Extrinsic and intrinsic dc photoconductivity in a conjugated polymer

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Steady-state photoconduction was studied in typically 100-nm-thick films of a polyphenylenevinylene derivative with ether linkages in the backbone. Samples were prepared in sandwich configuration between indium tin oxide (ITO) and Al electrodes. Forward photocurrents measured upon irradiating through the positively biased ITO electrode decreased by typically three orders of magnitude when a 8–10-nm-thick silicon monoxide (SiO) layer had been deposited on top of the ITO to prevent photoinjection of positive charge carriers. Insertion of a SiO layer can thus be used as a tool to separate extrinsic from intrinsic sources of optical charge-carrier generation. Analysis of the dependences of extrinsic and intrinsic photocurrents on temperature, electric field, and photon energy indicate that they can be described in terms of Onsager's theory of geminate pair dissociation in either one or three dimensions. [S0163-1829(97)02231-5]

I. INTRODUCTION

Photoconductivity has been one of the phenomena supporting the notion that π-conjugated polymers behave like inorganic semiconductors. The pertinent argument has largely been based upon the coincidence of the optical-absorption edge and the threshold energy for optical generation of charge carriers.[1-8] It seems to suggest that photon absorption creates a pair of charge carriers whose mutual Coulombic binding energy is of order kT only.[9] This situation is encountered in inorganic semiconductors as a result of the combined effects of band-type motion of charge carriers with low effective mass and a modestly large dielectric constant ($\geqslant 10$). Neither of these premises is fulfilled in conjugated polymers, however. The dielectric constant is not different from that of typical molecular crystals ($\cong 3.5$), and charge transport occurs via hopping among different segments of the same or adjacent polymer chains on which carriers are localized thus rendering coherence effects unimportant.

To resolve the puzzle one has to rely on early work concerning photoconductivity in molecular crystals.[10] It is well established that, upon exciting a molecular crystal through a semitransparent electrode, the onset of photoconductivity coincides with the absorption edge because excitons diffusing to the interface may find it energetically favorable to dissociate by transferring one of the constituent charges to an acceptor level inside the electrode, e.g., the Fermi level in the case of a metal.[11,12] Its twin inside the crystal can easily escape the attractive image potential and contribute to photoconductivity. Organic molecules with appropriately located molecular orbitals, present either at the interface or in the bulk, may act in a similar way, thus giving rise to sensitized photoconductivity. In fact, it is difficult at times to suppress these extrinsic sources of photoconductivity and determine the action spectrum of intrinsic charge-carrier generation.[13] The latter is blueshifted relative to the absorption spectrum, the energy offset being a crude measure of the energy it costs to dissociate an exciton into a pair of the charge carriers.

There is growing evidence that similar phenomena take place in conjugated polymers. The fact that the quantum efficiency of optical charge-carrier production in π-conjugated polymers of the polyphenylenevinylene (PPV) type is $\ll 1$ and both temperature and field dependent[5] is incompatible with the notion that photon absorption generates a pair of free charge carriers. Otherwise it would also be difficult to understand why inadvertant impurities or deliberately added dopants, like oxidation products with high electron affinity,[7] should be able to increase the photocarrier yield substantially. In that respect C_{60} turned out to be a particularly efficient sensitizer for excited-state dissociation.[14] The observation of an increase of the photocarrier yield in an alkoxy-substituted PPV of about 0.9 eV above the absorption edge[15] has been taken as another indication that the system behaves like a classic molecular solid. Fluorescence quenching in high electric fields provides independent evidence of the exciton binding energy being about 0.4 eV,[16-18] noting, however, that this value differs from the above mentioned energy gap between the claimed intrinsic photoconductivity threshold and the optical $S_1 \leftarrow S_0 0-0$ transition energy.

The aim of the present work is to discriminate between extrinsic and intrinsic contributions to the stationary photoconductivity in a conjugated polymer. The material chosen for this study is poly(oxy-1,4-phenylene-1,2-ethenylene-2,5-dioctyl-oxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene), in the following abbreviated as PPV-ether.[19]
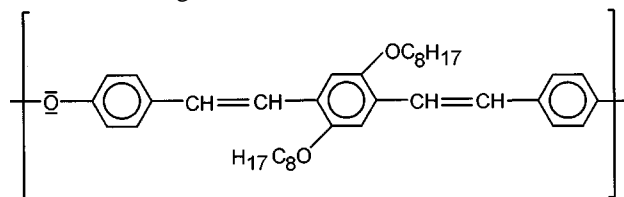
It consists of well-defined distyrylbenzene blocks connected by ether linkages. One of its advantages is that it can be

prepared at a level of purity inaccessible with standard precursor PPV. Due to the partial interruption of π conjugation by the ether linkage, it can be considered as a model compound for a conjugated polymer consisting of structurally well-defined subunits.

II. EXPERIMENT

PPV-ether was synthesized by polycondensation using the HORNER reaction yielding vinylene double bonds in all-trans configuration as evidenced by IR spectroscopy. A photoluminescence yield of 82% in solution testifies on the absence of nonradiative quenching centers, such as oxidation products, in the polymer chain.[19]

By spin coating from chloroform solution clear films of a typical thickness of 100 nm could be deposited on top of indium tin oxide (ITO)-covered glass slides. In order to study the effect of charge carrier injection from ITO a certain section of the contact area was covered by a 8–10-nm-thick evaporated layer of silicon monoxide (SiO, Balzers), known to block photoinjection. Before completing the sandwich structure by evaporating Al top contacts of 0.07 cm^2 the sample was kept in a vacuum chamber at a pressure of $\cong 10^{-6}$ mbar at 295 K for 12 h to remove residual solvents.

