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Enhanced carrier photogeneration by defects in conjugated polymers and its mechanism

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Upon irradiating poly(*p*-phenylene vinylene) thin films with white light in air (total exposure ~5 J/cm^2), an enhancement of about forty times in photocarrier generation and a similar reduction in the photoluminescence intensity are observed. The wavelength and electric-field dependence of the photoconductivity are, however, essentially unchanged. These results demonstrate the sensitivity of the conjugated polymers to photo-oxidation and the importance of extrinsic photogeneration processes in these materials. The microscopic physics of carrier generation and luminescence quenching are established, and we discuss the implications for various conjugated polymer devices.

INTRODUCTION

Although the origin of photocarriers contributing to steady-state photoconductivity (PC) measurements in poly (*p*-phenylene vinylene) (PPV) has been the subject of intense discussion in the past few years,[1-13] a clear picture of the mechanisms explaining carrier photogeneration remains elusive. The onset of PC at the optical-absorption edge has been cited as evidence for direct carrier generation analogous to that in inorganic semiconductors.[8,13] Other work has suggested, however, that an optical transition in PPV produces strongly correlated electron-hole pairs (i.e., excitons or bound charge pairs) with quantum yield for generation of photocarriers much smaller than unity and strongly dependent upon the applied electric field.[5,7,11,12,14] Recent experimental work has documented strong quenching of the excitons responsible for the photoluminescence (PL) by oxidation defects.[15] These were found to consist of impurities that originate from aldehyde or ketone groups.[16,17] Photo-oxidation of PPV results in chain breaks with terminal aldehyde groups. There, it was proposed that the PL quenching is due to dissociation of the emitting excitons. In the present paper, we report studies of how controlled introduction of PL quenching defects affects the PC to test the hypothesis of exciton dissociation. We report an order of magnitude increase in PC accompanied by a decrease in the PL after calibrated illumination of pristine PPV in air. The light intensity, the electric field, and wavelength dependence of steady-state PC in both pristine and photo-oxidized samples are studied. We attribute the dramatic increase of PC upon oxidation to increased photocarrier generation through dissociation of the photoexcited bound pairs at the photoinduced defects. An onset of field-dependent PC at about 10^4 V/cm was found which remained unchanged with photo-oxidation.

EXPERIMENT

PPV thin films of 1000 Å were fabricated on glass via a modified sulfonium precursor synthesis[17] and subsequently were converted at 200 °C in a reducing atmosphere (85% H_2/15% N_2). The thicknesses of the PPV films were measured with a commercial profilometer, Tencor Inst. model Alpha-Step 200. For the PC measurements, coplanar Al or Au contacts (with interelectrode distance of 400 μm) were thermally evaporated onto the PPV films at a vacuum of about 10^{-6} Torr. White light, from a halogen lamp of 150 W, was used for the irradiation (photo-oxidation) of the samples under ambient conditions. The total light exposure was estimated to be about 5 J/cm^2. The PC measurements were done under flowing dry nitrogen and no changes in photocurrent were observed prior to oxygen exposure of the pristine sample. Optical absorption of PPV was measured before and after irradiation in air with a commercial UV/VIS/NIR photospectrometer model Cary 5. A programmable electrometer (model Keithley 617) and a high-voltage power supply (model SRS PS325) were used for the steady-state and time-dependent photocurrent measurements. The light-excitation source used was a xenon lamp dispersed by a compact holographic grating monochromator (model PTI 01-001) broadcasting into a quartz fiber bundle. A series of neutral density filters was used to regulate the light intensity. The electrometer, the power supply, and the monochromator were all controlled by a personal computer. All measurements were performed under ambient temperature.

