PHYSICAL REVIEW B VOLUME 57, NUMBER 15 15 APRIL 1998-I

Intrinsic and extrinsic photocarriers in polyparaphenylenevinylene

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(Received 17 March 1997; revised manuscript received 2 September 1997)

We report on photoconductivity in polyparaphenylenevinylene films under continuous wave illumination in the presence of air traces. Near room temperature the photocurrent buildup is extremely slow, steady state not being reached after 1 h illumination. When light is turned off the photocurrent decay kinetics is slower and slower and it takes about 24 h to reach thermal equilibrium. The instantaneous lifetime follows a power-law time dependence $\tau_{\text{inst}}(t)=i_p(t)/|di_p(t)/dt|\propto t^{\alpha}$, $0<\alpha<1$ and the decay kinetics can be accurately fitted to a stretched exponential relaxation law $i_p(t)=i_p(0)\exp-(t/\tau)^{\beta}$ where $\beta=1-\alpha$. When temperature is decreased down to ≈ 255 K the exponent β and the relaxation time τ are found to be temperature dependent, β being linearly dependent upon T: $\beta=T/T_0$ with $T_0=1175$ K. The nonlinear decrease of β between 255 and 190 K is interpreted as a transport mode transition at $T_t\approx 225$ K. When temperature is further decreased in the range 160–77 K the slow component is frozen and leaves room to a fast signal that rapidly reaches steady state and is slightly dependent upon temperature. The magnitude of the slow photocurrent is proportional to the square root of the light intensity whereas that of the fast one is proportional to the light intensity. Modulated photocurrent studies allowed us to show that the fast signal exists in the whole temperature range. Examination of the temperature dependence of the fast photocurrent at low temperature led us to interpret the fast signal as being an intrinsic photocurrent due exciton dissociation. Such an interpretation rests on the recent work of Albrecht and Bässler on the yield of geminate pair dissociation in an energetically random hopping system with built-in energetic disorder. The slow component is interpreted as being extrinsic due to dissociation of polaron pairs through interaction with oxygenated defects to create positive polarons. Recombination and the functional form of the extrinsic component decay is attributed to the dispersive diffusion of the positive polarons in a random distribution of negatively charged defects. [S0163-1829(98)04411-7]

I. INTRODUCTION

Interest in polyparaphenylenevinylene (PPV) and its derivatives stems from the recent development of soluble precursors allowing easy processing of PPV-based light emitting devices.[1,2] Although many studies have been devoted to these nondegenerate ground state conjugated polymers[3,4] some of their photophysical properties are still debated, in particular the early phenomena leading to charge carriers generation. Coincidence of the optical absorption edge and the onset of photoconductivity (PC) was interpreted as being proof of free carriers generation via interband transition.[5,6] In contrast it was suggested that photon absorption produces strongly correlated electron-hole pairs[7–14] that either dissociate[7,8] or form bound polaron pairs.[10,11,14] As far as recombination of carriers is concerned it has been suggested that the long tail observed in picosecond transient PC is due to the slow motion of bipolarons in the bulk.[6] Along the same lines the long term relaxation of carriers following continuous wave (cw) illumination has been interpreted as being due to the slow dispersive diffusion of bipolarons to the surface and dissociation into polarons.[5] In contrast slow recombination was tentatively attributed to the effect of traps, including carbonyl groups either thermally or photochemically created.[10,11]

This paper deals with PC in PPV films in the presence of air traces. Oxygen generates surface and bulk defects that induce large changes in the PC buildup and decay kinetics as compared to what is observed under vacuum. Under illumination the photocurrent buildup is extremely slow and steady state is not reached after many hours. After termination of illumination PC exhibits a slower and slower nonexponential decay kinetics lasting for hours. Nonexponential relaxation of photocreated carriers has been reported earlier in PPV,[5] in poly(2,5-diheptyloxy-*p*-phenylenevinylene),[10b] and in a variety of materials like CdS:Ag:Cl,[15] in the interface of $Al_xGa_{1-x}As$-GaAs,[16] in the layered perovskite $Nd_2Ti_3O_9$.[17] This nonequilibrium conductance following illumination has been interpreted as being due to a dispersive diffusion mechanism restricting recombination.[5,17] More generally slow relaxation towards equilibrium has been observed in many physical systems like dielectric relaxation in glassy media,[18] strain recovery in polymers,[19] or relaxation in the electronic properties of doped amorphous hydrogenated silicon.[20] In most cases, nonexponential relaxation was described in terms of the stretched exponential relaxation law (Kohlrausch's law[21])

$$\Phi(t)=\Phi(0)\exp-\left(\frac{t}{\tau}\right)^{\beta}, \tag{1.1}$$

where $0<\beta<1$.

In the PPV films under study the time dependence of photocurrent decay can be accurately fitted to Eq. (1.1) for long time periods in a wide temperature range, the exponent β and the relaxation time τ being temperature dependent. When temperature is decreased the relaxation rate slows down and, at a sufficiently low temperature, gets frozen leaving room to a photocurrent having quite fast buildup and decay kinetics.

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Modulated photocurrent studies allowed us to show that the fast component exists in the whole temperature range. The low-temperature data of the fast photocurrent exhibits a sub-Arrhenius-type dependence, the interpretation of which allowed us to suggest a model of creation and recombination of intrinsic and extrinsic photocarriers.

After describing experimental details in Sec. II, we present in Sec. III A the main characteristics of PC in freshly converted films, kept under vacuum. In Sec. III B are reported the photocurrent buildup and decay in the presence of surface and bulk defects due to the presence of air traces, and in Sec. III C is reported temperature and light power dependence of PC in the presence of air traces. In Sec. III D modulated photocurrent studies as a function of temperature and light power are reported. The results are discussed and interpreted in Sec. IV.

II. EXPERIMENT

The sulfonium polyelectrolyte precursor is prepared by a standard procedure using tetrahydrothiophene.[22,23] The precursor monomer is synthesized by reacting paradichloroxylene with tetrahydrothiophene and polymerized by reacting the monomer with NaOH and purified by dialysis against water.

Films of the precursor are cast from a methanolic solution onto suprasil substrates and thermally converted by heating at 300 °C under vacuum (2×10^{-6} mbar). Typically, the films thickness is of the order of 1 μm. Surface gold strips with a 1 mm interelectrode spacing are evaporated and contacted to the external circuit with an Ag-loaded epoxy resin and films are attached to the cold finger of an Oxford cryostat.

Photocurrent measurements are made under cw conditions using the 457.9 nm line of a Spectra-Physics argon laser. The light power falling onto the interelectrode spacing (1×8 mm) was typically 6 μW cm^{-2}. Ohmicity was checked up to 3×10^3 V cm^{-1}, measurements being made under an electric field of 2×10^3 V cm^{-1}.