Stationary photocurrent measurements were performed in a temperature-controlled cryostat using a calibrated xenon lamp as a light source and employing lock-in techniques for signal detection. All data reported were recorded in a point-wise fashion, and refer to photocurrents established immediately after applying a rectangular light pulse. In case of no SiO layer on top of the ITO, the mode of data recording turned out to be unimportant, since the photocurrent was constant throughout the irradiation period. However, some decay was noted in the presence of SiO, indicating that the latter also has some effect on carrier discharge. In order to minimize space-charge effects, the sample was shorted after each measurement, irradiated with red light for 10 s, and kept in the dark for another 5 min before the next data point was taken immediately after turning on the light.

Dark currents were of order 10^{-10} A/cm^2, typically one order of magnitude lower than the lowest photocurrents considered for data evaluation. The rather low value of the dark current testifies on the purity of the PPV-ether used. It translates into a specific conductivity of 5×10^{-16} (Ω cm)$^{-1}$. Since it is independent of the presence of a SiO layer, whose dark conductivity is $\cong 10^{-13}$ (Ω cm)$^{-1}$, it must either originate from thermally activated dissociation of a small amount of inadvertant dopants or from electron injection from the aluminum electrode. In view of the large energy barrier the latter process appears to be unlikely. Because of the low dark conductivity, one can safely rule out a redistribution of the electric field inside the cell due to charge accumulation near the SiO/PPV-ether interface. Even in the extreme case (i) that the dark current was entirely due to electron transport towards the positively biased ITO/SiO electrode and (ii) that no discharge occurs through the SiO layer, it would have taken about 2000 s to fully charge the SiO capacitor.

III. RESULTS

Figures 1 and 2 show the action spectra of the photocurrents observed with a 95-nm-thick PPV-ether film sand-
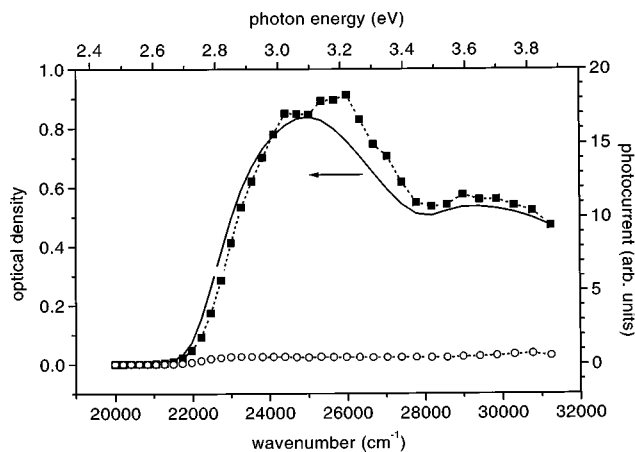

FIG. 1. Absorption (full curve) and photocurrent action spectra of a 95-nm-thick PPV-ether film sandwiched between ITO and Al electrodes. Irradiation was through the ITO. Full squares refer to forward (i.e., ITO positive) open circles to reverse photocurrents. The electric field was 2.1×10^5 V/cm, and the temperature was 298 K. Photocurrents have been corrected for the spectrum of the xenon lamp and the transmittance of ITO. At 25 000 cm^{-1} the photon flux was 1.3×10^{15} photons (cm^2 s)$^{-1}$.

wiched between an Al and an ITO electrode with or without a protective SiO layer upon irradiation through the ITO electrode. It is obvious that (i) the magnitude of the photocurrent is strongly polarity dependent, and (ii) the presence of the SiO layer has a significant influence if ITO is positively biased. The reverse photocurrent j_-, i.e., ITO biased negatively, is unaffected by the SiO layer. At an applied external field of 2.1×10^5 V/cm, the photocurrents measured at the spectral maxima are $j_+=1.4\times10^{-7}$ A and $j_{+,\text{SiO}}=3\times10^{-10}$ A, while $j_-\cong j_{-,\text{SiO}}=2\times10^{-9}$ A. Another noteworthy feature is the different shape of the action spectra of j_+ and $j_{+,\text{SiO}}$. The presence of a SiO layer on the top of the ITO also affects the dependences of the forward photocurrent on electric field as well as on temperature. While $j_{+,\text{SiO}}(E)$ is a steeply rising function of the electric field within the entire field range studied (10^5–10^6 V/cm), $j_+(E)$ rises su-
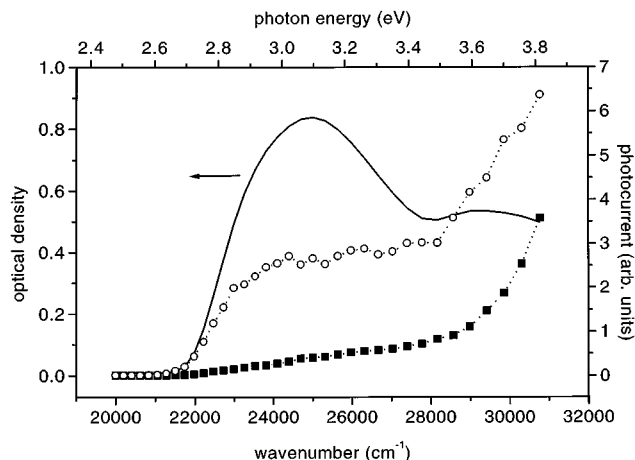

