the results obtained by Sinclair *et al.*,[1(b)] who found $I_p(0°)/I_p(90°)\approx 2$ (at approximately 100 ps) for nonoriented *trans*-polyacetylene. These polyacetylene data are consistent with the high degree of crystallinity in *trans*-$(\mathrm{CH})_x$. Note that in polyacetylene the decay of the transient photoconductivity is much faster than the decay of the photoinduced dichroism. Thus, the results of Sinclair *et al.*[1(b)] are characteristic of the system after the initial decay of polarization memory in the amorphous regions, but before significant decay of the polarization memory in the crystalline regions.

The simplest explanation for the small measured value of $I_p(0°)/I_p(90°)$ would be that the material is essentially amorphous. This, however, is not the case; significant crystallinity has been reported for P3HT films cast from solution.[30] More importantly, transient pump-probe absorption measurements have demonstrated photoinduced dichroism which persists out to at least 300 ps, indicative of significant parallel chain order.[26] For P3HT the photoinduced dichroism at 1.17 eV associated with the self-localized excitations decays smoothly to $\Delta\alpha_\parallel/\Delta\alpha_\perp\approx 1.4$ at 200 ps, decreasing to 1.2 at 400 ps.[26]

The small measured value of $I_p(0°)/I_p(90°)$ must be understood in the context of the time decay of the photoinduced dichroism.[26] Since the anisotropy of the transient photocurrent was measured with a preamplifier (4.2 GHz bandwidth) in the detection system, the effective temporal resolution of the entire system is about 130 ps. Thus, the value obtained for $I_p(0°)/I_p(90°)$ is an average over this time. Over the same time interval, the photoinduced dichroism at 1.17 eV has an average value of about 1.6. The smaller value for $I_p(0°)/I_p(90°)$ implies that either the photoinduced carriers are produced principally in the amorphous regions (where the dichroism would decay much more rapidly), or that the photoconductivity is dominated by the highest-mobility carriers, which would lose their polarization memory more quickly than the average. Since the magnitude of the peak photoconductivity is quite large (within an order of magnitude of that of polyacetylene), the latter alternative appears to be the correct explanation.

Since $I_p(0°)/I_p(90°)\approx 1.1$, throughout the subnanosecond regime $\alpha_\parallel\eta_\parallel>\alpha_\perp\eta_\perp$. This inequality implies that subsequent to the absorption of a photon in an intrachain (‖) process, there is a significant branching ratio for the generation of free polarons and that this branching ratio is sufficiently large to favor intrachain rather than interchain photogeneration of polarons (i.e., $\alpha_\parallel\eta_\parallel>\alpha_\perp\eta_\perp$). This is the case even though intrachain-generated polarons have higher energy than the confined neutral bipolaron exciton [at least within the Su-Schrieffer-Heeger (SSH) model]. Although the dynamics of the initial photogeneration process take place with the system far from equilibrium, the photogenerated excitations quickly cool (subpicosecond time scale) and a quasiequilibrium is established. In this regime the intrachain branching ratio for polaron production may result from the increased entropy of polarons over bipolarons at low excitation densities (so that the free energy is lowered if some fraction of the excitations are polarons, even though bipolarons have the lower internal energy).[31]

The decay time, ~ 100 ps, of the transient photocurrent in P3HT is somewhat shorter than that found in any of the forms of polyacetylene.[1-3] This rapid decay is similar to that found in amorphous semiconductors,[32] and probably results from the presence of a relatively high density of relatively deep (compared with $k_B T$) traps with energies such that the activated probability of release is small even at room temperature. The temperature independence of the (pretrapping) transient-photocurrent signal is consistent with a rapid-trapping model. Confirming evidence comes from the picosecond time-resolved photoinduced absorption,[26] which measures only the number of excitations and is insensitive to whether they are mobile or trapped. From the time decay of the density of photoinduced gap states as observed through nondegenerate pump-probe measurements,[26] we conclude that the lifetime of the excitations is about a factor of 3 greater than the time over which they are mobile (as inferred from the decay of the photocurrent). Although the probability of activated release from traps is small, it dominates the much more sensitive steady-state measurements (the observed activation energy is 0.11 eV), and it may contribute to the t^{-1} decay of transient photocurrent.

By comparing the onset of photoconductivity with that of the principal absorption band, one can learn whether an interband transition (with the initial generation of free electron-hole pairs) or an exciton (with the electron and hole bound by their Coulomb attraction) is involved. For P3HT the data of Fig. 4 demonstrate that both the transient and the steady-state photoconductivity follow the absorption spectrum to within the experimental accuracy. Moreover, the linearity of the photocurrent with light intensity implies a direct photogeneration mechanism. We conclude, therefore, that the photogenerated carriers result from a direct interband transition. This is to be contrasted, for example, with the experimental results obtained from studies of the polydiacetylenes, in which the onset of photoconductivity is blue-shifted by nearly 0.5 eV with respect to the absorption.[5] The absence of an exciton in P3HT implies that the effective electron-electron interaction is relatively weak in this polymer.

CONCLUSIONS

Transient-photoconductivity measurements (in the subnanosecond-time regime) on films of poly(3-hexylthiophene-2,5-yl) reveal a fast, temperature-independent photoconductive response which decays within about 100 ps after photoexcitation. Information on the anisotropy of the transient photocurrent is obtained from nonoriented films by using polarized light and varying the direction of the polarization with respect to the biasing electric field; the results indicate a weak polarization dependence with a 10% larger photocurrent with light polarized parallel to the field. We conclude from analysis of these data that the branching ratio for intrachain photoproduction of polarons is sufficiently large that such carriers make the largest contribution to the initial photocurrent; the transient photoconductivity in P3HT is dominated by polarons formed via photoexcitation of electrons and holes on the same chain rather than on different chains. Rapid trapping is implied by the more rapid decay of the photocurrent in comparison with the decay of the photoinduced absorption (the latter measures only the number of excitations and is insensitive to whether they are mobile or trapped). For both transient and steady-state photoconductivity, measurements of the spectral response demonstrate that the magnitude of the photocurrent follows the absorption profile. This is consistent with the photogeneration of free carriers via an interband transition. Since there is no shift of the onset of photoconductivity with respect to the onset of absorption, there is no significant Coulomb binding of the electron and hole into a neutral exciton. We conclude, therefore, that in P3HT the effective electron-electron interaction is relatively weak.

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