

Persistent photoconductivity in poly(*p*-phenylenevinylene): Spectral response and slow relaxation

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(Received 2 March 1992; revised manuscript received 16 July 1992)

We report the spectral response and slow decay of the steady-state photoconductivity in poly(*p*-phenylenevinylene) (PPV) films. The spectral response of the photoconductivity is in good agreement with that calculated from the absorption data with the assumption of rapid recombination at the surface of the film; the results indicate direct photogeneration of free charge carriers via an interband transition. The photoconductivity is, therefore, consistent with a description of the electronic structure of PPV in terms of a semiconductor band model (rather than an exciton model). The very slow stretched-exponential relaxation of the photoinduced conductivity is reminiscent of the persistent photoconductivity observed in inorganic semiconductors. By assuming that the photocurrent is carried predominantly by mobile polarons near the surface, one can construct a model for the persistent photoconductivity in which the recombination of long-lived bipolarons is inhibited in the bulk where bipolarons have a lower free energy than polarons. The persistent photoconductivity, therefore, is caused by the slow dispersive diffusion of photogenerated bipolarons to the surface where they dissociate into polarons and where both polaron transport and recombination occur.

I. INTRODUCTION

The electronic and optical properties of conducting polymers have been successfully described by the Su-Schrieffer-Heeger (SSH) model in which the π electrons of the one-dimensional conjugated macromolecular chains are treated in the tight-binding approximation and coupled to distortions in the polymer backbone by the electron-phonon interaction.¹ In the SSH model, photoexcitation across the π - π^* band gap creates free carriers (electrons and holes) which self-localize to form the nonlinear excitations of conducting polymers: solitons, polarons, or confined soliton pairs (bipolarons), depending on the ground-state degeneracy. Through photoinduced absorption measurements (excitation spectroscopy), the localized gap states associated with these novel quasiparticles have been observed in a number of conducting polymers; for example, polyacetylene,² polythiophene,³ poly(3-alkylthiophenes),⁴ and poly(phenylenevinylene) (PPV).⁵ The photoinduced infrared-active vibrational modes,⁶ the well-defined vibronic side bands in both absorption and emission,⁷ and the Stokes shift in photoluminescence⁸ directly demonstrate the importance of the electron-phonon coupling in PPV and more generally in this class of quasi-one-dimensional semiconducting polymers.

The applicability of the band picture supplemented by electron-phonon interactions, as described by the SSH model, has been criticized because of the neglect of the electron-electron Coulomb interaction. Recently, Rauscher *et al.*⁹ have interpreted their site-selective fluorescence data from PPV in terms of an exciton picture and argued that the band model is not appropriate to PPV. Electron-energy-loss-spectroscopy data,¹⁰ however, show a momentum dispersion consistent with a well-defined band structure. Therefore, it is important to uti-

lize alternative experimental methods to probe the importance of electron-electron interactions on the electronic structure (bands versus excitons) in PPV. Clearly, the traditional comparison of the spectral response of photoconductivity with the absorption spectrum near the absorption edge provides fundamentally important information. By determining whether the onset of photoconductivity coincides with that of the fundamental absorption edge, as in polyacetylene¹¹ and poly(3-hexylthiophene),¹² or the onset of photoconductivity occurs at a higher energy than the fundamental absorption edge, as in polydiacetylene,¹³ one can demonstrate that an interband transition is involved (with excitation of free-electron-hole pairs) or, alternatively, that bound excitons are generated.

We find that the spectral response of the steady-state photoconductivity in PPV follows the absorption profile, similar to the results observed in other conducting polymers.^{11,12} Using DeVore's theoretical analysis,¹⁴ the photoconductivity spectral distribution has been calculated from the measured absorption profile with results in excellent agreement with the experimental photoconductivity data. From this analysis, we conclude that the maximum in photoconductivity near the absorption edge results from enhanced surface recombination. This detailed comparison of the photoconductivity and photoabsorption indicates the photogeneration of free charge carriers via interband transition; we find no evidence of a significant exciton binding energy.

After termination of the illumination, the photoinduced conductivity exhibits slow relaxation and, in the long-time regime, follows the stretched-exponential form

$$\sigma(t) = \sigma_0 \exp[-(t/\tau)^\beta], \quad 0 < \beta < 1. \quad (1)$$

Nonexponential relaxation towards equilibrium has been observed in a wide variety of complex physical systems.¹⁵

The decay forms are algebraic (dispersive relaxation),¹⁶ stretched-exponential (Kohlrausch¹⁷ or Williams-Watts¹⁸ law), or logarithmic in time. Many examples have been reported; in glassy,¹⁵ mechanical (viscoelastic),¹⁷ and dielectric^{18,19} relaxation, in photoconductivity²⁰ of semiconductors, and in the electrochemical doping kinetics in a conducting polymer.²¹ Attempts to explain the nonexponential relaxation often assume a phenomenological model involving a statistical distribution of the relaxation times τ for different clusters or excitations, etc. (parallel relaxation).¹⁵ Palmer, Stein, Abrahams, and Anderson (PSAA),²² however, proposed a serial interpretation in which the path to equilibrium involves many sequential correlated steps. PSAA showed that the Kohlrausch law emerges naturally from such hierarchically constrained dynamics.

It is well known that, in nondegenerate conjugated polymers such as PPV, bipolarons localized on different polymer chains are the stable charged excitations and dominate the transport in the bulk of the specimen.¹ On the other hand, polarons can also exist as stable excitations. Although close in energy, polarons have higher energy than bipolarons (the gain in energy due to the structural binding energy is nearly offset by the Coulomb repulsion of the doubly charged bipolaron).¹ Near the surface, however, where the disorder is greatest and where the interchain dielectric screening is least effective, polarons can be the lowest-energy mobile charged species. The stretched-exponential decay of the persistent photoconductivity (PPC) can thus be described by a hierarchical model with the assumption that the photocurrent is carried predominantly by mobile *polarons* near the surface, but that within the bulk of the film charge is stored as bipolarons. Since recombination is inhibited in the bulk where bipolarons have a lower free energy than polarons, one can construct a model in which the PPC is caused by the slow dispersive diffusion of bipolarons to the surface. This serial relaxation model is conceptually similar to that proposed by Queisser and Theodorou²⁰ to explain the kinetics of PPC near semiconductor interfaces.

The paper is organized as follows: Experimental details and experimental results are described in Secs. II and III, respectively. The discussion in Sec. IV is composed of two parts. In Sec. IV A, we use DeVore's theoretical analysis to calculate the spectral response of the steady-state photoconductivity from the measured absorption profile, with results in excellent agreement with the measured photoconductivity data. In Sec. IV B, we develop the PPC model and compare the results with the observed stretched-exponential decay. We summarize and present our conclusions in Sec. V.