We noticed that, when filling the sample chamber with helium gas, small amounts of air were introduced and drastically changed the photocurrent buildup and decay kinetics. As shown below under these conditions the photocurrent keeps increasing under illumination for many hours without reaching steady state [Fig. 1(b)]. Therefore films were irradiated for a standard time length of 1 h at the end of which, at 300 K, the photocurrent to dark ratio is about 1.5×10^3 and the buildup rate is about 4×10^{-11} A min^{-1}. Under these conditions the decay kinetics is reproducible from one run to the next. In what follows the term ''pseudo-steady state'' is used to characterize the photocurrent value measured at the end of this illumination period. Standard electrometer, light chopper, lock-in amplifier, and computer equipment are used for dc and modulation experiments.

III. RESULTS

A. PC of PPV films under vacuum

In freshly converted films sheltered from light, the dark conductivity measured under vacuum is about 5×10^{-14} Ω^{-1} cm^{-1} at room temperature. Intrinsic dark conductivity was reported to be $<10^{-15}$ Ω^{-1} cm^{-1} and to increase in the presence of oxygen[24] so that the nonilluminated films under study may be considered as being relatively free of oxygenated impurities. We found that the dark current is thermally activated with an activation energy $E_{\text{dark}}=0.80-0.85$ eV. As seen in Fig. 1(a) under illumination with the 457.9 nm line of an argon laser a photocurrent reaching steady state in a few seconds is observed, in agreement with previous reports.[24–27] After termination of illumination the photocurrent rapidly decays to thermal equilibrium. Measurements on several films showed that the photocurrent is thermally activated with an activation energy $0.21<E_p<0.28$ eV. These values were repeatedly found in films originating from the same batch. It should be noted that the activation energies of the dark conductivity and of the photocurrent found in this work are larger than those previously reported: $E_{\text{dark}}=0.21$ eV (Ref. 5) and $E_p=0.14$ eV.[5,10]

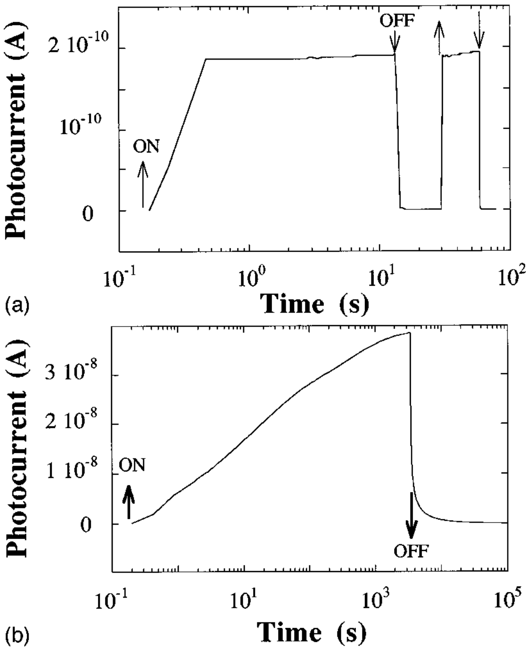

FIG. 1. Photocurrent buildup ($\lambda_{\text{exc}}=457.9$ nm) and decay observed in a PPV film (a) in a freshly converted film kept under vacuum. Steady state and return to equilibrium in the dark are rapidly reached. (b) The same film in the presence of air traces; steady state is not reached after 1 h illumination and when light is turned off thermal equilibrium is reached about 24 h later.

The light power dependence of the photocurrent was studied at room temperature by varying the light intensity with neutral density filters. A power-law dependence

$$i_p \propto P^{\gamma} \tag{3.1}$$

was observed with an exponent $\gamma=0.84-0.86$. This value is indicative only because as shown below γ may vary from 0.5 to 1 depending upon the defect density and temperature. A value close to one means that the film is relatively free of oxygenated defects.

B. PC buildup and decay kinetics in the presence of air traces

As seen in Fig. 1(b), in the presence of air traces, illumination at 300 K with the 457.9 nm laser line results in a completely different signal as compared to the signal observed under vacuum [Fig. 1(a)]. The photocurrent is characterized by a very slow buildup and nonexponential decay kinetics. Starting from a dark current at 300 K $i_{\mathrm{dark}} = 2\times 10^{-11}$ Å a sluggish photocurrent buildup is recorded, steady state being not yet reached after an illumination period of 1 h. When light is turned off a nonexponential increasingly slower decay is observed, return to thermal equilibrium being apparently completed about 24 h later. Reproducible decays were obtained but we observed that the current measured when decay is apparently over often differs by 2–3% from the dark current measured before illumination. Degassing to a pressure $\approx 2\times 10^{-6}$ mbar allowed us to reobtain the fast signal observed on fresh films [Fig. 1(a)].

The occurrence of excess nonequilibrium conductance was reported in poly (2,5-diheptyloxy-*p*-phenylenevinylene) by Frankevich *et al.*[10(b)] and in PPV by Lee and co-workers[5] but in the latter case nonexponential decay was observed on a much shorter time scale, return to thermal equilibrium being obtained within about 2000 s.

The nonexponential character of the photocurrent decay in Fig. 1(b) is evidenced when considering the time dependence of the instantaneous lifetime defined as

$$\tau_{\mathrm{inst}}(t) = \frac{i_p(t)}{\left|\dfrac{di_p(t)}{dt}\right|}, \tag{3.2}$$

where $i_p(t)$ is the photocurrent. In the case of an exponential decay $\tau_{\mathrm{inst}}(t)$ is a constant. In Fig. 2(a) is shown a log-log plot of $\tau_{\mathrm{inst}}(t)$ at 300 K as a function of the time elapsed from termination of illumination. The instantaneous lifetime follows a time-dependent power law

$$\tau_{\mathrm{inst}}(t) \propto t^{\alpha}, \tag{3.3}$$

with $\alpha = 0.701$, on a time period of about 5 h. At longer times the decay kinetics is much too slow to yield accurate derivation. As discussed in Sec. IV, Eq. (3.2) may be accounted for by considering that charge carriers recombination is restricted by a dispersive diffusion mechanism.

Integration of Eq. (3.2) with $\tau_{\mathrm{inst}}(t) \propto t^{\alpha}$ yields the stretched exponential relaxation law [Eq. (1.1)] that applied to the photocurrent reads

$$i_p(t) = i_p(0)\exp - \left(\frac{t}{\tau}\right)^{\beta}, \tag{3.4}$$

with $\beta = 1-\alpha$. As shown in Fig. 2(b) the photocurrent decay at room temperature can accurately be fitted to Eq. (3.4) for about 24 h. A slight deviation is observed at long times that is mainly due to a poor knowledge of the residual conductance to be deduced from the total current. The fitting procedure yields $\beta = 0.31$ and $\tau = 80$ s. The value of the exponent β is in fair agreement with the value $(1-\alpha)$ obtained from the time dependence of the instantaneous lifetime.

C. Temperature and light power dependence of PC in the presence of air

When temperature is decreased a complex behavior is observed allowing to distinguish three temperature ranges.