RESULTS AND DISCUSSION

Figure 1 illustrates the enhancement of PC in PPV with photo-oxidation. The electric-field dependence of PC J_{ph}/E (photocurrent density divided by electric field)

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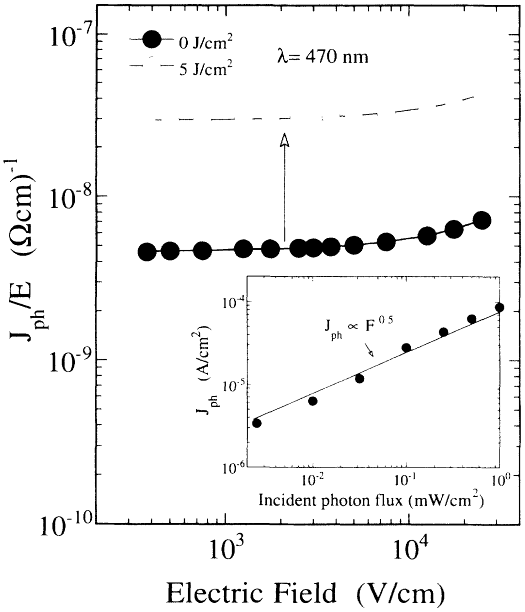

FIG. 1. Photocurrent density divided by electric field (J_{ph}/E) as a function of the applied electric field for before photo-oxidation (5 J/cm^2) and after exposure on white light (5 J/cm^2). Measurements were performed with a 470-nm monochromatic illumination of about 1 mW/cm^2. The inset shows the dependence of steady-state photocurrent of pristine PPV with incident photon flux. The square-root dependence of photocurrent is indicated with a straight line.

for before photo-oxidation and after exposure to white light ($\sim$5 J/cm^2) is shown as a function of electric field. These measurements were performed with a 470-nm monochromatic illumination of about 1-mW/cm^2 flux. An almost tenfold increase in J_{ph} is observed upon photo-oxidation. For both cases the PC was found to be electric-field independent for fields lower than 10^4 V/cm, followed by an onset of field dependence which remained unchanged with photo-oxidation. In principle, the PC enhancement due to photo-oxidation could originate either from changes in mobility μ, photogeneration efficiency η_g, or recombination kinetics. Since no detectable changes in the dark conductivity ($\sigma = en\mu$) of our samples were observed, we believe that the principal cause of the increased PC is enhanced photogeneration associated with the photoincorporated carbonyl defects. The electric-field dependence of J_{ph}/E could also be explained as a photogeneration effect, with the field assisting dissociation of excitons as has been observed by Kersting *et al.*[18] and Hammer and Friend.[19] Independent studies of charge collection time-of-flight experiments in PPV have shown that the photogeneration efficiency of holes is much smaller than unity and strongly field dependent.[9,14] The present data indicate that the electric-field effects are similar to those of carbonyl. That is, if the electric field is strong enough, it can provide the necessary energy to release the electron from the attraction of hole, thus enhancing photogeneration.

The inset to Fig. 1 shows the dependence of steady-state photocurrent of pristine PPV with incident photon flux (F). The photocurrent follows a square-root dependence on incident intensity ($F^{0.5}$) over the entire measured range (1 μW/cm^2 to 1 mW/cm^2). These kinetics were observed for all excitation wavelengths between 400 and 600 nm and did not change with photo-oxidation. We make the plausible assumption that the observed dependence is due to bimolecular photocarrier recombination caused by their spatial restriction, often observed in this type of electrode geometry. On the other hand, a linear relation has been observed in a configuration where the PPV thin film is sandwiched between two metal electrodes.[20–23] Under bimolecular kinetics the positive carriers (positive polarons or bipolarons) are likely to recombine with separately generated negative carriers (negative polarons or bipolarons) before reaching the cathode. Thus the carrier recombination time τ will be given by $\tau = (\beta_r \Delta n)^{-1}$, where β_r is the recombination coefficient and Δn the spatially dependent volume density of photocarriers. According to Giro *et al.* and Bube[24,25] the average volume density of photocarriers measured perpendicularly to the electrode surface of a sample of thickness d is

$$\Delta n = \frac{2}{d}\left[\frac{\eta_g F}{\alpha \beta_r}\right]^{0.5}[1-\exp(-\alpha d/2)]\ , \tag{1}$$