II. EXPERIMENT

Samples used for this study were thin films of the precursor polymer spin cast from solution and subsequently converted to poly(*p*-phenylenevinylene) by heat treatment. The water-soluble precursor²³ polymer was first spin cast onto 0.5-in.² glass or alumina substrates (spin speed 800–1000 rpm) under nitrogen gas. The precursor film was then sealed in an evacuated tube and converted

into the conjugated form by heat treatment at 300°C for 3 h. The resulting PPV films are uniform with excellent optical quality; films prepared in the similar way have been used for waveguide experiments.²⁴ Film thicknesses were controlled in the 0.2–0.3- μm range as measured by a Dektak surface profiler, corresponding optical densities of 1.5–2.5 at the peak in the absorption spectra. The sample thickness was also estimated to be about 0.3 μm from the interference fringes resulting from multiple internal reflection at frequencies below the absorption edge. Based on this thickness and the measured optical density at the peak of the absorption spectrum (OD \sim 2.5), the peak absorption coefficient was estimated as $\alpha = 2 \times 10^5 \text{ cm}^{-1}$ in agreement with that reported earlier.²⁵

Gold electrodes were evaporated onto the top surface of the samples using appropriate masks to form a surface-cell configuration. For the steady-state photoconductivity measurements, the electrodes were 6 mm in length separated by a gap of 0.2 mm. The dark conductivity of the PPV films is approximately $5 \times 10^{-9} \text{ S/cm}$ at room temperature with an activation energy of about 210 meV, as measured with a Keithley 467 picoammeter/voltage source. The intrinsic dark conductivity of the precursor-route PPV film is known to be less than 10^{-15} S/cm at room temperature; the dark conductivity of the order of $10^{-10} \sim 10^{-8} \text{ S/cm}$ is usually obtained upon exposure to oxygen during handling in air.²⁶ The applied electric field across the 0.2-mm gap was $2.5 \times 10^3 \text{ V/cm}$. The dark I-V measurement shows Ohmic behavior up to at least 400-V bias voltage across the 0.2-mm gap (electric field of $2 \times 10^4 \text{ V/cm}$). For photoconductivity (PC) measurements, 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.

For the steady-state and the modulated (low-frequency) PC measurements, a 500-W tungsten-halogen lamp, dispersed by a single-grating monochromator (with relevant order filters), was employed as the light source. The power density of exciting light incident upon the sample surface were in the range 0.4–0.5 mW/cm^2 unless otherwise specified. The light was focused on the gap area between the electrodes using proper focus lenses. To normalize out the spectral response of the measurement system, the probe head used to obtain the PC data was replaced by a broadband pyroelectric detector (Moletron Model J3-02) or by a calibrated silicon photodiode. The spectral response of the detection system was recorded under identical conditions and used as the background for the normalization of the photocurrent spectrum. For each PPV film sample, the absorption spectra were measured (either simultaneously during the modulation experiment or subsequently with a Perkin-Elmer Lambda-9 spectrophotometer).

The steady-state PC response has a faster and a slower component (lasting as long as several tens of minutes). A computer-controlled digital multimeter (Keithley 195A DMM) was used to record the growth and decay data of the persistent photoconductivity (PPC) in 3-s intervals. In the modulated PC experiment, standard photomodulation techniques were employed; the excitation light was

chopped with a Stanford SR450 mechanical chopper, and the resulting modulated signal was processed through a Stanford SR530 lock-in amplifier tuned to the chopping frequency. The resulting PC spectra were normalized for equal photon flux at all photon energies.

The steady-state modulated (19.1 Hz) PC at 2.45 eV is calculated to be about 7×10^{-9} S/cm at room temperature for an incident photon flux of about 10^{15} photons/cm² s. For temperatures above 200 K, the activation energy of the steady state PC is about 140 meV, significantly smaller than the dark conductivity (σ_d); the latter being about 210 meV. The measured PC response is genuine and not due to a bolometric effect from sample heating. For bolometric heating, the signal is expected to be approximately proportional to the dark conductivity, whereas we find that the two have significantly different activation energies. Furthermore, the PC action spectrum shows a peak at 2.45 eV where the absorption is weak (see Sec. III). The frequency dependence of the modulated PC is sublinear, whereas a bolometric signal is expected to decrease as $\omega^{-1.5}$. Finally, the estimated temperature rise (at 300 K) for the modulated PC (0.4 mW/cm² chopped at 19.1 Hz) is estimated to be less than 19 mK from which we estimate $\sigma_{ph} = 10^{-3} \sigma_d$. This is in sharp contrast to the observed result, $\sigma_{ph} \approx \sigma_d$. The extremely long decay time (tens of minutes) of the PPC is absolutely inconsistent with sample heating as the source of the signal.

III. RESULTS

The spectral response of the steady-state PC of the spin-cast PPV film is shown in Fig. 1 together with optical-absorption spectrum. The solid curve is the calculated spectral response, based upon DeVore's theory¹⁴ which takes into account enhanced recombination for carriers generated near the surface (see Sec. VI). The PC spectral response data in Fig. 1 were taken at room temperature using a lock-in amplifier with a chopping frequency of 19.1 Hz and normalized to a constant number of incident photons. The PC spectra at lower temperature (down to 240 K) are basically similar to those at room temperature. The experimental PC data are normalized to unity at the peak, $E = 2.45$ eV ($\lambda = 505$ nm), to compare with the computed PC curve. The spectral resolution was set at about 2 nm. The optical-absorption spectrum was measured at room temperature prior to the PC measurement.

The optical-absorption spectrum of fully converted PPV shows that the onset of the π - π^* interband transition occurs at about 2.4 eV, coincident with the threshold for a significant steady-state PC response, with a broad absorption maximum at about 2.9 eV. The well-defined band edge and the resolved vibronic structure indicate relatively good crystallinity even in the spin-cast PPV films, consistent with x-ray-diffraction data.²⁵

Figure 1 clearly illustrates that the PC response turns on with the absorption and shows a peak at about 2.45 eV, just above the onset of absorption. Figure 2 presents the PC spectra measured with several chopping frequencies (6.53, 19.1, 198, and 796 Hz); the data near the ab-

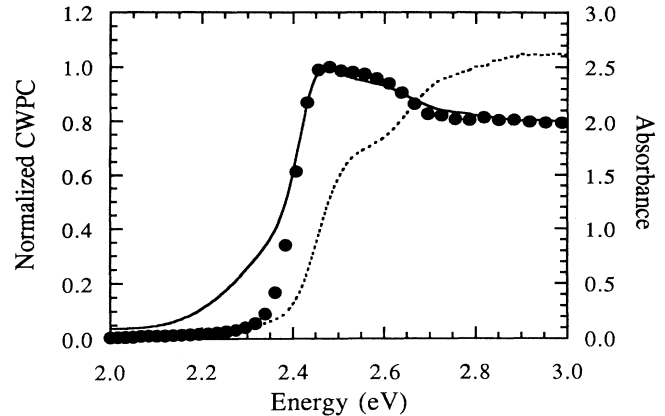


FIG. 1. Spectral response of the modulated photoconductivity (closed circles) and the absorption (dotted line) of a PPV film measured at room temperature ($T = 295$ K). The theoretical fitting curve (solid line) is calculated from the absorption profile using DeVore's theory with fitting parameters $\delta = 1.0$ and $\xi = 1000$. The modulated PC data are measured by a lock-in amplifier with a chopping frequency 19.1 Hz and normalized to the equal number of incident photons. To compare with the computed PC curve, the experimental PC data are normalized to unity at the peak, $E = 2.45$ eV (505 nm).