FIG. 2. The same as in Fig. 1, except that the ITO electrode carried a 8–10-nm-thick silicon monoxide (SiO) layer. The scale of the photocurrent is also the same.
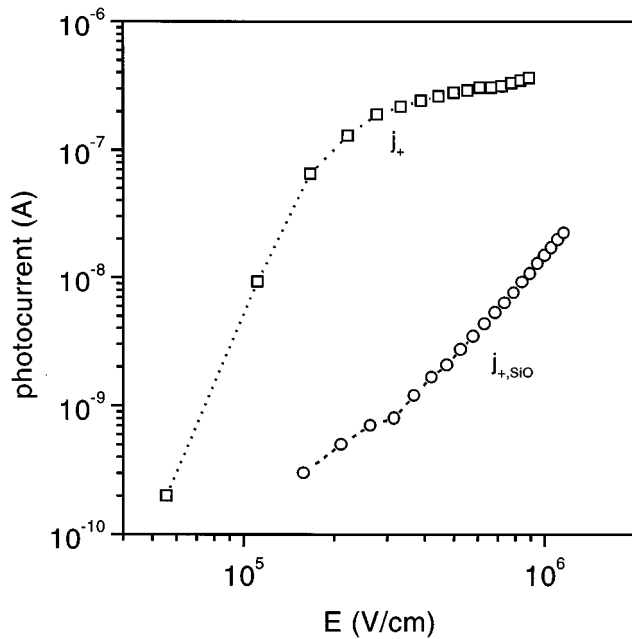
FIG. 3. Dependence of the photocurrent in PPV-ether on an electric field. Squares and circles: Forward photocurrent measured upon irradiating through a neat ITO contact (j_+, $h\nu_{exc} = 25\,320\ cm^{-1}$) and a SiO-covered ITO contact ($j_{+,SiO}$, $h\nu_{exc} = 27\,400\ cm^{-1}$), respectively. The temperature was 298 K.

perlinearly only at low fields and tends to saturate for $E > 10^6$ V/cm (Fig. 3). The temperature dependence of $j_{+,SiO}$ is non-Arrhenius-like (Fig. 4). For $T > 290$ K, Arrhenius behavior with an activation energy of 0.25 ± 0.02 eV is asymptotically approached, while, for $T < 200$ K, $j_{+,SiO}$ becomes temperature independent. The temperature dependence of j_+ is much weaker. Figure 5 presents data sets measured with different samples. They document that absolute photocurrents are reproducible within a factor of 2, and do not exhibit an hysteresis effect. Ignoring the subtle deviation from simple Arrhenius behavior, one would end up with an activation energy $E_{a,+} = 37 \pm 5$ meV. It is worth noting that the
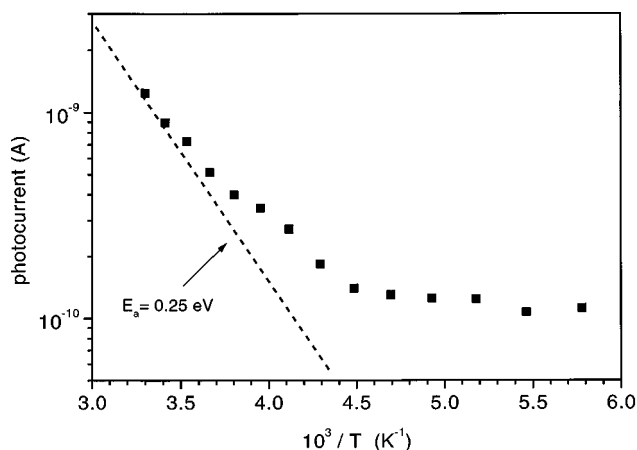

FIG. 4. Temperature dependence of the intrinsic photocurrent measured upon irradiating a PPV-ether film through ITO/SiO at positive bias ($E = 3.2 \times 10^5$ V/cm, $h\nu_{exc} = 27\,400\ cm^{-1}$).
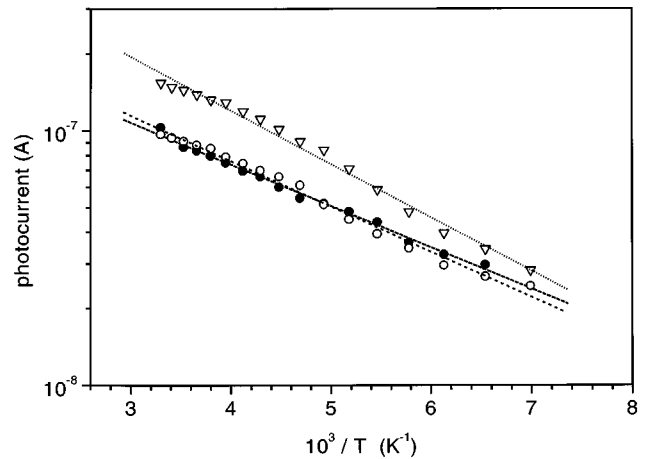