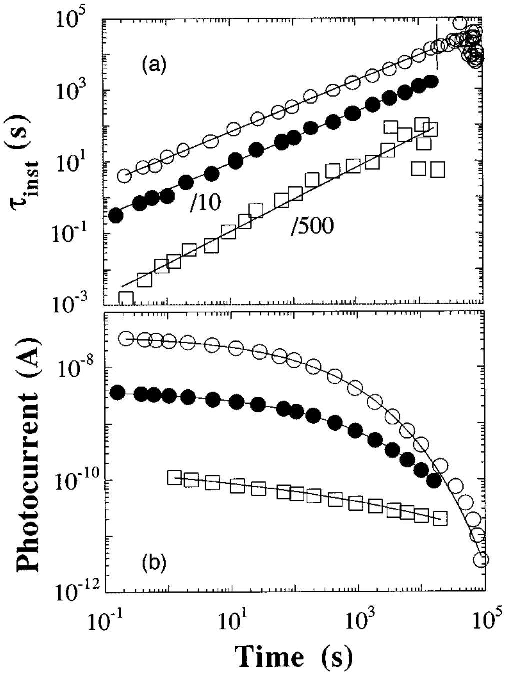

FIG. 2. (a) Time dependence of the instantaneous lifetime [Eq. (3.2)]. The solid lines are the fits to the power law: $\tau_{\mathrm{inst}}(t) \propto t^{\alpha}$ with $\alpha = 0.701$ at 300 K (open circles). Beyond about 16 500 s the photocurrent decay is too slow to yield accurate derivation, therefore data beyond this time (indicated by a vertical line) were not taken into account. At 265 K (closed circles), $\alpha = 0.722$. At 210 K (open squares), $\alpha = 0.887$. (b) photocurrent decays; the solid lines are the fits to the stretched exponential relaxation law [Eq. (3.4)]. At 300 K (open circles), $\beta = 0.31$ and $\tau = 80$ s. At 265 K (closed circles), $\beta = 0.27$ and $\tau = 143$ s. At 210 K (open squares), $\beta = 0.11$ and $\tau = 1.5$ s. As seen $\alpha + \beta \approx 1$.

Between 325 K and about 190 K both the instantaneous lifetime and the photocurrent decay kinetics are fairly fitted to Eqs. (3.3) and (3.4), respectively, (Fig. 2). At each temperature $(\alpha+\beta)$ is found to be close to one but, in contrast with Lee's results[5] both the exponent β and the relaxation time τ are found to be temperature dependent. This is shown in Fig. 3. β linearly decreases from 0.32 at $T = 325$ K to 0.27 at 255 K and extrapolates close to zero at zero K: $\beta(T) = T/T_0$ with $T_0 = 1175$ K [Fig. 3(a)]. In the same temperature range the relaxation time increases from 22 s at 325 K up to 220 s at 255 K [Fig. 3(b)].

At lower temperature, between about 255 and 190 K, both the instantaneous lifetime and the decay kinetics can still be fitted to Eqs. (3.3) and (3.4), respectively. β rapidly decreases from 0.27 at 255 K down to 0.14 at 255 K where it reaches a plateau at an average value ~ 0.12, while τ goes through a maximum around 250 K, $\tau_{\max} = 200$ s, and decreases down to about 0.5 s at 190 K. At 170 K the decay cannot be fitted to Eq. (3.4); the photocurrent at this temperature is a mixture of the slow component with the fast one described below (Fig. 4).

A further decrease in temperature leads to quite different signals: at $T \leqslant 160$ K the buildup and decay are unexpectedly much faster. Inset in Fig. 4 shows for example the signal recorded at 89.5 K: the photocurrent, which is 4 to 5 orders of magnitude smaller than at 300 K, reaches steady

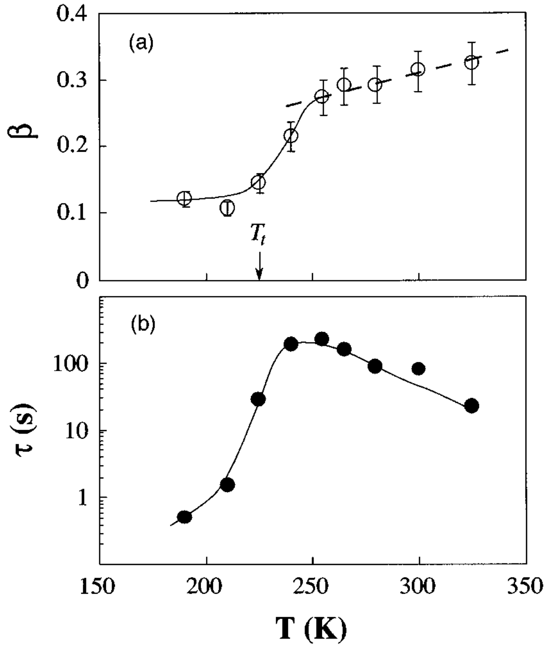

FIG. 3. (a) Temperature dependence of the exponent β in Eq. (3.4). β is measured with an estimated error of 10%. The broken line is the linear fit between 325 and 255 K: $\beta = T/T_0$, which extrapolates to 0.054 at 0 K. The slope yields $T_0 = 1175$ K. Below 255 K, β reaches rapidly a plateau (see the solid line). The arrow indicates the transition temperature T_t. (b) Temperature dependence of the relaxation time τ in Eq. (3.4). The solid line is a guide for the eyes.

state in a few seconds and after termination of illumination decays rapidly to the dark current value.

These findings suggest the existence of two components, different in nature, contributing to photoconductivity: a slow component dominating PC in the high-temperature range that is gradually frozen when T is decreased, leaving room to a much faster one at $T \leqslant 160$ K. Strong support to this assumption comes from the variations with temperature of the exponent γ characterizing the photocurrent light power dependence [Eq. (3.1)]. Typical log-log plots of i_p as a function of the relative light power are shown in Fig. 5. Near 300 K, $\gamma = 0.5$ is measured in agreement with previous works[5,24,25] but when temperature is decreased the exponent steadily increases reaching $\gamma = 1$ at $T \leqslant 130$ K and keeps this value down to 77 K, i.e., in the temperature range where fast photocurrent buildup and decay kinetics are seen.

Evidence for the existence of two components also comes from the variations of the photocurrent with temperature. Figure 6 shows that at high temperature, between 325 and ≈ 160 K, the pseudo-steady-state data, measured after a standard illumination period of 1 h, are thermally activated with an energy $E_{HT} \approx 0.25$ eV. But below 160 K the photocurrent becomes less and less sensitive to temperature changes. Inset in Fig. 6 shows that the photocurrent suffers, between 130 and 77 K, very small changes with temperature, decreasing by a factor of 2.5 only.