sorption edge are plotted on a semilog scale. At each frequency, the spectra are normalized to a constant number of incident photons and also normalized to unity at the peak, $E = 2.45$ eV. For comparison, the calculated PC response (see Sec. IV) is shown as the solid curve. The frequency dependence of the PC response below E_g is different from that above E_g : Below E_g , the signal decreases much faster with increasing chopping frequency, while all of the spectra above E_g parallel the theoretical curve. This indicates that E_g corresponds to the mobility edge as well as the threshold for charge-carrier generation, because below the mobility edge the activated mo-

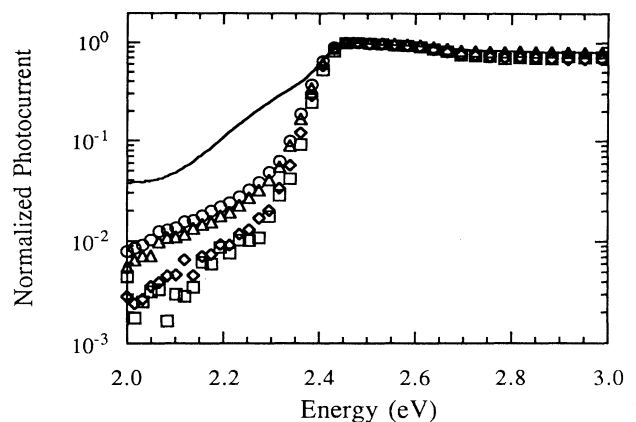


FIG. 2. Semilog plot of the modulated PC spectra near the absorption band edge with several chopping frequencies: 6.53 (open circles), 19.1 (triangles), 198 (diamonds), and 796 Hz (squares). The theoretical curve (solid line) is also plotted for comparison.

bility of localized carriers leads to much slower response.

Figure 3 shows the spectral response of the saturated PC under continuous illumination, compared with that of the modulated PC measured by a lock-in amplifier; again the calculated curve is shown for comparison. Several minutes are required to reach steady state under continuous illumination, and several tens of minutes are required for the photocurrent to decay to the equilibrium dark conductivity level after termination of photoexcitation. Therefore, it takes more than 30 min to obtain each data point of the saturated PC, which is the difference between the steady-state conductivity (sample illuminated) and the dark conductivity. The magnitude of the saturated PC at 2.45 eV is calculated to be about 6×10^{-8} S/cm at room temperature for an incident photon flux of about 10^{15} photons/cm²s, which is an order of magnitude larger than the dark conductivity. We conclude from Figs. 1–3 that there is no significant energy range over which there is substantial absorption but no photoconductivity, as would be expected if there were a significant exciton binding energy (and observed, for example, in the spectral response of the photoconductivity of polydiacetylene¹³).

The saturated PC shows a somewhat weaker spectral dependence above the absorption edge than the modulated PC. This difference appears to be mainly due to the importance of different recombination mechanisms: bimolecular recombination in the (persistent) saturated PC, and monomolecular decay at shorter times. Bimolecular recombination is important in the saturated PC as can be seen in Fig. 4, where the saturated PC is shown to be proportional to the square root of the excitation intensity I_L . A similar intensity dependence of the steady-state PC was reported by Tokito *et al.*²⁶ By contrast, the modulated PC is approximately linear in I_L with slightly different exponents for different chopping frequencies. In all cases, the intensity dependence was measured at the peak photocurrent (2.45 eV) at room temperature and the power density of exciting light incident upon the sample surface was varied from $4.5 \mu\text{W}/\text{cm}^2$ to $0.45 \text{ mW}/\text{cm}^2$ using neutral density filters.

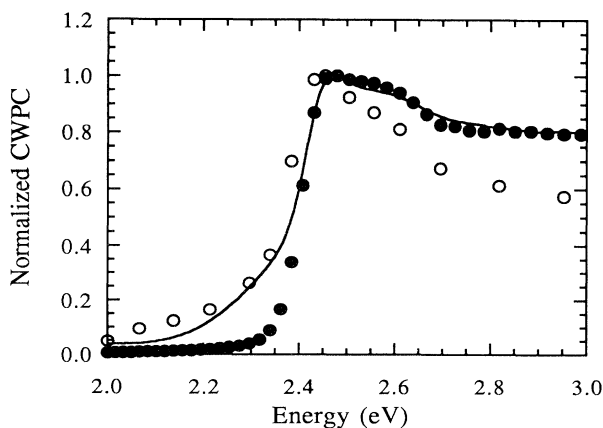


FIG. 3. The saturated PC spectrum (open circles) normalized to an equal number of incident photons is compared with both the modulated PC spectrum (closed circles) and theory (solid line) of Fig. 1.

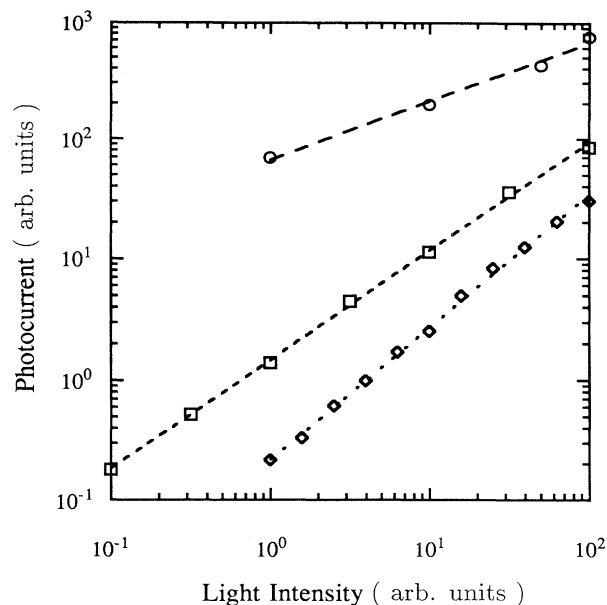


FIG. 4. The light intensity dependence of the saturated PC (open circles) and the modulated PC with chopping frequencies 6.53 (squares) and 198 Hz (diamonds) at the peak photocurrent. The saturated PC is proportional to the square root of the excitation intensity I_L and the modulated PC is linearly proportional to I_L .

The linear dependence of the modulated PC on light intensity suggests monomolecular recombination kinetics. In the case when a single monomolecular recombination time τ governs the recombination of photoexcited charge carriers, the frequency dependence is given by

$$\sigma(\omega) = \frac{\sigma(0)}{[1 + (\omega\tau)^2]^{1/2}} \quad (2)$$

Therefore, the modulated PC is expected to be approximately independent of frequency in the low-frequency limit ($\omega\tau \ll 1$) and to decrease with increasing frequency as ω^{-1} in the high-frequency limit ($\omega\tau \gg 1$).