FIG. 5. Temperature dependence of the forward photocurrent measured upon irradiating a 95-nm-thick PPV-ether film through a neat ITO electrode. Data represented by triangles and circles were taken with different samples, and full and open circles were taken at rising and falling temperature, respectively. The data indicate both the absence of hysteresis effects and the level of reproducibility of absolute photocurrents with different samples ($E = 2.1 \times 10^5$ V/cm and $h\nu_{exc} = 25\,320\ cm^{-1}$).

intensity dependence of the photocurrents is in all cases strictly linear, independent of whether or not the incident light is strongly (at $25\,000\ cm^{-1}$) or weakly absorbed (at $22\,220\ cm^{-1}$) (Fig. 6). This testifies to the absence of bimolecular charge-carrier recombination and in the case of unipolar current injection, on the absence of space-charge effects. It proves that the photocurrent is a measure of the number of charge carrier generated per unit time. Room-temperature absorption and fluorescence spectra of a PPV-ether film are portrayed in Figure 7.
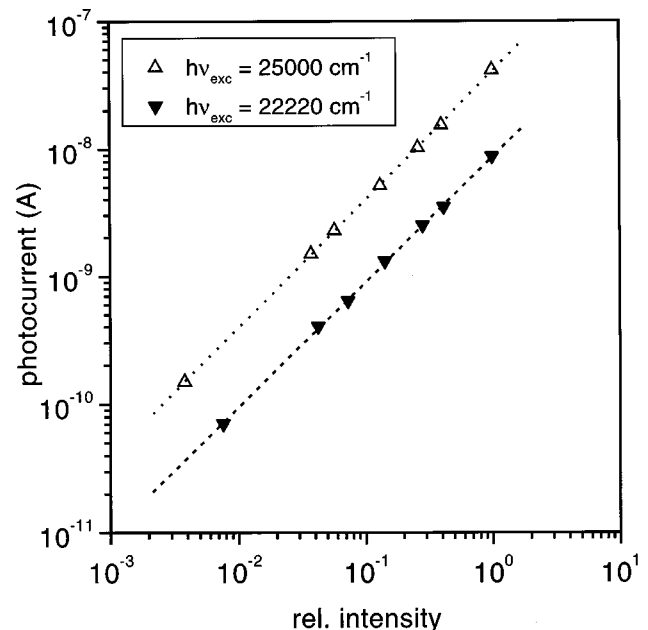

FIG. 6. Intensity dependence of the forward photocurrent in a 105-nm-thick PPV-ether film irradiated through a neat ITO electrode ($E = 1.9 \times 10^5$ V/cm and $T = 298$ K). One intensity unit corresponds to a photon flux of 1.3×10^{15} photons $(cm^2\ s)^{-1}$.
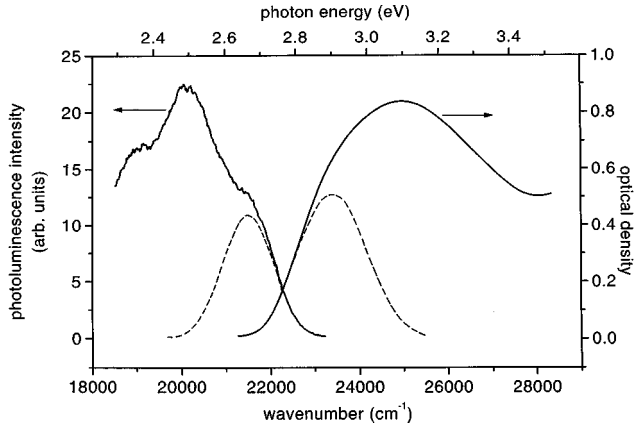
FIG. 7. Room-temperature absorption and photoluminescence spectra of a 95-nm-thick PPV-ether film. Dashed profiles represent the inhomogeneously broadened $S_1 \leftarrow S_0$ 0–0 and $S_1 \rightarrow S_0$ 0–0 bands, respectively.

IV. DISCUSSION

A. Optical charge-carrier injection

The dependence of the observed photocurrents on the polarity of the irradiated ITO electrode and on the presence of a SiO layer, known to prevent injection while effecting discharge of charge carriers only weakly, is an unambiguous signature of injection occurring. Since the highest photocurrents are measured when native ITO is positively biased, it is obvious that hole injection from ITO is the essential charge-carrier delivering process. The underlying mechanism must be dissociation of an optically excited state at the interface via transfer of the excited electron from the lowest unoccupied molecular orbital of the donor to the electrode, quite in analogy to what had been observed previously with an oligo-para-phenylenevinylene model compound[20] and with PPV in contact with a molecularly doped polymer.[21] The remaining positive charge can be collected by the electric field, provided that it escapes geminate recombination with its counter (image) charge.