From the above results, the existence at low temperature of a fast component the magnitude of which is proportional to light power seems well established. The question arises to know whether or not this component exists in the whole

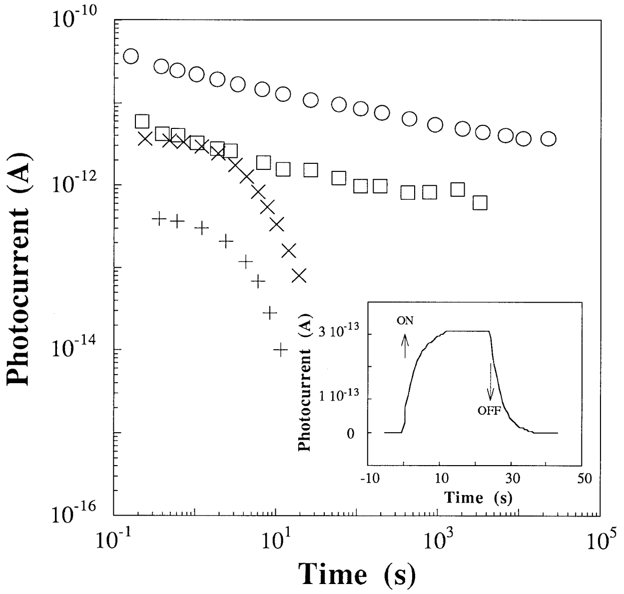

FIG. 4. Variations of the photocurrent decay kinetics below 190 K. (open circles): 190 K; (open squares): 170 K; (crosses): 158 K; (plus): 101 K. Below about 190 down to about 170 K the decay is slower and slower and cannot be fitted to a stretched exponential relaxation law. At about 160 K down to 77 K a new and fast photocurrent is recorded. Inset shows the photocurrent buildup and decay kinetics at 89.5 K; the photocurrent follows the response time of the electrometer, reaches steady state in a few seconds and when light is turned off rapidly decays to the dark value.

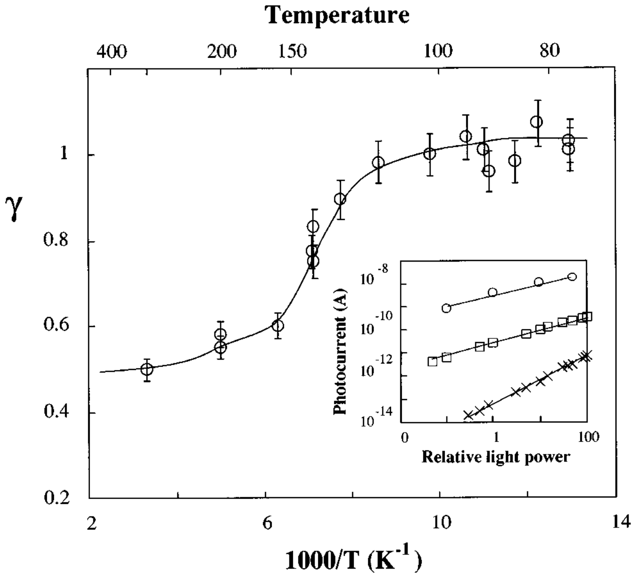

FIG. 5. Temperature dependence of the exponent γ characterizing the light power dependence of the photocurrent: $i_p \propto P^{\gamma}$. When temperature is decreased γ steadily increases from 0.5 at 300 K up to 1 at 130 K down to 77 K. Estimated error 5%. Inset shows some typical curves i_p vs P, where the solid lines are the fits to a power law. (open circles): $T = 300$ K, $\gamma = 0.498$; (open squares): $T = 200$ K, $\gamma = 0.577$; (crosses): $T = 77$ K, $\gamma = 1.01$.

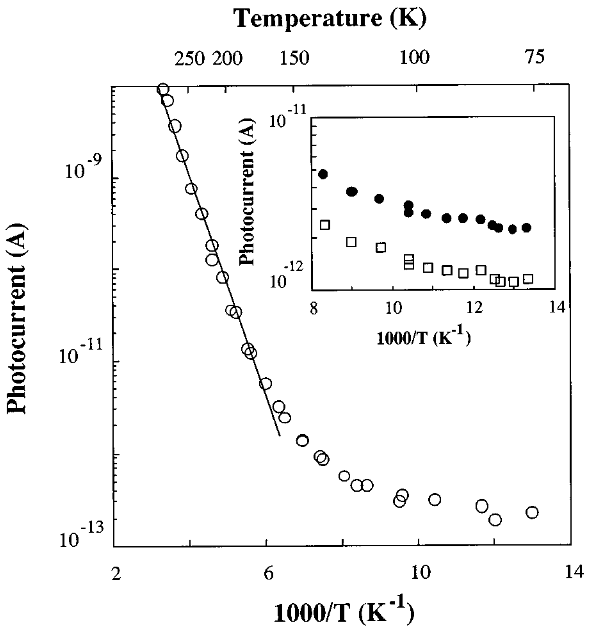

FIG. 6. Temperature dependence of the photocurrent in a PPV film in the presence of air traces. (open circles): pseudo-steady-state data (i.e., measured after an illumination period of 1 h) at high temperature ($160 \leqslant T \leqslant 325$ K). The photocurrent is thermally activated with an activation energy $E_{HT} \approx 0.25$ eV. Inset shows low temperature data ($77 < T < 160$ K) measured with a light intensity about ten times larger. (closed circles): dc measurements; (open squares): electrometer response when light is modulated at any frequency between 5 and 2800 Hz. Between 130 and 77 K the photocurrent is slightly dependent upon temperature, it decreases by a factor 2.5. Comparison of dc and modulated data shows that the chopped signal is just one half of the dc signal, excluding a bolometric effect at low temperature.

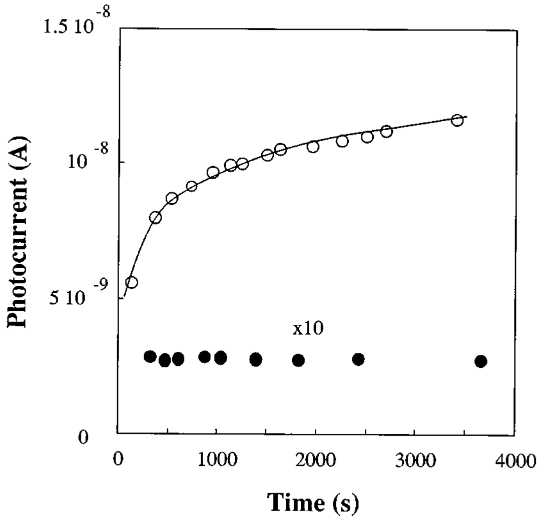

FIG. 7. Buildup of the dc photocurrent and of the modulated photocurrent at 300 K. Illumination starts at $t=0$. (open circles): dc photocurrent. The solid line is a guide for the eyes. (closed circles): lock-in response at $f=15$ Hz, data are multiplied by 10.

temperature range. In order to obtain more informations we carried out modulation experiments to separate the fast signal from the overwhelming slow one.

D. Modulated photoconductivity

In a first experiment, starting from the equilibrium conductance the film was illuminated with the 457.9 nm line of an argon laser. We successively recorded the dc photocurrent, measured by means of an electrometer, and the amplitude of the modulated photocurrent, at a frequency $f = 15$ Hz, by means of a lock-in amplifier. The results at 300 K are shown in Fig. 7. Whereas the dc photocurrent slowly grows in time without reaching steady state, the lock-in response rapidly reaches steady state. At the end of an illumination period of 3500 s the amplitude of the modulated photoconductivity is about 40 times smaller than the dc response. This result suggests the existence at room temperature of a fast photocurrent the generating process of which is different from that of the slow component.