Figure 5 shows the dependence of the peak photocurrent at $E = 2.45$ eV on chopping frequency ω in the range 10–4000 Hz at room temperature. The data shown in Fig. 5 cannot be fit to the simple frequency dependence predicted by Eq. (2); the modulated PC response decreases as $\omega^{-0.66}$ for chopping frequencies above about 100 Hz, suggestive of much slower decay kinetics than the monomolecular recombination with a single lifetime. The power-law dependence on chopping frequency has been commonly seen in the photoinduced absorption arising from long-lived bipolaron states in conducting polymers;²⁷ the power law has been understood as arising from a distribution of characteristic times for the decay of long-lived excitations. This interpretation was confirmed through studies of photoinduced absorption in highly ordered films of conducting polymer in polyethylene prepared by gel processing.²⁸ In these oriented and ordered films, the dependence of the photoinduced absorption signal on chopping frequency was consistent

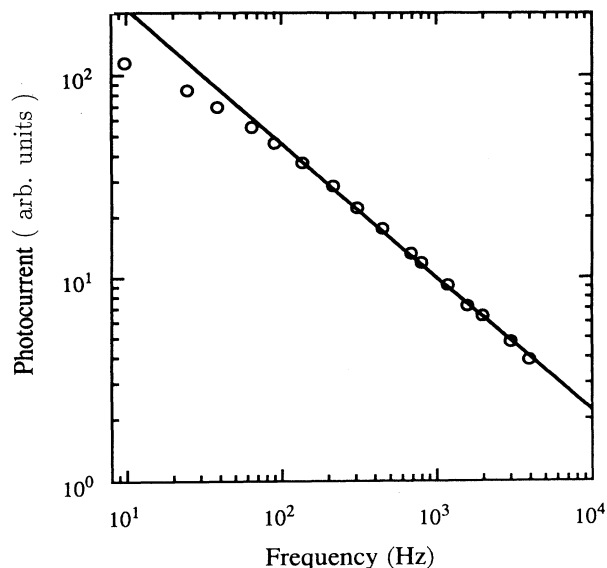


FIG. 5. The dependence of the peak photoconductivity upon chopping frequency is measured in the range 10–4000 Hz. The solid line is the power law ($\omega^{-0.66}$) which fits the data above 100 Hz.

with Eq. (2), whereas the same material showed a power-law dependence prior to ordering by tensile drawing.

Figure 6(a) shows the buildup and decay of the steady-state PC at $\hbar\omega=2.45$ eV at room temperature as a function of time. The power density of exciting light incident upon the sample surface was $4.5 \mu\text{W}/\text{cm}^2$. The data are normalized to unity at $t=0$, the moment at which photoexcitation is terminated. The very slow decay of PC is reminiscent of the persistent photoconductivity (PPC) observed in inorganic semiconductors.²⁹ After a fast initial decay, the excess photoinduced conductivity approaches the equilibrium dark value with an increasingly sluggish rate of decay. Queisser and Theodorou²⁰ observed this type of nonexponential relaxation of PPC in the interfaces of $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ heterostructures.

Figure 6(b) shows the time dependence of the buildup and decay of PPC at different wavelengths as the pump energy is varied through the interband transition. The data are normalized to a constant number of incident photons. The saturated level of the PPC with respect to the photon energies has been plotted previously in Fig. 3.

Figure 7(a) shows the data from Fig. 6(a) and the instantaneous lifetime, defined as

$$\tau_{\text{ins}} = \frac{\sigma(t)}{|d\sigma(t)/dt|}, \quad (3)$$

on a log-log plot. The instantaneous lifetime is a constant for exponential decay with a single lifetime (monomolecular recombination) and is linearly proportional to time for either bimolecular recombination or power-law decay. The data in Fig. 7(a) show that the instantaneous lifetime is a sublinear function of time, $\tau_{\text{ins}} \sim t^\alpha$ with $0 < \alpha < 1$ (solid line), which indicates that recombination of the photoexcited carriers is restricted in some way. We also plot the instantaneous lifetime for the case of logarithmic

decay (dotted line) reported by Queisser and Theodorou.²⁰ Although the downward curvature after about 1000 s is beyond the measurement accuracy, the PPC decay is consistent with a logarithmic decay, $\sigma(t) = \sigma_0 - A \ln t$, in the long-time regime. We will show in Sec. IV B that the PPC decay can be understood as resulting from dispersive diffusion of the long-lived bipolarons to the surface.

Integration of Eq. (3) with $\tau_{\text{ins}} \sim t^\alpha$ yields the stretched-exponential decay form of Eq. (1). The solid curve in Fig. 7(b) is the result of Eq. (1) with $\beta=0.47$ and $\tau=154$ s; the PPC data in Fig. 6(a) are fit quite well by Eq. (1). Two thirds of the data points are removed to show the fitting curve clearly. The fitting parameter β in Fig. 7(b) is in reasonable agreement with $\alpha=1-\beta$ obtained from the instantaneous lifetime in Fig. 7(a).

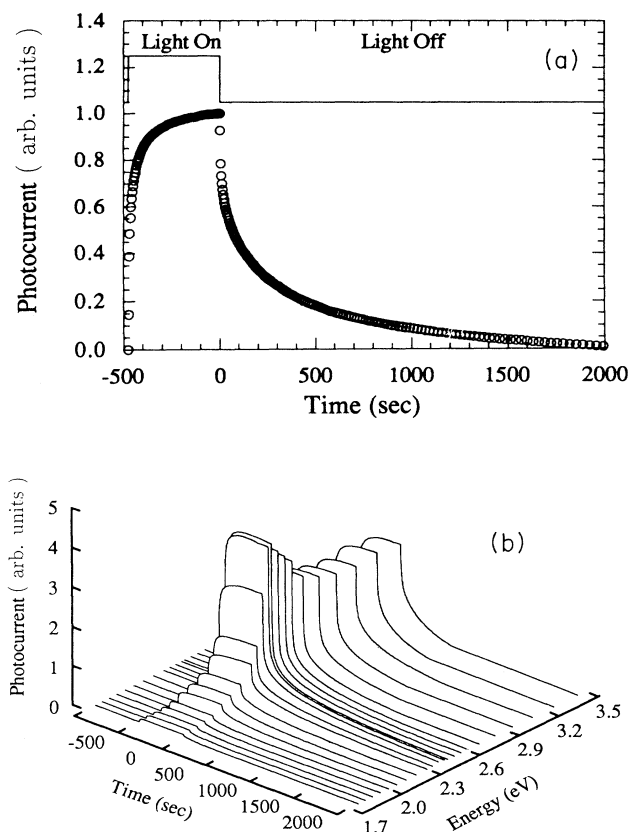


FIG. 6. (a) The buildup and decay of the steady-state PC at $\hbar\omega=2.45$ eV at room temperature as a function of time. The power density of exciting light incident upon the sample surface is about $4.5 \mu\text{W}/\text{cm}^2$ and the applied dc bias voltage is 50 V across a 0.2-mm gap. The data are normalized to unity at $t=0$, the moment at which photoexcitation is terminated. The very slow decay of PC is reminiscent of the persistent photoconductivity (PPC). (b) The time dependence of the buildup and decay of PPC at different wavelengths as the pump energy is varied through the interband transition. The data are normalized to a constant number of incident photons. The illumination was turned on at -500 s and turned off at 0 s.