In general, a sensitized photocurrent is given by

$$j_+(E,T,h\nu)=eI_0\varphi_+(E,T,h\nu)\frac{l_d}{l_d+\alpha^{-1}}, \qquad (1)$$

where I_0 is the incident photon flux, α^{-1} the penetration depth of the incident radiation, l_d the diffusion length of the excitations [i.e., $l_d/(l_d+\alpha^{-1})$ is the fraction of excitations reaching the interface], and φ_+ is the probability that an excited state at the interface generates a free charge carrier. Since at the absorption maximum $\alpha^{-1}\cong 50$ nm, and bearing in mind that in a conjugated polymer a singlet exciton will visit very few chain segments only before becoming immobilized,[22] $l_d \ll \alpha^{-1}$, and Eq. (1) reduces to

$$j_+(E,T,h\nu)=eI_0\varphi_+(E,T,h\nu)\alpha l_s, \qquad (2)$$

l_s being the thickness of the photoelectrically active layer adjacent to the electrode. φ_+ is the product of a primary dissociation probability φ_0 and the probability $\varphi_{esc,s}$ that the carrier left inside the dielectric medium will avoid geminate recombination with its counter, i.e., image charge. Given the
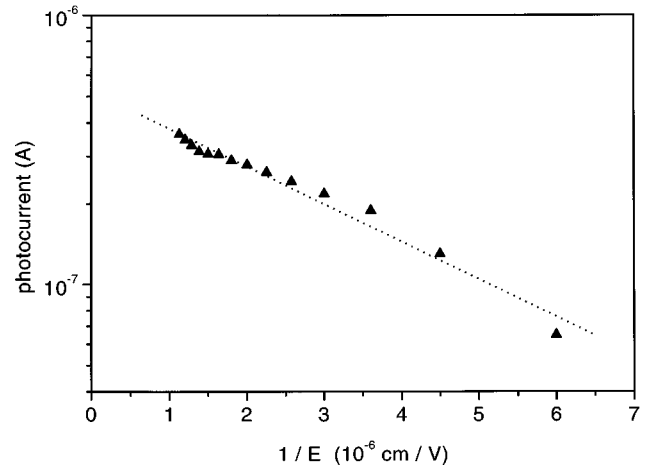

FIG. 8. Field dependence of the extrinsic photocurrent in PPV-ether ($h\nu_{exc}=25\,320$ cm^{-1} and $T=298$ K).

planar geometry, the field and temperature dependence of the escape probability $\varphi_{esc,s}$ should be given by Onsager's theory[23,24] for geminate pair dissociation in one dimension if adapted to random systems in which the energy of the hopping sites is subject to statistical variation. In the absence of disorder effects,

$$\varphi_{esc,s}=\varphi^{1D}=\frac{\int_0^1 \exp(-2\xi t-\eta/t)dt}{\int_0^\infty \exp(-2\xi t-\eta/t)dt}, \qquad (3)$$

where $\eta=e^2/16\pi\varepsilon\varepsilon_0 kTr_0$, $\xi=eEr_0/2kT$, and t is the normalized spatial coordinate perpendicular to the surface. It turns out that in the high-field limit $\varphi_{esc,s}(E)$ reproduces as a straight line over almost two decades if plotted on a $\ln\varphi$ vs E^{-1} scale with the slope being proportional to $-(\varepsilon r_0)^{-1}$, and r_0 being the distance from the interface at which the carrier starts its random walk. Experimental data for j_+ are, in fact, consistent with Onsager's theory (see Fig. 8). It is remarkable that the slope is almost the same as reported recently for sensitized hole injection from ITO into an oligo-para-phenylenevinylene doped into a polystyrene matrix.[20] By comparing the slope with that of a theoretical plot calculated for a given set of values for r_0 and temperature, one can infer the experimental r_0 values. Assuming a dielectric constant of 4 yields $r_0\cong 2$ nm. If one identifies this value with the thickness of the contact zone from which excited state dissociation proceeds, one can estimate the absolute carrier yield. It extrapolates to a value close to unity in the $E\rightarrow\infty$ limit for undiluted PPV-ether. This means that within a skin depth of $l_s\cong 2$ nm all excited states decay via electrode sensitized dissociation, and the fraction that escapes recombination with its image charge is determined by field- and temperature-assisted diffusion, tractable in terms of Onsager's theory.

The action spectrum of sensitized injection from ITO is determined by normalizing the photocurrent to the number of photons absorbed within a skin depth of thickness l_s. The result, shown in Fig. 9(a), demonstrates that the dissociation yield is not strictly independent of photon energy—as it is in
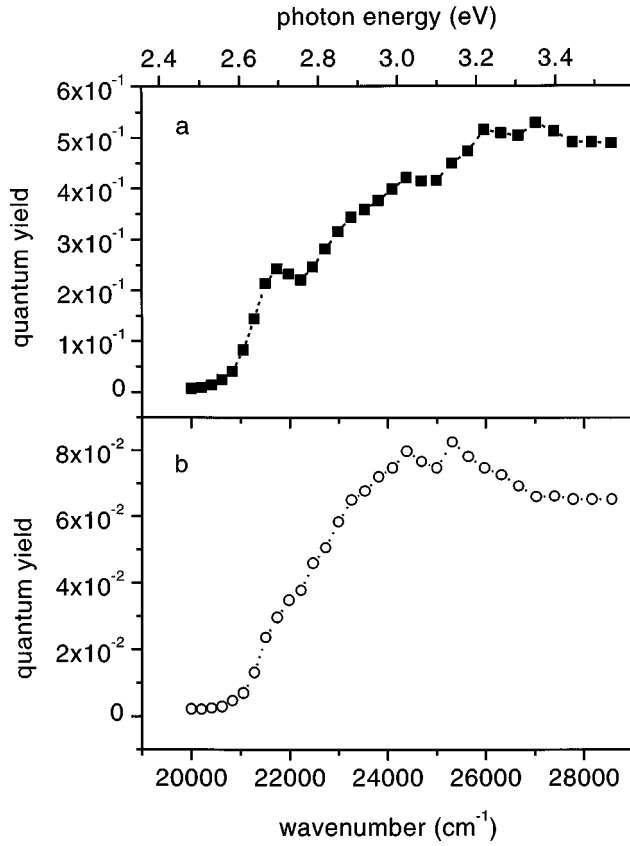
FIG. 9. Spectral dependence of the quantum yield of the forward (a) and reverse (b) photocurrent measured with a PPV-ether film upon irradiating through a neat ITO electrode at a field of 2 $\times 10^5$ V/cm and $T = 298$ K. The quantum yield has been defined as the number of charge carriers generated per photon absorbed within a skin depth of 2 nm next to either the ITO or the Al electrode.