where η_g is the quantum yield for photogeneration of carriers, and α^{-1} is the wavelength-dependent absorption depth of photons. Under these conditions η_g is proportional to

$$\eta_g \propto \alpha J_{\mathrm{ph}}^2[1-\exp(-\alpha d/2)]^{-2}\ . \tag{2}$$

Therefore, in the case where the photocurrent is limited by bimolecular recombination, the charge photogeneration efficiency is measured by the square of the photocurrent. The data of Fig. 1 therefore reflect carrier-generation enhancement of a factor of 40 due to photo-oxidation.

The quenching of emissive excitons by oxidation defects has been shown to be extremely efficient, resulting in reductions of the PL efficiency and a lifetime of a factor of 2 at carbonyl defect densities in PPV of only one per 400 phenylene vinylene repeat units. Figure 2 plots the quantum yield of PL (η_{PL}) and photogeneration efficiency (η_g) in terms of the carbonyl defect density determined elsewhere.[17] Both the steady-state PL and PC were initiated by 470-nm excitation. The PL was measured at 555 nm and the generation efficiency η_g was calculated from the photocurrent according to relation (2). It is obvious from Fig. 2 that defect incorporation has a much more rapid effect on the photoluminescence than the photocarrier generation. On the other hand, the photocarrier generation efficiency remains insensitive to low carbonyl density indicating that there may exist some intrinsic photogeneration in PPV. While intrinsic photogeneration has been widely assumed in PPV, literature results on PPV PL lifetimes indicate that most work has been done on quite oxidized samples where our results show that the majority of the PC is extrinsic. For refer-

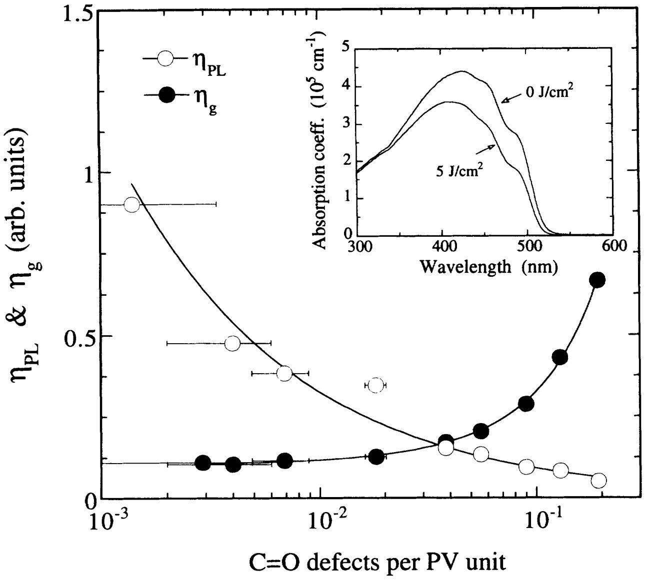

FIG. 2. Quantum yield of PL (η_{PL}) and photogeneration efficiency [η_g, estimated from relation (2)] as a function of the carbonyl defects per phenylene vinylene (PV) unit. The inset shows the optical absorption of the PPV film before (0 J/cm^2) and after photo-oxidation (5 J/cm^2). The maximum C=O density shown on the x axis (0.2 C=O/PV unit) coresponds to total exposure of 2.5 J/cm^2.