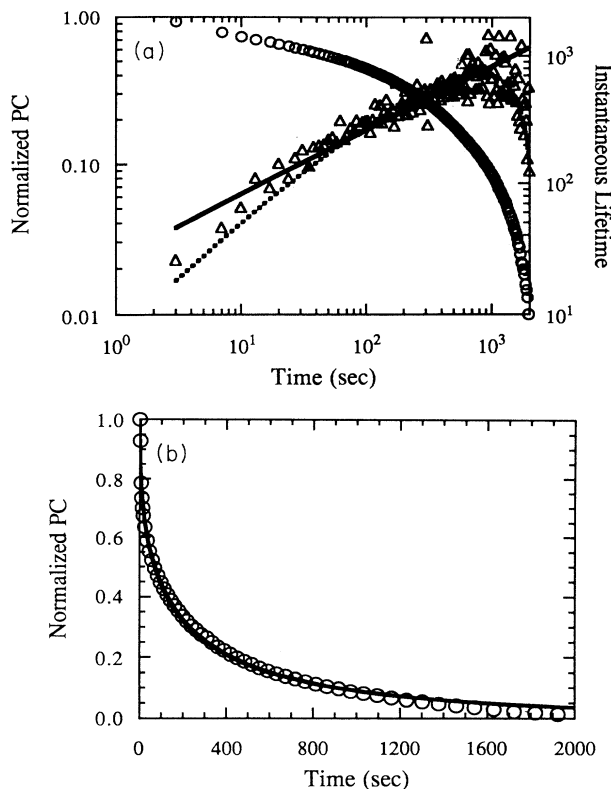


FIG. 7. (a) The data in Fig. 6(a) and the instantaneous lifetimes, defined as Eq. (3), on a log-log plot. The instantaneous lifetime is a sublinear function of time, $\tau_{\text{ins}} \sim t^\alpha$ with $\alpha=0.5$ (solid line). We also plot the instantaneous lifetime for the case of logarithmic decay (dotted line) reported by Queisser and Theodorou (Ref. 20). (b) PPC decay as a function of time after termination of the illumination at room temperature. The open circles are experimental data in Fig. 7(a) and the solid line is the fitting curve from Eq. (1) with fitting parameters $\beta=0.47$ and $\tau=154$ s. Two-thirds of data points are removed to show the fitting curve clearly.

IV. DISCUSSION

A. Spectral response

The steady-state PC of PPV, in the powder form, was first investigated by Horhold and Opfermann.³⁰ Using films (5 or 10 μm in thickness) synthesized by the thermal conversion of the precursor polymer at 300 $^\circ\text{C}$ for an hour, Tokito *et al.*²⁶ reported the spectral response of the steady-state PC. The long-lived photocurrent showed a relatively sharp peak at about 530 nm ($E=2.34$ eV), below the $\pi-\pi^*$ interband absorption maximum, and the photocurrent increased approximately as the square root of the light intensity, $I_{\text{ph}} \sim I_L^{0.54}$. Tachiguchi *et al.*³¹ reported a maximum in the steady-state photocurrent at about 2.4 eV for a nonstretched PPV film (about 10 μm in thickness) converted at 250 $^\circ\text{C}$. From time-of-flight measurements, they found a mobility of about 2×10^{-4} $\text{cm}^2/\text{V s}$ for the long-lived photocarriers with lifetimes larger than several μs and showed that the predominant mobile carriers were holes. In the fully converted,

precursor-route, stretch-oriented PPV film, Bradley *et al.*³² reported a peak at about 2.64 eV (470 nm) in the excitation spectrum for transient (nanosecond time regime) photoconductivity, somewhat higher energy than the results of Tokito *et al.*²⁶ and Tachiguchi *et al.*³¹ The steady-state PC data in Fig. 1 show a peak at about 2.45 eV (505 nm). Thus, although the maximum in the photoconductive response near the absorption edge is a general feature, the precise position of the maximum is sample dependent.

These observations are somewhat surprising, since the conventional model of photoconductivity via an interband transition predicts a threshold energy for electron-hole pair production at the fundamental optical-absorption edge with relatively high sensitivity for $\hbar\omega$ at photon frequencies above E_g . Since the carrier photogeneration rate is proportional to the number of photons absorbed, a peak would be expected for thin films (thickness less than optical-absorption depth) at the photon frequency corresponding to the maximum in the absorption spectrum. For thick films (thickness much larger than optical-absorption depth), this model would predict that the photocurrent would be insensitive to the photon frequency for energies greater than the energy gap. On the other hand, if the absorption is excitonic in origin, there would be no photoconductivity until the photon frequency is sufficient to overcome the exciton binding energy.

The experimental results demonstrate that the PC response exhibits a maximum near the absorption edge and decreases at higher photon energies, where the absorption coefficient continues to increase. To explain this, DeVore¹⁴ calculated the spectral response of the steady-state PC for the surface-cell geometry by solving the rate equation and including in the recombination kinetics carrier diffusion to the surface, where the recombination rate is assumed to be enhanced. DeVore showed that if the sample thickness is larger than the carrier diffusion length and/or the surface recombination rate is much larger than the volume recombination rate, there would be a peak in the photoresponse at an energy in the vicinity of the absorption edge. Detailed comparisons of DeVore's theory with experiment are rare in the literature, largely as a result of the difficulty in obtaining the thin-film samples required for simultaneous measurements of the steady-state PC response spectrum and the absorption spectrum. In conducting polymers, however, it is relatively easy to obtain thin-film samples with excellent optical quality. We therefore use the DeVore theory to compare the PC response spectrum with that predicted from the absorption spectrum.

DeVore's analysis is carried out for a photoconductor in the form of a large sheet with thickness d . The sample is illuminated on one face and, at each point through the sample, charge carriers are generated at a rate proportional to the absorbed photon density at that point. Because of the gradient in the carrier density, the charge carriers diffuse. Carriers in the bulk (away from the surface) are assumed to undergo monomolecular recombination at a rate τ , while those that diffuse to the surface recombine at a rate which may be represented by a surface recombination velocity S , which is the product of the

carrier velocity and the probability that recombination occurs when the particles reach the surface. The numerical value of S depends on the equilibrium concentration of charge carriers in the dark, the height of the surface barrier, and the density of surface states, etc.³³ Diffusion from the bulk of the sample towards the active surface

$$\sigma_{\text{ph}}(\alpha) = \frac{1 - e^{-\alpha d}}{1 + \xi \coth(\delta/2)} \left[1 + \frac{\xi \delta [\delta \coth(\delta/2) - \alpha d \coth(\alpha d/2)]}{\delta^2 - (\alpha d)^2} \right], \quad (4)$$

where α is the absorption coefficient and D is the diffusion constant for the photoexcited carriers. Therefore, we can calculate the spectral response of the steady-state PC from the absorption profile, assuming that every absorbed photon creates a charge carrier, i.e., assuming that all the oscillator strength results from band-to-band transitions.

With δ and ξ as fitting parameters, Eq. (4) has been used to fit the spectral response of the steady-state PC in Fig. 1, where the solid curve corresponds to $\delta=1.0$ and $\xi=1000$. The fitting parameters with $\delta \sim 1$ and $\xi > 100$ provide good fits to the experimental data. For a large value of ξ , δ is chosen to match the location of the peak near the absorption edge. The ratio of the peak PC to the asymptotic value at large absorption constant yields the value of ξ for a chosen δ . Values for $\xi > 100$ correspond to rather strong surface recombination; for $\delta \sim 1$, increasing ξ above 100 has relatively little effect upon the resulting spectrum.