a molecular crystal—but increases as the latter increases. A similar phenomenon has been observed with an oligo-para-phenylenevinylene blend.[20] This might indicate that higher excited states are more liable to dissociation. An alternative explanation is that part of the excess photon energy is transferred to the hole which, therefore, thermalizes at a slightly larger distance from the interface and, concomitantly, has a higher chance to avoid recombination with its image charge. Detailed measurements of $\varphi_+(E,T)$ as a function of photon energy would be needed to distinguish among these possibilities.

The photocurrent at reverse polarity can, in principle, be due to (i) hole injection from the Al back-electrode, (ii) electron injection from ITO, or (iii) volume photoionization. The second alternative can be ruled out since j_- is independent of whether or not the ITO contact carries a SiO coating. This concurs with work on molecular crystals, e.g., anthracene, which showed the electron injection is usually orders of magnitude less efficient than hole injection.[25] The third alternative can also be discarded since $j_- \gg j_{+,\text{SiO}}$, anticipating already that $j_{+,\text{SiO}}$ reflects bulk-photoionization (see Sec. IV B). If j_- is due to hole injection from the back-electrode via exciton dissociation, its action spectrum must be modified by the filter effect due to sample absorption, i.e.,

$$j_-(E,T,h\nu) = eI_0\varphi_{+,\text{Al}}\alpha l_s \exp(-\alpha L), \qquad (4)$$
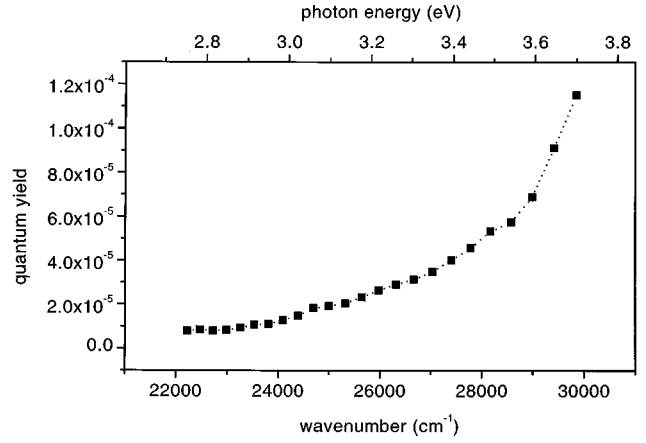

FIG. 10. Spectral dependence of the quantum yield of the intrinsic photocurrent measured upon irradiating a PPV-ether film through the ITO/SiO electrode at positive bias. The quantum yield has been defined as the number of charge carriers generated per photon absorbed ($E = 2.1 \times 10^5$ V/cm, $T = 298$ K).

L being the sample thickness. In fact, the spectral dependence of the efficiency of photoinjection ($\varphi_{+,\text{Al}}$) at positively biased Al obtained from j_- by appropriate normalization [see Fig. 9(b)], is very similar to that of φ_+, except that the yield is a factor of about one order of magnitude smaller. This can be accounted for by efficient energy transfer from the excited state to metal electrons which competes with oxidative excited state dissociation, and which does not occur at an ITO electrode.

B. Bulk photoionization

If the photocurrent $j_{+,\text{SiO}}$ observed upon irradiation through a positively biased, SiO-covered ITO electrode were due to weak electron injection from the back-electrode, its spectral dependence should match that of j_- since both had to originate from the same excited species being either oxidized or reduced depending on electrode polarity. This is at variance with experiment. We therefore attribute $j_{+,\text{SiO}}$ to bulk photoionization. In that case the photocurrent is proportional to the number of absorbed photons in the bulk $[1 - \exp(-\alpha L)]$ and the dissociation yield φ_b of the optically generated excited state,