In order to learn whether or not the modulated signal at high temperature has the same origin as the low-temperature steady state photocurrent we studied the light power dependence at 300 K of the lock-in response at various frequencies. Figure 8 shows that when the chopping frequency f is increased the exponent γ increases from 0.66 at 5 Hz up to 1 at $\approx 1600-2000$ Hz. As seen when f is increased from 5 to 15 Hz the amplitude of the modulated signal is decreased by about three orders of magnitude, increasing the modulation frequency up to 2100 Hz results in a decrease by one order of magnitude only. The linear power dependence of the lock-in response at high frequencies suggests monomolecular recombination kinetics. As noted earlier,[5,28] if so, the photocurrent frequency dependence is given by

$$i_p(f) = \frac{i_p(f=0)}{[1+(2\pi f \tau_1)^2]^{0.5}}. \tag{3.5}$$

Following Eq. (3.5) the modulated signal is independent of frequency at low frequency ($2\pi f \tau_1 \leqslant 1$) and decreases as f^{-1} at high frequency ($2\pi f \tau_1 \gg 1$). In Fig. 9 is shown a

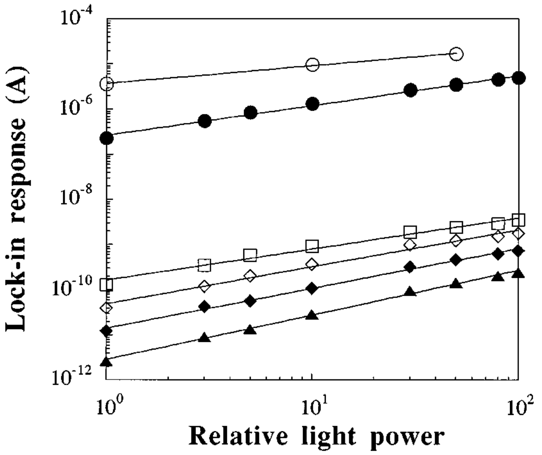

FIG. 8. Light power dependence of the lock-in response at 300 K at various frequencies. (open circles): 0 Hz, $\gamma=0.5$; (closed circles): 5 Hz, $\gamma=0.66$; (open squares): 15 Hz, $\gamma=0.69$; (open lozenges): 200 Hz, $\gamma=0.82$; (closed lozenges): 800 Hz, $\gamma=0.88$; (closed triangles): 2100 Hz, $\gamma=0.99$.

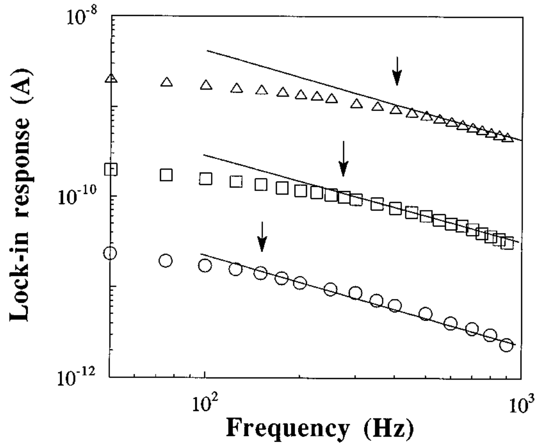

FIG. 9. Frequency dependence of the lock-in response at different temperatures. (open triangles): 302 K; (open squares): 245 K; (open circles): 200 K. The drawn lines have f^{-1} slope. Arrows indicate the frequency f_1 at which the lock-in response is linearly dependent upon frequency [Eq. (3.5)].

log-log plot of the lock-in response as a function of frequency at various temperatures. At 300 K the lock-in response starts decaying as f^{-1} beyond a characteristic frequency $f_1 \approx 480$ Hz. When T is decreased f_1 decreases and is of the order of 140 Hz at 200 K. Thus when T is decreased the contribution of the component proportional to $P^{0.5}$ decreases so that the magnitude of the component proportional to P is larger at lower frequencies.

Finally, we used PC modulated experiments to check that the low-temperature signal is a genuine photocurrent and is not due to a bolometric effect. In Fig. 6 (inset) is shown the effect of light chopping at 175 Hz; the modulated signal is just one half of the value of the dc current. This is true whatever the chopping frequency in the range 5–2800 Hz.

IV. DISCUSSION

Analysis of PC in PPV in the presence of air traces may be summarized as follows: (i) near room temperature under cw illumination PC is dominated by a slowly growing photocurrent the magnitude of which is proportional to the square root of the light intensity, (ii) after termination of illumination the instantaneous lifetime follows a power-law time dependence: $\tau_{\mathrm{inst}}(t) \propto t^{\alpha}$ and the photocurrent decay kinetics is accurately described by a stretched exponential functional form where the exponent $\beta = 1 - \alpha$, (iii) β is linearly dependent upon temperature down to 255 K where it abruptly decreases and reaches a plateau at 255 K; in the same temperature range τ first decreases and goes through a maximum at ≈ 250 K, (iv) in the temperature range $\approx 130-77$ K, the photoresponse is only due to a fast photocurrent the magnitude of which is proportional to the light intensity, (v) photocurrent modulation studies show that a fast photocurrent proportional to the light intensity exists in the whole temperature range; at high temperature it is much smaller than the slow one.

In what follows we recall, in Sec. IV A, the various interpretations given in the literature concerning charge carriers creation and recombination in PPV. In Sec. IV B 1 we identify the fast component on the basis of its low temperature dependence. In Sec. IV B 2 we discuss the nature of the slow component, the functional form of its decay and suggest a tentative model of positive polaron diffusion to negatively charged defects. Finally, in Sec. IV B 3, we interpret the changes of β and τ when temperature is decreased as being due to the approach of a transport transition temperature and discuss the associated change in the transport process.

A. Current views on charge carriers creation and recombination in PPV

Mainly on the basis of the similarity between the photoexcitation spectrum and the optical absorption spectrum it was assumed by Lee and co-workers[5,6] that initial excitation results in the creation of free charge carriers via interband transition. In contrast Frankevich *et al.*[10] and Hsu *et al.*[14] suggested the primary act is the formation of intrachain singlet excitons and bound polaron pairs (P^+, P^-) the branching ratio depending upon excitation energy. A bound polaron pair consists of a positive polaron and a negative polaron residing on adjacent chains, close enough to interact with each other.[10,13(b)] Picosecond photoinduced absorption studies were interpreted as showing that 80 to 90% of the excitations are polaron pairs and about 10% excitons[13(a)] and it was shown that in poly(2-methoxy-1,4-phenylene vinylene) after an initial rapid decay in the picosecond time frame about 40% of the pairs slowly decay and persist for nanoseconds.[14] Therefore due to their relatively long lifetime and high production rate polaron pairs are believed to play an important role in steady-state PC. Study of the magnetic field effect on steady-state PC brings support to this assumption.[10] Various mechanisms may account for the decay of polaron pairs as suggested by Mizes and Conwell[11] and Garstein:[29] (i) jump of one charge on the adjacent chain followed by formation of an on-chain polaron pair or of an exciton which subsequently decay; (ii) the positive and negative polarons move randomly on their own chains and separate thermally or in the presence of an electric field giving birth to free polarons contributing to PC; (iii) interaction with defects, generating free positive polarons that conduct. Another possible source of photocarriers is the dissociation of hot intrachain excitons either thermally or by defects. In the latter case a defect traps the electron leaving the hole free to become a positive polaron.