In the context of the DeVore theory, the different energies of PC maximum near the absorption edge reported previously in the literature^{26,30-32} can be understood to arise from differences in either sample thicknesses or surface recombination rates due to different sample preparation conditions.

When the PC is linear in light intensity (as in the case for the modulated PC data in Fig. 4), and when all the light is absorbed by the sample, the number of the steady-state photocarriers is $n = \eta G \tau$, where η is the quantum efficiency for creation of charged excitations and G is the generation rate and τ is the average lifetime of the photocarriers. Therefore, the steady-state PC is given by

$$\sigma_{\text{ph}} = e \eta \mu G \tau, \quad (5)$$

where μ is the average mobility. Although it is very difficult to determine τ because there is no single characteristic time for the decay of long-lived charge carriers (see Fig. 5), the frequency dependence of the PC (Fig. 5) or photoinduced-absorption (PA) (Ref. 27) data imply τ in the order of millisecond. Then $\sigma_{\text{ph}} \sim 10^{-8}$ S/cm for $G \sim 3 \times 10^{19}$ photons/cm³s gives $\eta \mu \sim 2 \times 10^{-6}$ cm²/V s. If we assume the quantum efficiency to be $\eta \sim 1\%$ as in *trans*-(CH)_x,^{11,34} the resulting mobility of the long-lived charged carriers is in good agreement with the time-of-flight-experiment result of Tachiguchi *et al.*³¹ The diffusion constant D is estimated through Einstein relation as $D = \mu kT/e \sim 5 \times 10^{-6}$ cm²/s, so the diffusion length is $(D\tau)^{1/2} \sim 0.7$ μm , i.e., of the order of sample

persists so long as any excess carriers remain.

If δ is defined as the ratio of sample thickness d to diffusion length $(D\tau)^{1/2}$, $\delta = d/(D\tau)^{1/2}$ and ξ is the ratio of surface to volume recombination rates, $\xi = S(\tau/D)^{1/2}$, DeVore's theory leads to the following expression for the spectral dependence of the photoconductivity:

thickness. Therefore, since $(D\tau)^{1/2} \sim d \sim 0.3$ μm , $\delta \sim 1$, consistent with the result from the fit to Eq. (4) ($\delta=1.0$). Since $\delta=1.0$ was chosen from the peak position of the PC spectrum with less arbitrariness, this agreement is quite satisfactory considering the rough estimate of τ ($\tau \sim 1$ ms). Using $\tau=1$ ms and $D \sim 5 \times 10^{-6}$ cm²/s, we can estimate the lower bound of the surface recombination velocity from $\xi > 100$, $S = \xi(D/\tau)^{1/2} > 7$ cm/s. This large surface recombination velocity implies that long-lived bipolarons diffuse towards the active surface to dissociate and recombine there. Evidently, the recombination is relatively efficient at the surface; $\xi > 100$ implies that within the bulk of the film, the recombination of charge carriers is inhibited.

It is well known that in conducting polymers, bipolarons can be lower in energy than separated polarons; within the SSH model, bipolarons always have lower energy. On the other hand, the Coulomb repulsion favors separated polarons with charge $\pm e$ over bipolarons with charge $\pm 2e$. In real physical systems, the dielectric screening of the Coulomb interaction can be sufficiently large that charge is stored predominantly in bipolarons whether the charge carriers are generated by doping or by photoexcitation.

We assume, therefore, that within the bulk of the PPV film, charge is stored in bipolarons and that $B^{2+} + B^{2-}$ is more stable than $2B^0$, where B^0 is the neutral polaron exciton (a bound state of $P^+ + P^-$). We assume, in addition, that polarons are lower in energy (than bipolarons) only near the surface. If bipolarons are lower in energy than separated polarons, *there is a fundamental barrier to recombination*. Near the surface, $B^{2\pm} \rightleftharpoons 2P^\pm$, followed by recombination of $P^+ + P^- \rightarrow B^0 \rightarrow |g\rangle$, where $|g\rangle$ is the ground state (either radiatively via luminescence or non-radiatively via multiphoton processes). Thus, with these assumptions, carrier recombination takes place only near the surface (where bipolarons first dissociate into polarons), in agreement with the experimental results.

In Fig. 1, one sees excellent agreement in overall shape between the experimental PC spectrum and the theoretical prediction. The PC response shows a peak at about 2.45 eV, where the absorption is moderate, as predicted from DeVore theory in the case of significant surface recombination. Although the PC spectrum follows the theoretical curve above the band edge ($E_g = 2.4$ eV), the data fall below the theoretical curve below E_g . The reason for this disparity is that while the theory assumes that every absorbed photon creates a pair of charge carriers, the absorption in the long-wavelength tail may arise

from electronic transitions to band-edge states which may be localized by disorder. In other words, E_g corresponds to the threshold for the photogeneration of *mobile* charge carriers, or the mobility edge separating localized states from extended states.³⁵ Indeed, as noted earlier, in Figs. 2 and 3, the PC shows a strong dependence on modulation frequency below E_g , indicating that E_g corresponds to the mobility edge, because the activated mobility of carriers leads to much slower response for photoexcitation into states below the mobility edge. The interpretation in terms of the mobility edge at $E_g = 2.4$ eV is also consistent with the observation of Rauscher *et al.*⁹ of a "localization threshold" $\nu_{\text{loc}} = 19,020 \text{ cm}^{-1}$ (2.36 eV) in the fluorescence spectrum measured at 6 K, although they interpreted it in the context of an exciton picture. They observed a well-defined energy, $\nu_{\text{loc}} = 19020 \text{ cm}^{-1}$ (2.36 eV), in the tail of the absorption edge below which the fluorescence emission is quiresonant with a Stokes shift of 100 cm^{-1} . Above this localization threshold, spectral diffusion is observed, with the emission being independent of excitation.

Although we showed that the steady-state PC action spectra can be understood in detail within the semiconductor band picture, it is important to establish whether the data are consistent with the exciton picture commonly used in molecular crystals. Gailberger and Bassler³⁶ argued that the optical absorption in PPV or PPPV creates strongly correlated electron-hole pairs (excitons). They described the photocarrier generation in terms of the Onsager theory of geminate-pair dissociation in one-dimensional chains. From the temperature dependence of the dc photocurrent in PPPV at an excitation wavelength of 400 nm, they found the activation energy of $E_a = 0.165$ eV (our data yield a similar value, $E_a = 0.14$ eV in PPV at an excitation wavelength of 505 nm). Within the Onsager theory,³⁷ E_a is the exciton binding energy with an initial separation r_0 at low fields