$$j_b(E,T,h\nu) = eI_0\varphi_b(E,T,h\nu)[1 - \exp(-\alpha L)]. \qquad (5)$$

This assignment is supported by both the temperature and field dependencies of the photocarrier yield, that differ in a characteristic way from that of the injection currents (see Figs. 3, 4, and 5) and by the action spectrum determined via Eq. (5) (Fig. 10). The non-Arrhenius-type temperature dependence of φ_b is in full accord with the prediction of previous Monte Carlo simulations of geminate pair dissociation in a three-dimensional hopping system with energetic disorder.[26] A more detailed discussion of these results is deferred to a later publication. Suffice it to mention here that the high-temperature asymptote is a measure of the average Coulombic binding energy of the dissociating geminate pair. Its extrapolation to $T \to \infty$ yields the primary dissociation yield $\varphi_{b,0}$. Experimentally, $\varphi_{b,0} \cong 0.5$ is found for $h\nu = 27\,400$ cm^{-1}, upper and lower bounds being 1.0 and 0.25,
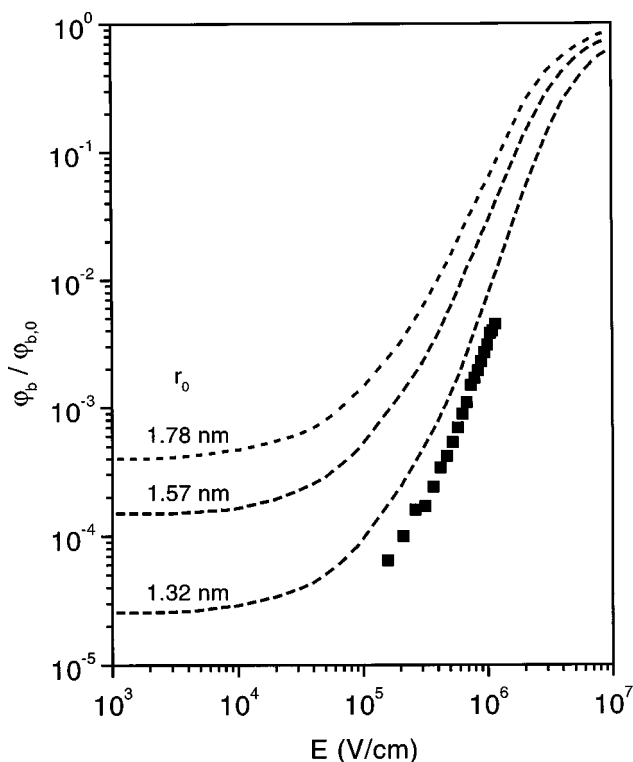
FIG. 11. Comparison between the experimental field dependence of the intrinsic photocarrier yield in undiluted PPV-ether, and theoretical 3D Onsager fits for $\varepsilon = 4$ and variable thermalization distance r_0 (from Ref. 28).
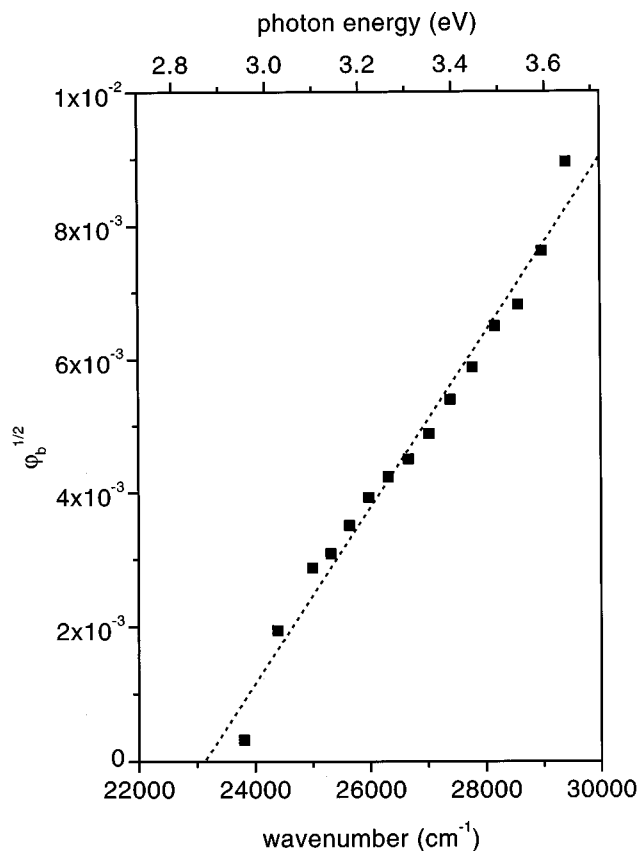

FIG. 12. A plot of the square root of the intrinsic charge-carrier generation yield as a function of photon energy. Data have been taken from Fig. 10 after subtracting a constant background yield of 1×10^{-5}.

respectively. Knowledge of $\varphi_{b,0}$ allows a comparison of $\varphi_b / \varphi_{b,0}$, which is the dissociation yield of a primary optically generated geminate pair, with the predictions of theoretical concepts. The simplest of these is Onsager's theory of geminate pair dissociation in three dimensions premised upon (i) the existence of an infinite sink for carriers at $r = 0$, (ii) a δ-shaped initial distribution of intrapair distances,[27] (iii) the neglect of disorder effects, and (iv) a field independent primary dissociation yield φ_0. Figure 11 compares the experimental field dependence of $\varphi_b / \varphi_{b,0}$ with the calculations by Pai and Enck.[28] The data fit perfectly into the pattern of dissociation yields as a function of electric field parametric in the initial intrapair distance r_0. Assuming $\varepsilon = 4$, $r_0 = 1.2$ nm is obtained. It translates into a zero-field activation energy of $E_0 = 0.3$ eV which compares well with the extrapolated zero-field activation energy of the short-circuit photocurrent in a PPV photovoltaic device.[29]