As far as charge carriers recombination is concerned, Lee and co-workers[5] suggested that in steady-state PC bipolarons being more stable in the bulk must suffer dispersive diffusion to the surface to yield polarons which subsequently recombine. In picosecond PC studies it was suggested that the initial fast transient component, the magnitude of which is proportional to the light intensity and is very slightly temperature dependent, is due to a pretrapping mechanism while the slower component, which is proportional to the square root of the light intensity, was attributed to a trap-controlled transport.[6] Alternatively it was speculated that recombination of positive polarons with carbonyl traps is a slow process giving rise to the long tail observed in steady-state photoconductivity.[10(b),11]

B. Interpretation of results

1. Nature of the fast monomolecular component

In order to identify the fast component we start by discussing the complex photocurrent temperature dependence reported in Fig. 6. Two ranges are to be distinguished. At high temperature, between 325 and about 160 K, where the slow component dominates PC, an activation energy $E_{HT} \approx 0.25$ eV may be measured. More significant are the quite small photocurrent variations observed at low temperature, below 130 K, where monomolecular recombination prevails. In order to interpret the observed sub-Arrhenius-type temperature dependence we refer to the recent work of Albrecht and Bässler[30] on the yield of geminate pair dissociation in a random hopping system with built-in energetic disorder. This work is relevant to the present discussion because very likely energetic disorder is introduced in PPV by variations in the conjugation lengths.[11(e)] Using Monte Carlo simulation techniques, Albrecht and Bässler modeled the distribution of site energies by a Gaussian function of variance σ. They studied the dependence of the dissociation yield of geminate electron-hole pairs as a function of temperature, for different values of σ and of the initial pair distance r_0 (thermalization distance), dissociation being aided by an external electric field. Their results show that disorder enhances dissociation of the pairs, giving rise to significant deviations from the expected temperature dependence of the dissociation yield in a Coulombic system. The effect is more pronounced at low temperature giving rise to a sub-Arrhenius-type temperature dependence (see their Fig. 1) quite similar to the low-temperature data reported in Fig. 6. The yield at a given temperature is found to increase exponentially with the disorder potential σ, and to decrease exponentially when r_0 increases. As started by Albrecht and Bässler the activation energy that may be eventually measured by a conventional analysis is not the binding energy of the precursor electron-hole pair, but is much smaller than the binding energy of excitons.

On this basis we identify the fast component as an intrinsic photocurrent resulting from thermal dissociation of excitons and subsequent creation of conducting positive polarons and immobile negative polarons.[26] Decay of polaron pairs might be at the origin of such excitons, one charge jumping on the adjacent chain to create an on-chain exciton.[11] As exciton dissociation competes with geminate recombination this photocurrent rapidly reaches steady state and linearly depends upon light power. Such a mechanism has been suggested to give account of the linear intensity dependence of picosecond photoinduced absorption in poly(2-methoxy-1,4-phenylenevinylene).[14] As noted by Albrecht and Bässler, the concept of increased geminate pair dissociation in disordered media also provides a clear explanation of the quasitemperature independence of the fast component, the magnitude of which is proportional to light intensity, which is measured in picosecond PC transient experiment by Lee and co-workers.[6]

A test of the above interpretation would consist in comparing the photocurrent temperature dependences in PPV specimens having different built-in disorder potentials, a far from obvious issue. It turns out that photochemically converted PPV (Ref. 23) was recently shown to be more disordered than the standard PPV converted by thermolysis at 300 °C under vacuum.[31] Photochemical conversion of the PPV precursor is carried out at 120 °C, under vacuum, by illuminating with the filtered UV-visible light spectrum emerging from a xenon lamp.[23] Optimized photoconverted PPV was shown to have an absorption edge very close to that of thermoconverted PPV and a quasisimilar fluorescence spectrum. The slight observed differences are due, as revealed by Raman spectroscopy, to a broader distribution of the conjugation segments and to the presence of a larger amount of short conjugation segments.[31(a)] The photocurrent temperature dependence in experimental conditions as those used for standard PPV films.[31(b)] In Fig. 10 the normalized data for both thermoconverted and photoconverted samples are compared; it is seen that these films have different temperature dependences. From about 125 down to 77 K the photocurrent in the thermoconverted sample is almost constant in contrast with the thermoconverted film which slightly decays. This is in qualitative agreement with the Monte Carlo simulation studies of Albrecht and Bässler: in photoconverted films the dissociation yield of geminate pairs is larger because the disorder potential σ is larger.

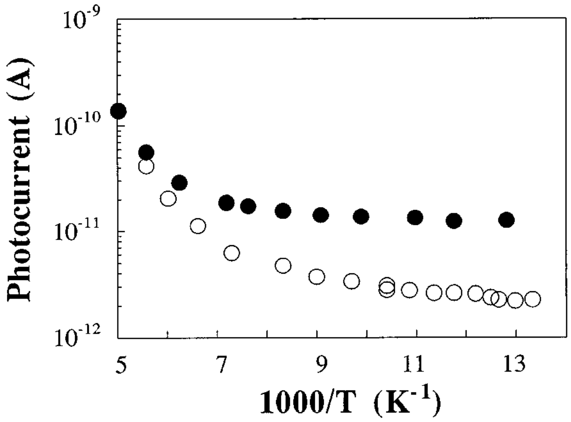

FIG. 10. Temperature dependences of a standard PPV sample (open circles) and of a photochemically converted sample (closed circles). The curves are normalized at 200 K.

2. Nature of the slow bimolecular component

As shown above, at high temperature, the PC signal is overwhelmingly dominated by a slow component that is to be identified. For environmental reasons most of the photogenerated polaron pairs can neither rapidly dissociate nor recombine, because polarons in the pairs are separated by barriers, the Coulomb binding energy confining each of the polarons in the pair being about 0.35 eV.[11] Therefore we suggest that most of the surviving pairs are dissociated through interaction with defects, following

$$(P^+,P^-)+D \rightarrow P^+ + D^-, \tag{4.1}$$

where D is an oxygen molecule adsorbed on the film surface or an oxygenated defect in the bulk, for example a carbonyl group. Due to the high production rate of polaron pairs a large density of conducting positive polarons is thus generated under illumination giving rise to the extrinsic part of PC that we identify with the slow component. If the recombinations $P^{+}+O_2^{-}$ and/or $P^{+}+D^{-}$ are restricted, steady state cannot be reached in a sizeable time, the density of P^{+} increases with time giving rise to slow buildup under illumination. So the ratio of the intrinsic component to the extrinsic one in PC depends upon the density of defects. If it is small the fast intrinsic photocurrent dominates PC and rapidly reaches steady state. This is the case under vacuum. If, on the contrary, this density is large, as in the presence of air, extrinsic PC dominates at high temperature. When temperature is decreased both photogeneration and recombination of positive polarons are restricted so that at low temperature only the intrinsic photocurrent is observed. The feature will be thereafter shown to be correlated with the temperature dependence of the exponent β.