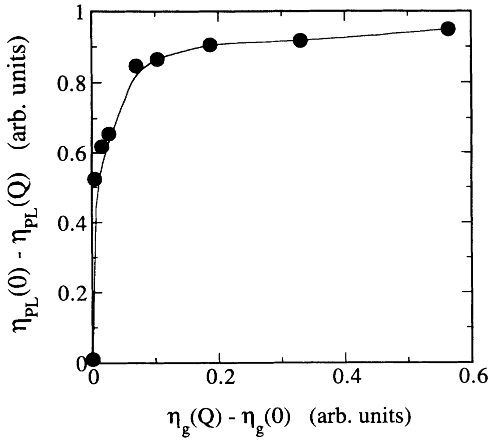

FIG. 3. Correlation of relative change upon photo-oxidation on the quantum yield of PL [$\eta_{PL}(0)-\eta_{PL}(Q)$] and photogeneration efficiency [$\eta_g(Q)-\eta_g(0)$].

ence, the inset shows the relatively small effect of the maximum photo-oxidation dose (5 J/cm^2) on the optical absorption of the PPV film which reflects a slight bleaching and shortening of the conjugation length due to carbonyl introduction.

If in fact the mechanism for extrinsic carrier photogeneration is dissociation of emissive excitons, then the PL and PC behaviors with defect incorporation should be related by

$$\eta_{PL}(0)-\eta_{PL}(Q)\propto\eta_g(Q)-\eta_g(0) , \qquad (3)$$

where Q is the concentration of quenching defects. In general, proportionality between PL quenching and photogeneration enhancement has been used in the field of molecular crystals to support the scenario that emissive excitons are the precursors to photocarriers.[26] Figure 3 plots the left-hand side versus the right-hand side of relation (3) for the carbonyl defect densities shown in Fig. 2. The lack of proportionality of the two magnitudes indicates that extrinsic PC cannot be derived from the dissociation of the emissive excitons at photo-oxidation defects. We now speculate on an alternative mechanism that may lead to the photo-oxidation assisted carrier photogeneration. The sensitivity of excitons to quenching is mainly attributed to their relatively facile exciton diffusion in PPV (Ref. 15) allowing them to efficiently find defect sites. It is therefore plausible to conclude that the extrinsic photocarrier generation is caused by separation of charge pairs which are not as mobile as excitons. It has been hypothesized that the predominant species created upon photoexcitation is an interchain charge transfer ("spatially indirect") exciton which has also been referred to as a bound polaron pair.[12] These are nonemissive, immobile, and created in abundance in excess of 80% per absorbed photon. Moreover, transient absorption measurements indicate that their number is significantly reduced by oxidation of PPV but not as much as are emissive excitons.[15] In addition to that, the bound polaron pair decay dynamics are *not* dependent on defect density. The reduction in bound polaron pair density has therefore been ascribed to quenching of the precursor to the interchain pairs, namely, hot intrachain excitons or carrier pairs.[15] These are therefore excellent candidates for a neutral species which could be dissociated by oxidation defects to initiate the majority of the extrinsic PC we observe. These do not live long enough to diffuse and would be consistent with a rapid turn-on in the extrinsic PC similar to what is observed for the case of mixed poly(2-methoxy 5-(2′-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) and C_{60}.[27]

We note that our data cannot differentiate between the case of initially created charge pairs being (1) vibrationally hot excitons, which would have become nonemissive polaron pairs, and (2) free carriers, which were confined to a conjugation segment and would have recombined nonradiatively. Nevertheless, the pronounced effect of photo-oxidation on the PC implies that the generation of photocarriers in pristine PPV is an inefficient process where the majority of photoexcited charges remain in bound pairs even at very long times. Presumably, in the case of excitons and polaron pairs this means that their binding energy must be much larger than the thermal energy k_BT to prevent dissociation at room temperature.[28] If we assume the case of free carriers, the energy restricting them to a single chain segment must still be greater than k_BT.