Before discussing the action spectra of bulk photoionization, it seems appropriate to consider absorption and fluorescence spectra of PPV-ether first because they provide some information concerning the energy distribution of excited states. From previous spectroscopic work it is known that both the absorption and fluorescence spectra consist of an inhomogeneously broadened $S_1 \Leftrightarrow S_0 0 - 0$ transition of approximately Gaussian shape followed by vibronic progressions. If non-site-selectively recorded only one vibrational feature with energy $\cong 1500$ cm^{-1} can be distinguished which, in fact, is the convolute of several vibrations of the phenylene-vinylene skeleton.[18,30–32] The maxima of the origin bands in absorption and emission bear out a Stokes shift δ that arises from the electronic relaxation an excited state

suffers while migrating incoherently within the manifold of hopping states. The latter are identified as segments of the polymer that accidentally differ in energy due to random packing and/or random effective conjugation length. If dynamic equilibrium is attained, $\delta = \sigma_{abs}^2 / kT$, σ_{abs} being the variance of the inhomogeneous $S_1 \leftarrow S_0 0 - 0$ profile.

A crude band profile analysis of the 298-K absorption and emission spectra (Fig. 7) yields a $S_1 \leftarrow S_0 0 - 0$ band centered at 23 400 cm^{-1} with $\sigma_{abs} = 740$ cm^{-1} [the full width at half maximum (FWHM) is $\sigma \sqrt{2 \ln 2}$], a $S_1 \rightarrow S_0 0 - 0$ band centered at 21 550 cm^{-1} with $\sigma_{em} = 560$ cm^{-1} and $\delta = 1850$ cm^{-1}. The experimental value of δ is less than σ^2 / kT (2700 cm^{-1}), indicating that the lifetime of the excited states is unsufficient for attainment of equilibrium.

With this information in mind we shall now be discussing the action spectrum of bulk photoionization. It starts rising monotoneously above $\cong 23 200$ cm^{-1} from a background level that appears to be independent of photon energy. If one attributes that background to some residual injection or photodetrapping, and subtracts it from genuine bulk photoionization, one arrives at a yield that follows $\varphi \propto (h\nu - h\nu_0)^2$ (Fig. 12). Similar power-law dependences have been reported for intrinsic photoionization in molecular crystals.[33] Considering the uncertainties in determining the background photocarrier yield and of the spectral deconvolution procedure, one can safely conclude that the threshold for intrinsic photoionization (23 100 cm^{-1}) is close to the center of the $S_1 \leftarrow S_0 0 - 0$ absorption band. Importantly, there is no correlation be-

tween the action spectrum and the absorption spectrum. In particular, no change in the action spectrum is observed when exciting into the vibronic replica instead of the $0-0$ band. This is an unambiguous signature of primary photoionization occurring prior to vibronic cooling.

The straightforward conclusion is that the primarily excited Franck-Condon state dissociates with a certain probability into an e-h pair on adjacent chain segments. On the basis of the structureless absorption spectrum and the primary yield coming close to unity, we consider it unlikely that primary photoionization is due to a direct, i.e., optically driven charge-transfer transition buried underneath the excitonic on-chain transition.[34] Excited-state dissociation must, on average, be an endothermic process because charge transfer has to proceed against the attractive Coulombic potential. The likelihood for this to occur increases with the excess energy of the dissociating Franck-Condon state. While in organic crystals an energy gap usually exists between the excitonic absorption edge and onset of intrinsic photoconductivity this gap narrows, and may even approach zero in random media because the expense in Coulombic energy may be compensated for by a gain in site energy, albeit with low probability. From the fact that the fluorescence spectrum of PPV-ether is characteristic of an individual chromophore rather than of a dimer or an excimer,[35] one can also exclude the possibility that the energy of a given e-h pair is less than that of a parent singlet state. Otherwise fluorescence spectra should carry features of a charge-transfer transition. This is not the case for PPV-ether. The situation after photoexcitation of PPV-ether is therefore not different from that in a classic molecular solid. An excitation with some excess energy can form a short-lived geminate e-h pair that can either recombine to reestablish fluorescent S_1 state of one of the parent chain segments or dissociate in accord with the 1938 version of Onsager's theory of geminate pair dissociation in three dimensions.

V. CONCLUDING REMARKS

The present work substantiates the conclusion drawn for previous work on oligo-para-phenylenevinylene,[20] indicating that the photoinjection of holes from an ITO anode is the main contributor to photoconductivity in conjugated polymers and their oligomeric counterparts. Eliminating this process by introducing a blocking layer provides a handle on intrinsic photoionization which does occur, albeit with different signatures as far as its dependence on electric field, temperature, and photon energy is concerned. The action spectrum of the latter increases at photon energies in excess of the $S_1 \leftarrow S_0 0-0$ transition energy in qualitative agreement with the results of Chandross et al.[15] on PPV. In conjunction with the measured activation energy of this process, this confirms the earlier notion that an energy of $\gg kT$ is needed for generating a free e-h pair from an excitonic precursor state. On the other hand, the results do not allow to extract a value for the exciton binding energy either. If one identified the latter with the sum of the zero-field activation energy (0.3 eV) and the difference between the photon energy at which this value has been measured (3.4 eV) and the mean singlet exciton energy (2.9 eV), one would end up with a value of 0.8 eV. However, this procedure overestimates the exciton binding energy because it implicitly assumes that primary photoionization is an elastic process. This ignores the energy dissipation in the course of a thermalization process of the kind which is usually invoked to explain photoionization in molecular crystals.

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