An important feature is the functional form [Eq. (3.4)] of the extrinsic photocurrent decay kinetics. When light is turned off a rapid decrease of PC by a few percent is observed that may be attributed to the decay of the intrinsic component. It is followed by the slow nonexponential relaxation which, as reported in Sec. III B, lasts for hours. Under the preceding assumptions, after termination of illumination, a high density of polarons lies in the film and we interpret slow relaxation as resulting from the dispersive diffusion of positive polarons in a random density of negatively charged defects until recombination.

Dispersion and slow relaxation of the carrier density $n(t)$ toward equilibrium in disordered media is often described by the stretched exponential relaxation law. This was accounted for on the basis of the continuous time random-walk (CTRW) model[32–34] that assumes that each carrier undergoes a random walk, composed of alternating steps and pauses, biased in the direction of the applied field with a pausing-time distribution $\Psi(t)\propto t^{-(1+\beta)}$, $0<\beta<1$. In semiconductors dispersion is due to the existence of an exponential energy distribution of states above the valence-band edge or below the conduction-band edge: $\exp(-E/kT_0)$ where the width kT_0 is related to the dispersion parameter $\beta(T)=T/T_0$.[34] Alternatively Palmer *et al.*[35] suggested a serial interpretation where the path to equilibrium involves sequential correlated activation steps leading to a time-dependent relaxation rate $k(t)$ in the rate equation

$$\frac{dn(t)}{dt}=-k(t)n(t). \tag{4.2}$$

In the case at hand, following the CTRW model, the linear dependence of the exponent β, in the temperature range 325–255 K, may be interpreted as indicating the existence of an exponential tail of states above the valence-band edge due of width $kT_0\approx 100$ meV giving rise to dispersion. Environmental differences and variations in the conjugation lengths in the polymer chains might generate such a density of states in the gap. In order to give account of the dispersive diffusion of positive polarons towards defects it may be considered that the rate constants in Eq. (4.2) decreases with time as

$$k(t)\propto t^{-\alpha}, \quad \text{where} \quad 0<\alpha<1. \tag{4.3}$$

Consequently, in agreement with experimental data, the instantaneous lifetime increases with time as $\tau_{\text{inst}}(t)=1/|k(t)|\propto t^{\alpha}$ and the solution of Eq. (4.2) with Eq. (4.3) is the stretched exponential function [Eq. (3.4)], with $\beta=1-\alpha$. Such a time dependence of $k(t)$ may be accounted for if the diffusion coefficient of the positive polarons carries the time dependence

$$D_{\text{pol}}(t)\propto t^{-\alpha}. \tag{4.4}$$

Such a functional form was used by Kakalios and co-workers[20] in the case of the diffusive motion of bonded hydrogen in doped amorphous hydrogenated silicon.

3. Variations of β and τ below 255 K

Examination of Fig. 3(a) shows that the exponent β linearly depends upon temperature from 325 to about 255 K where it rapidly starts decreasing to a plateau at about 225 K. This change occurs in a narrow range, about 25 K. As shown in Fig. 3(b) the relaxation time τ also shows a change around 255 K; τ first increases in the range 325–255 K, goes through a maximum, and decreases abruptly by a factor of about 400 between 255 and 190 K.

In glasses, either molecular or electronic, β is expected to increase up to one at high temperature but is not expected to decrease down to zero when T is decreased. Contraction of the configuration space when T is decreased is reflected by the reduction of β and it is anticipated that near the glass transition temperature T_g either β is stabilized or reaches a plateau. Many examples are found in the literature (see for example the recent review by Phillips[36]). Nevertheless, in PPV, the decrease of β below 255 K should hardly be associated with a glass transition temperature. Therefore we suggest that a change in the charge transport process occurs at a transition temperature $T_t\approx 225$ K.

Quite importantly we observe that, at T_t, β decreases by a factor of about 2 [Fig. 3(a)], a meaningful change that is to be interpreted. First we note that in the frame of the CTRW model a smaller β means a longer pausing time and suggest that the rapid decrease at T_t is correlated with a change in the dimensionality of the transport process. Shlesinger and Montroll,[33] in their model of dielectric relaxation in a frozen medium, e.g., a polymeric material, have explicitly treated the case of defects diffusion in the three-dimensional (3D) and one-dimensional (1D) cases. They reached the conclusion that if diffusion in 3D is characterized by β, in 1D the exponent takes the value $\beta/2$. Thus, in 1D the maximum value of the exponent is 0.5. Therefore we suggest 3D diffusion of positive polarons above T_t and 1D diffusion below T_t. In PPV the 3D-1D transition should be accompanied by a change in the transport process. We suggest that, following Mizes and Conwell proposals,[11] below T_t, the positive and negative polarons stay on their own chains where they move randomly; some steps allow the pair to separate, either thermally or by interaction with a defect residing on the chain. But most steps are inefficient and the most probable event is pair recombination. When temperature is decreased below T_t, as the pausing time increases the recombination rate increases. Consequently, the average relaxation time decreases, as experimentally observed [Fig. 3(b)]. When temperature is sufficiently low, the escape probability is zero and 1D diffusion gets frozen, leaving room to the weak intrinsic photocurrent due to electron-hole pair dissociation.

V. CONCLUSION

Several conclusions are drawn from this experimental study. One is that charge carriers creation and recombination in PPV strongly depend upon the bulk and surface density of defects. It is not entirely new. The crucial role played by defects in PPV PC was demonstrated previously by various works,[10,24] but in addition we have shown that the photocurrent buildup and decay kinetics are dependent upon the presence of defects, either adsorbed oxygen on the surface or carbonyl groups in the bulk. Our main conclusions are consistent with the recent proposals that photon absorption leads to excitons and polaron pairs creation.

In the presence of air traces, i.e., when defects density is large, we demonstrated that PC is due to the superimposition of two photocurrents. One grows and decays slowly and depends upon the square root of the light intensity. We reached the conclusion that it is an extrinsic photocurrent resulting from the interaction of the photogenerated polaron pairs with defects to create positive polarons. The restricted recombination of charge carriers, which is responsible for the slow buildup and decay kinetics, are interpreted as being due to the dispersive diffusion of positive polarons in a random density of negatively charged defects. This conclusion rests on the linear temperature dependence of the exponent β in the range 325–255 K. Following the CTRW model an exponential band tail of width about 100 meV, due to defects, lies above the valence-band edge.

An important conclusion follows from the observation that the linear temperature dependence of β stops at about 255 K. Below this temperature β rapidly decreases and reaches a plateau. We argued that such a variation is due to a transport mode transition at $T_t \approx 225$ K. An important experimental fact is the decrease of β by a factor of about 2 at T_t, interpreted, on the basis of the Shlesinger and Montroll model,[33] as a 3D to 1D transition. This implies, between T_t and the temperature where the extrinsic component gets frozen, a different charge carrier transport mechanism. We made the proposal that on-chain polaron pairs move randomly as suggested earlier;[11] as a consequence the polaron pairs rapidly decay, a conclusion that agrees with the strong decrease of the relaxation time below T_t.