$$E_a = \frac{e^2}{4\pi\epsilon\epsilon_0 r_0}, \quad (6)$$

where ϵ_0 is the dielectric constant of the medium. Because changes in the initial kinetic energy of the photoelectron will result in changes in r_0 , variation in the activation energy will be expected at different excitation wavelengths, as is observed in *a*-Se.³⁸ However, we find that the PC action spectra at each temperature from 350 to 240 K normalized at 2.45 eV ($\lambda = 505$ nm) is observed to collapse onto the same curve. Therefore, the activation energy is essentially independent of the excitation energy from about 2.2 to about 3.5 eV, contrary to the prediction of the Onsager theory. We find no measurable energy difference (within our spectral resolution of about 2 nm) between the onset of the PC response and the absorption threshold. In addition, the temperature dependence of the peak transient PC in the subnanosecond regime shows thermally activated behavior only for temperatures above about 200 K. Below 200 K, the transient peak PC is *independent of temperature*.^{39,40} Clearly, the temperature-independent behavior below 200 K cannot be described by the Onsager model. Furthermore, we

also observed that E_a decreases with increasing light intensity, as inferred from the temperature dependence of the peak transient photocurrent from 300 down to 200 K at 2.91 eV ($\lambda = 425$ nm).³⁹ This observation is in contradiction to the interpretation of E_a as the exciton binding energy because in the Onsager model the exciton binding energy does not depend on the photoexcitation level. Therefore, the activation energy should not be interpreted as the exciton binding energy.

In addition to the above difficulties with the exciton picture in explaining the photoconductivity response in PPV, it is also difficult to understand the PC action spectrum from the absorption profile. If the PC shows structure related to the excitonic excitations, then there should be corresponding structure in the absorption profile, as observed in many semiconductors. However, in PPV no structure is observed at 2.45 eV in the absorption profile while the PC shows a peak. Gailberger and Bassler³⁶ argue that this peak near the absorption edge is an accidental effect due to the bimolecular recombination at higher energy. We have found, however, that in our measurements the saturated PC action spectrum is essentially identical to the modulated PC spectrum (see Fig. 3); both show the peak near 2.45 eV even though the saturated PC is proportional to $I^{0.5}$ while the modulated PC is proportional to I (see Fig. 4). Thus, the data are not consistent with the argument of Gailberger and Bassler. In contrast, we showed in the above discussion that all aspects of the PC action spectrum are predicted directly from the absorption spectrum within the band model using the DeVore theory.

Within the exciton picture, free carriers must be produced as a secondary process, by exciton diffusion as invoked in low-mobility molecular crystals such as anthracene⁴¹ or σ -bonded polysilanes.⁴² Charge carriers are generated when excitons, bound electron-hole pairs formed when a photon is absorbed, diffuse to the vicinity of the surface where the bound pair dissociates. In this model, a plot of the reciprocal of the photocurrent (or of the number of charge carriers produced by photoexcitation) versus the reciprocal of the absorption coefficient, $(i_{\text{photo}})^{-1}$ versus α^{-1} , should yield a straight line, where the ratio of the intercept to the slope of the line gives the exciton diffusion length. Such behavior is well established, for example in the data of Kepler *et al.*⁴² However, a plot of $(i_{\text{photo}})^{-1}$ vs α^{-1} does not yield a straight line for PPV, as shown in Fig. 8.

In addition, within the exciton picture, the PC response is expected to be similar to the absorption spectrum, i.e., larger for higher absorption because more excitons would be created near the surface. On the contrary, the PC action spectrum shows just the opposite behavior. We therefore conclude that on the basis of the experimental observations, carrier generation by exciton diffusion and subsequent surface dissociation is ruled out as the dominant mechanism in PPV. In fact, it is well established that in PPV, similar to other π -conjugated polymers, the long-lived charge carriers are bipolarons, as seen in the photoinduced absorption measurement.¹

From detailed examination of the predictions of the exciton model, we conclude that the picture in which the

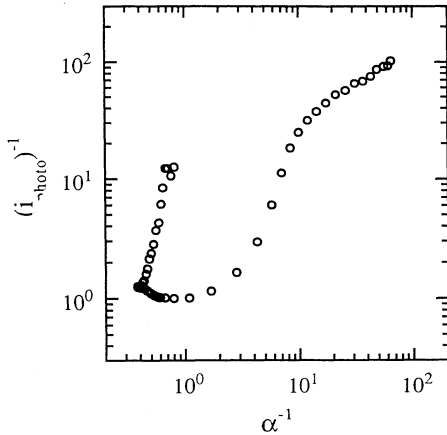


FIG. 8. Log-log plot of $(i_{\text{photo}})^{-1}$ vs α^{-1} (where α is proportional to the optical density); the data are taken from Fig. 1 (the ordinate is in arbitrary units). The straight-line behavior expected within the exciton model is not observed.

initial photoexcitations are bound electron-hole pairs (excitons) is not capable of explaining the spectral, temperature, light intensity, and field dependences of the photoconductivity. In contrast, we showed that the semiconductor band picture is fully consistent with the data. In particular, as emphasized in the Introduction, by determining whether the onset of photoconductivity coincides with that of the fundamental absorption edge or the onset of photoconductivity occurs at a higher energy than the fundamental absorption edge, one can determine if an interband transition is involved (with the generation of free electron-hole pairs) or if bound excitons are generated (with the electron and hole bound by their Coulomb attraction). The fact that the measured steady-state PC spectrum follows the theoretical curve calculated from the measured absorption coefficient proves that the charged carriers are photogenerated via a direct interband transition. From this detailed comparison of the photoconductivity and photoabsorption, we find no evidence of a significant exciton binding energy.

B. Slow relaxation of the persistent photoconductivity

The very slow relaxation of photoinduced conductivity after the termination of photoexcitation [shown in Figs. 6(a) and 6(b)] is reminiscent of the persistent photoconductivity (PPC) observed in inorganic semiconductor systems.²⁹ Figure 7(b) shows that PPC decay follows the stretched-exponential form. The stretched-exponential decay has been observed in a wide class of complex disordered materials; it is apparently a general characteristic of glassy materials. Several mechanisms leading to the nonexponential relaxation have been proposed, including time-dependent barriers to recombination,¹⁸ hierarchically constrained dynamics,²⁰ percolation,⁴³ and time-dependent diffusion processes.⁴⁴

While the physical processes which generate the stretched-exponential decay are still controversial, two classes of models have been proposed, one of which pos-

tulates a statistical distribution of lifetimes of many uncorrelated degrees of freedom (parallel relaxation), reflecting the complexity of the dynamics in disordered structures. Then, with the assumption of additive contributions from each degree of freedom, the relaxing quantity is expressed as

$$n(t) = \int_0^{\infty} w(\tau) \exp(-t/\tau) d\tau. \quad (7)$$

A suitable choice of the distribution function $w(\tau)$ can account for any reasonable shape of the relaxation data. However, as PSAA (Ref. 22) point out, this approach is microscopically arbitrary. There is no apparent reason why the resulting decay should be a stretched exponential, as this does not result from any obvious distribution of lifetimes (such as, for example, a Gaussian). The $w(\tau)$ distribution must have a microscopic origin in the correlations between different degrees of freedom.