The wavelength dependence for the quantum yield of photocarriers, before and after exposure, is shown in Fig. 4. The quantum yield was obtained from photocurrent measurements and then corrected for bimolecular recombination according to relation (2). Changes in the optical density of the PPV film before and after photo-oxidation were taken into account (cf. inset of Fig. 2). Quantum yields for the oxidized and pristine samples are normal-

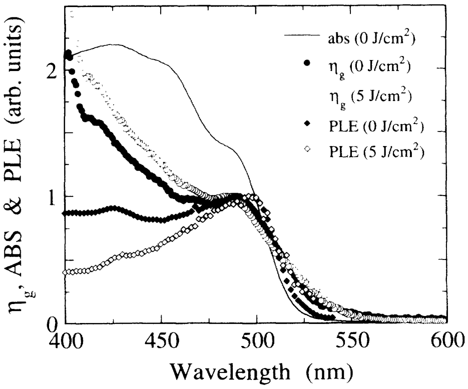

FIG. 4. Wavelength dependence for photogeneration efficiency (η_g) and photoluminescence excitation (PLE) for before (0 J/cm^2) and after photo-oxidation (5 J/cm^2). η_g was obtained from photocurrent and corrected for bimolecular recombination according to relation (2). η_g's are also normalized to unity at 490 nm for comparison. The optical absorption of pristine PPV is shown for reference.

ized to unity at 490 nm for comparison. Their resemblance through the entire wavelength range indicates that similar processes probably govern the generation mechanism of photocarriers in both cases. This is an additional support for the idea that the species that is dissociated by the carbonyl defects is the directly photogenerated hot exciton. Naturally, the excitation spectrum for carrier generation resembles that for production of bipolarons as measured by Leng *et al.*[11] in cw photoinduced absorption experiments since it is necessary to produce free charges first in order to obtain bipolarons.

Figure 4 also depicts the photoluminescence excitation (PLE) spectrum of PPV for the pristine and photo-oxidized samples for reference. We note that PLE decreases in the blue for the photo-oxidized sample, an effect which has been attributed to rapid internal conversion of the higher-lying excited states to the ground state. A more complete discussion of the physics behind the PL excitation spectrum and oxidation effects on it can be found elsewhere.[29] In terms of its implications for the photocarrier generation mechanism, we wish to point out that the PLE in the pristine sample reflects the probability of forming excitons versus absorbed photon energy. Since this is at variance with the changes to the spectrum of η_g due to oxidation, this provides additional evidence for our conclusion based on Fig. 3 that dissociation of the emissive species is not responsible for the extrinsic PC.

These data, when combined with previous transient PL and photoinduced absorption experiments, lead to a picture of the photocarrier generation. Initial photoexcitation creates hot intrachain excitons (S_1^*). Previous work shows that these either relax vibrationally to form emissive excitons (S_1) or interchain charge transfer occurs and bound polaron pairs (P^+-P^-) are formed. The lack of a quantitative correlation of the PC enhancement with the PL degradation (cf. Fig. 3) rules out the dissociation of relaxed emissive excitons S_1 as the dominant mechanism for extrinsic carrier generation. Similarly, the lack of carbonyl-related effect on the bound polaron pair (P^+-P^-) decay dynamics tends to rule these out as precursors to extrinsic carrier generation as well. We therefore believe our data show that some small fraction of the initially created hot excitons S_1^* dissociates resulting in intrinsic photogeneration on the same time scale that these other processes occur. Moreover, the dissociation of these hot excitons, when excited near a photo-oxidatively introduced defect, can be enhanced by orders of magnitude causing efficient extrinsic photocarrier generation and dramatic increases in the observed PC. This is analogous to what has been observed with C_{60} incorporation into conjugated polymers where PC also increases dramatically due to subpicosecond electron capture by the dopant.[30] We predict similarly rapid charge transfer and PC for the case of oxidation defects in PPV and related polymers.

Aside from the insight we have derived regarding the photophysics of the conjugated polymers, one practical consequence of the present work is worthy of mention. The dramatic enhancement of PC should be extremely useful for photodetectors based on conjugated polymers as recently reported by several groups.[20–23,31] Since the charge photogenerated per absorbed photon increases by over an order of magnitude upon oxidation and the absorption spectra of the samples are virtually unchanged, deliberate photo-oxidation of the conjugated polymers should provide a simple and valuable method to dramatically improve the performance of these devices. Moreover, images can be easily projected on a polymer and could form the basis for fabricating spatially patterned photodetectors which may have applications in image recognition.

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