Pseudo-steady-state and modulated PC measurements allowed us to show that in the whole temperature range a fast monomolecular photocurrent coexists with the extrinsic one. At $T < 160$ K, well below T_t, i.e., when the extrinsic component is frozen, only this photocurrent is observed. The salient feature is its quasi-independence upon temperature, which is understood in terms of the enhanced photoionization yield of photogenerated geminate electron-hole pairs. This should be due to built-in energetic disorder in the polymer, a conclusion that lies on the simulation work of Albrecht and Bässler.[30] The temperature dependence of photoconverted PPV, which is more disordered than standard PPV, brings qualitative support to this conclusion. Therefore we are led to conclude that this photocurrent is intrinsic resulting from the dissociation of photogenerated excitons upon photon absorption. Such a dissociation is believed to concern a small proportion of the excitation, most photons leading to polaron pairs generation.

It should be noted that the two photocurrents we separated by varying temperature and light frequency are also observed in time resolved PC.[6] The two components detected in these experiments have the same features as the photocurrents we identified as extrinsic and intrinsic; one is fast, its magnitude is proportional to the light intensity and is almost temperature independent around 80 K, the other is slow, its magnitude is proportional to the square root of the light intensity and disappears below 130 K. Picosecond transient PC studies in the whole temperature range, 300–77 K, might help reach a definite conclusion on the much debated question of the origin of charge carriers in PPV. Other directions for future work concern photochemically converted PPV in which energetic disorder is larger than in standard PPV.

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[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 539 (1990).

[2] D. Braun and A. J. Heeger, Appl. Phys. Lett. **58**, 1982 (1991).

[3] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[4] E. M. Conwell and H. A. Mizes, in *Handbook of Semiconductors*, edited by P. T. Landberg (North-Holland, Amsterdam, 1992), Vol. 1, p. 584.

[5] C. H. Lee, G. Yu, and A. J. Heeger, Phys. Rev. B **47**, 15 543 (1993).

[6] C. H. Lee, G. Yu, D. Moses, and A. J. Heeger, Phys. Rev. B **49**, 2396 (1994).

[7] U. Rauschler, H. Bässler, D. D. C. Bradley, and M. Hennecke, Phys. Rev. B **42**, 9830 (1990).

[8] K. Pichler, D. A. Halliday, D. D. C. Bradley, P. L. Burn, R. H. Friend, and A. B. Holmes, J. Phys.: Condens. Matter **5**, 7155 (1993).

[9] M. Gailberger and H. Bässler, Phys. Rev. B **44**, 8643 (1991).

[10] (a) E. L. Frankevich, A. A. Lymarev, I. Sokolik, F. E. Karasz, S. Blumstengel, R. H. Baughman, and H. H. Hörhold, Phys. Rev. B **46**, 9320 (1992); (b) E. L. Frankevich, A. Zakhidov, K. Yoshino, Y. Maruyama, and K. Yakushi, *ibid.* **53**, 4498 (1996).

[11] (a) H. A. Mizes and E. M. Conwell, Phys. Rev. B **50**, 11 243 (1994); (b) Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A **256**, 519 (1994); (c) Synth. Met. **68**, 145 (1995); (d) E. M. Conwell and H. A. Mizes, Phys. Rev. B **51**, 6953 (1995); (e) Synth. Met. **78**, 201 (1996).

[12] J. M. Leng, S. Jeglinski, X. Wei, R. E. Benner, Z. V. Vardeny, F. Guo, and S. Mazumdar, Phys. Rev. Lett. **72**, 156 (1994).

[13] (a) M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **72**, 1104 (1994); (b) *ibid.* **73**, 744 (1994).

[14] J. W. P. Hsu, M. Yan, T. M. Jedju, L. J. Rothberg, and B. R. Hsieh, Phys. Rev. B **49**, 712 (1994).

[15] M. K. Sheinkman, I. V. Markevich, and V. A. Khvostov, Sov.

Phys. Semicond. **5**, 1654 (1972); M. K. Sheinkman and A. Ya Skik, *ibid.* **10**, 128 (1976).

[16] H. J. Queisser, Phys. Rev. Lett. **54**, 234 (1985).

[17] B. Dulieu, J. Bullot, J. Wéry, M. Richard, and L. Brohan, Phys. Rev. B **53**, 10 641 (1996).

[18] G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[19] D. G. Legraud, W. V. Olszewski, and J. T. Bendler, J. Polym. Sci. Part B: Polym. Phys. **25**, 1149 (1987).

[20] J. Kakalios, R. A. Street, and W. B. Jackson, Phys. Rev. Lett. **59**, 1037 (1987); J. Kakalios, in *Hopping and Related Phenomena*, edited by H. Fritzsche and M. Pollack (World Scientific, Singapore, 1990), p. 441.

[21] R. Kohlrausch, Ann. Phys. (Leipzig) **12**, 393 (1847).

[22] F. E. Karasz, J. D. Capistran, D. R. Gagnon, and R. W. Lenz, Mol. Cryst. Liq. Cryst. **118**, 327 (1985); J. D. Stenger-Smith, R. W. Lenz, and G. Wegner, Polymer **30**, 1048 (1989).

[23] J. Bullot, B. Dulieu, and S. Lefrant, Synth. Met. **61**, 211 (1993).

[24] H. Antoniadis, L. J. Rothberg, F. Papadimitrakopoulos, M. Yan, M. E. Galvin, and M. A. Abkowitz, Phys. Rev. B **50**, 14 911 (1994).

[25] S. Tokito, T. Tsutsui, R. Tanaka, and S. Saito, Jpn. J. Appl. Phys. **25**, L680 (1986).

[26] J. Obrzut, M. J. Obrzut, and F. E. Karasz, Synth. Met. **29**, E103 (1989).

[27] H. Bleier, Y. Q. Shen, D. D. C. Bradley, H. Lindenberger, and S. Roth, Synth. Met. **29**, E73 (1989).

[28] N. F. Colaneri, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. B. Holmes, and C. W. Spangler, Phys. Rev. B **42**, 11 670 (1990).

[29] Yu. N. Garstein, Phys. Lett. A **235**, 389 (1995).

[30] U. Albrecht and H. Bässler, Chem. Phys. Lett. **235**, 389 (1995).

[31] (a) J. Wéry, B. Dulieu, E. Launay, J. Bullot, M. Baïtoul, and J. P. Buisson, Synth. Met. **84**, 277 (1997); (b) J. Wéry, B. Dulieu, F. Ragot, E. Faulques, and J. Bullot (unpublished).

[32] H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).

[33] M. F. Shlesinger and E. W. Montroll, Proc. Natl. Acad. Sci. USA **81**, 1280 (1984).

[34] H. Scher, M. F. Shlesinger, and J. T. Bendler, Phys. Today **44**, 26 (1991).

[35] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).

[36] J. C. Phillips, Rep. Prog. Phys. **59**, 1133 (1996).