The other model, introduced by PSAA,²² proposed a serial relaxation to equilibrium via a hierarchy of dynamical constraints. The latter model postulates a time-dependent relaxation rate. The relaxation processes are then no longer independent of each other, but evolve with time. The decay of the photoexcited carriers can be described by the rate equation

$$\frac{dn(t)}{dt} = -k(t)n(t). \quad (8)$$

The nonexponential decay must be related to the functional form of $k(t)$. Shlesinger and Montroll⁴⁵ derived the stretched-exponential decay law using the concept of continuous-time random walk (CTRW) with an algebraic pausing-time distribution $\psi(t) \sim t^{-(1+\beta)}$ that has been successfully applied to dispersive transport in amorphous semiconductors. The drift mobility of excess carriers in most amorphous photoconductors exhibits a power-law decay, $t^{-(1-\beta)}$, which was first explained by Scher and Montroll¹⁶ using the concept of CTRW. A common origin for the dispersion is an exponential energy distribution of traps, $\exp(-E_a/k_B T_0)$, where $k_B T_0$ is the width of the trap distribution and the dispersion parameter β is given by $\beta = T/T_0$. Kakalios, Street, and Jackson⁴⁴ established a link between the stretched-exponential decay and the dispersive transport characterized by a power-law time decay of the mobility or diffusion in hydrogenated amorphous silicon (*a*-Si:H).⁴⁶ The relaxation in the electronic properties of *a*-Si:H is attributed to the motion of bonded hydrogen which exhibits dispersive diffusion.

Although the data in Fig. 7(b) could be described with either a distribution of lifetimes or a time-dependent relaxation rate, we pursue the latter interpretation, which offers the potential for greater physical insight into the mechanism underlying the stretched-exponential decay. We demonstrate that the stretched-exponential decay of PPC in PPV film can be explained in terms of dispersive diffusion of bipolarons from the bulk to the surface. Thus, our model is conceptually similar to that of Queisser and Theodorou²⁰ and Kakalios, Street, and Jackson.⁴⁴

PPC effects have been observed in many materials and a variety of mechanisms have been proposed. Although there is no single origin of the PPC operating for different materials, there is a consensus that in each case there must exist a mechanism which prevents charge recombination. Any reasonable model for PPC in a conjugated polymer should be consistent with the well-established experimental fact that the photogeneration leads to polarons and/or bipolarons in nondegenerate π -conjugated polymers and that the long-lived charge carriers are bipolarons. In addition, we know from the detailed analysis of the PC action spectra in Sec. IV A that the surface recombination velocity is quite large, so that the surface dominates the recombination of bipolarons. Thus, any plausible model for the PPC in PPV must be consistent with these facts.

As described in Sec. IV A, our model assumes that photogenerated charges are stored in bipolarons within the bulk of the PPV film, while polarons are lower in energy only near the surface; carrier recombination takes place only near the surface where bipolarons first dissociate into polarons. Since the long-lived bipolarons have extremely small mobility, the photocurrent is carried predominantly by mobile polarons near the surface. Thus, the PPC decay is limited by the diffusion of bipolarons toward the surface. Because the decay is not an exponential function with a single lifetime, the diffusion must be restricted in some way. From Fig. 7(a), we demonstrate that the instantaneous lifetime in sublinear, indicative of the dispersive diffusion, not hydrodynamic diffusion described by the diffusion equation.

According to our model, the rate constant $k(t)$ will be proportional to the bipolaron hopping rate D/a^2 , where a is a characteristic hopping distance that the bipolaron moves in a single diffusion step, and D is the diffusion coefficient which contains the time dependence. Shlesinger and Montroll⁴⁵ found that if the diffusion of defects is executed as a CTRW composed of alternating steps and pauses, and if the pausing-time distribution has a power-law time dependence, then the relaxation function has the stretched-exponential form. Figure 7(a) indicates that the rate constant has the power-law time dependence

$$k(t) \sim t^{-\alpha}. \quad (9)$$

Using Eq. (9), we can integrate Eq. (8) to obtain the stretched-exponential decay law

$$n(t) = n_0 \exp[-(t/\tau)^\beta], \quad 0 < \beta < 1 \quad (10)$$

where $\beta = 1 - \alpha$. Thus, the stretched-exponential decay follows directly from the dispersive diffusion mechanism.

The analogy with dispersive electronic transport suggests that a temperature-dependent β is associated with a distribution of activation energies for recombination. However, we observed no significant temperature dependence in β from 300 down to 160 K. Therefore, the dispersive diffusion of bipolarons most likely occurs via a tunneling mechanism. We also measured the PPC decay over two orders of magnitude change of the light intensity

at room temperature and found that β and τ decrease slightly with increasing light intensity.

Although we have proposed a plausible model for the slow relaxation of the PPC in PPV films which yields the stretched-exponential form (under the assumption of bipolaron diffusion), the experimental data for times greater than about 10 s are also consistent with a logarithmic decay form. Many decades of observational time are required to unambiguously determine the various stages of the decay kinetics. Therefore, a complete understanding of microscopic dynamics of the photoinduced charge carriers will require extensive experimental studies with higher sensitivity. In separate experiments,³⁹ we have measured the transient PC in the subnanosecond time regime with a system resolution of about 50 ps; the time decay of the transient PC can also be fit to a stretched-exponential form. The nature of the transient response might, however, be quite different from that of the long-lived photocurrent. Further experiments in the microsecond and millisecond time regimes are planned to cover the whole range of transport and recombination dynamics from subnanosecond to times in excess of 10^3 s.

V. CONCLUSIONS

Two principal conclusions have been drawn from this experimental study: (i) The photoconductivity data are consistent with a description of the electronic structure of PPV in terms of a semiconductor band model (rather than an exciton model). (ii) The persistent photoconductivity is caused by the slow dispersive diffusion of photogenerated bipolarons to the surface where they dissociate into polarons and where both polaron transport and recombination occur.

The first conclusion follows from the good agreement of spectral response of the photoconductivity with that calculated (using DeVore's theory) from the absorption data with the assumption of rapid recombination at the surface of the film. This detailed comparison of the photoconductivity and photoabsorption data indicates the photogeneration of free charge carriers via an interband transition; we find no evidence of a significant exciton binding energy.

This analysis of the photoconductivity in terms of DeVore's theory indicates rapid surface recombination. This rapid surface recombination provides the basis for a serial relaxation model of the persistent photoconductivity which is conceptually similar to that proposed by Queisser and Theodorou²⁰ to explain the kinetics of persistent photoconductivity near semiconductor interfaces. The stretched-exponential decay of the persistent photoconductivity can be explained by assuming that the photocurrent is carried predominantly by mobile polarons near the surface, but that within the bulk of the film charge is stored as bipolarons. Since recombination is inhibited in the bulk where bipolarons have a lower free energy than polarons, the persistent photoconductivity and the stretched-exponential form of the decay are caused by the slow dispersive diffusion of bipolarons to the surface.

ACKNOWLEDGMENTS

We thank Dr. C. Zhang and Professor F. Wudl for supplying the PPV precursor polymer used for making the PPV films. We thank Dr. T. W. Hagler, H. Pakbaz,

and Dr. D. Braun for allowing us to use their instruments. One of authors (CHL) thanks the Ministry of Education, Republic of Korea for partial financial support (88-B055). This work was supported by the Office of Naval Research through Grant No. N00014-91-J-1235.

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