PHYSICAL REVIEW B **76**, 235203 (2007)

Charge carrier photogeneration and recombination in ladder-type poly(*para*-phenylene): Interplay between impurities and external electric field

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(Received 5 July 2007; revised manuscript received 4 October 2007; published 7 December 2007)

Charge carrier generation and decay in *m*-LPPP polymer films were examined by means of femtosecond transient absorption spectroscopy in the time window of 100 fs–15 ns. Two modes of polaron formation with distinct behavior were identified, impurity induced in the absence of an external electric field and electric field induced in pristine film. While field induced charge generation is relatively slow, occurring throughout the excited state lifetime, the rate of impurity induced charge generation is much faster and depends on excitation wavelength; it occurs on the several hundred femtosecond time scale under excitation within the main absorption band, but excitation into the red wing of the absorption band results in charge generation within less than 100 fs. Polaron decay through geminate electron-hole recombination occurs with widely distributed lifetimes, from ~0.8 ns to microseconds; the polarons characterized by the shortest decay time have a redshifted absorption spectrum (as compared to more long-lived polarons) and are attributed to tightly bound polaron pairs.

DOI: 10.1103/PhysRevB.76.235203 PACS number(s): 78.47.+p, 78.55.Kz, 78.66.Qn, 42.65.Re

INTRODUCTION

Charge carrier photogeneration and recombination are two basic processes determining application of conjugated polymers in organic optoelectronic devices. Despite very active investigations during recent decades, both these processes are still poorly understood. Two basic concepts are currently used to describe carrier generation. The direct carrier generation concept was mainly developed by Heeger and co-workers on the basis of investigations of poly(*p*-phenylene vinylene) type of polymers.[1–5] According to this model, charge carriers are generated directly by photon absorption; very rapid and intensity dependent recombination taking place on a femtosecond to picosecond time scale[6,7] is a consequence of this picture. Another, two-step carrier generation model grounds on the molecular exciton picture.[8–14] This model is to a large extent based on investigations of the methyl substituted ladder-type poly-*para*-phenylene (*m*-LPPP) polymer, and it is currently commonly accepted that polarons in *m*-LPPP are generated from nonrelaxed and relaxed excited states (excitons) on a subpicosecond-picosecond time scale.[11,13,14] Only a small fraction of about 10^{-3}–10^{-4} of the initially generated excitons yield free charge carriers at zero applied field.[15] A fraction of the generated polarons survive up to microseconds and reform fluorescent excited states,[16,17] but the main part recombine faster. Since the rapidly recombining polarons do not participate in photocurrent, they escape probing by electrical methods. The majority of them recombine nonradiatively, thus escaping fluorescence detection as well. Therefore, polaron absorption remains the best detection method for monitoring the initial polaron dynamics. Our present investigation shows that the majority of polarons recombine on a tens of nanosecond time scale, which is difficult to access both by ultrafast spectroscopy and nanosecond spectroscopy methods.

It is well known that impurities play an important role in photoconductivity of organic materials, but the relative importance of intrinsic carrier generation and generation by impurities still remains an open question. Other important questions are whether the generated polarons are free or form bound electron-hole pairs, and when and how the polaron pairs are separated or recombine. In some cases it is possible to distinguish between recombination of geminate electron-hole pairs and recombination of free charge carriers. The two processes are characterized by different recombination dynamics and carrier density dependence of the rates.[18] In this way, carrier generation and recombination are closely linked processes and both are important for the optoelectrical properties of conjugated polymers. Although these processes have been widely investigated, they were rarely addressed in the same experiment because they occur on quite different time scales. Therefore, the existing picture of carrier dynamics is built from rather scattered information, which rarely provides a clear account of the total sequence of events and their relationship. In the current investigation, we address all relevant processes of the charge carrier dynamics, charge carrier generation, recombination, and extraction by covering the time window of ~100 fs–15 ns in a single experiment.

EXPERIMENT

The *m*-LPPP polymer, provided by Scherf, was synthesized as described in Ref. 19, and polymer films were deposited in argon atmosphere by spin coating from toluene solution (1% by weight) on glass covered with indium tin oxide (ITO). The polymer film thickness was about 115 nm and the polymer was covered with thin semitransparent (24 nm), or thick (150 nm) aluminum layers, or uncovered. The charge carrier dynamics were monitored with the femtosecond time resolved absorption pump-probe and electromodulated differential absorption (EDA) techniques[11,14] by measuring the time resolved polaron absorption created by an excitation pulse and its modulation by an external electric field. The

EDA signal at a probe wavelength outside the steady state absorption band may be expressed as[20]

$$\mathrm{EDA}(\lambda,t,E) = l\{\sigma_e(\lambda)[n_e(t,E) - n_e(t,E=0)] + \sigma_p(\lambda)[n_p(t,E) - n_p(t,E=0)]\}, \qquad (1)$$

where l is the film thickness, $\sigma_e(\lambda)$ and $\sigma_p(\lambda)$ are the exciton and polaron absorption cross sections at λ wavelength, and $n_e(t,E)$ and $n_p(t,E)$ are the exciton and polaron densities at delay time t and applied field E. The first term in each square bracket expresses the field induced exciton quenching, while the second accounts for the field free polaron generation. The equipment for the transient absorption measurements was described in detail elsewhere.[21] Briefly, the samples were excited by frequency-doubled pulses generated in an amplified Ti:sapphire laser (1 kHz, 387 nm) or by sub-50 fs duration variable wavelength pulses from a parametric noncollinear generator. The differential absorption was probed by variable wavelength pulses generated in another noncollinear parametric generator. The spectrometer enabled very high measurement accuracy with standard deviation of less than 10^{-4} in differential absorption signal per pair of probe pulses with and without excitation. EDA measurements were performed by applying ~10 μs duration electrical pulses to the sample every second optical pulse. Positive bias was applied to the aluminum electrode and the difference in the sample optical density with and without field was measured.

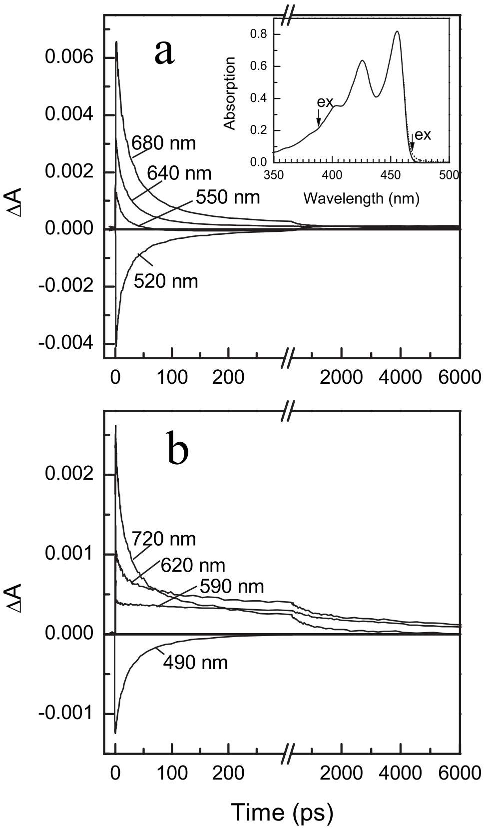

FIG. 1. Transient absorption kinetics excited at 470 nm and probed at different wavelengths for *m*-LPPP film covered by (a) a 150 nm Al layer and (b) without an Al layer. The inset shows the absorption spectrum of a freshly prepared film (solid line) and after 1 month (dotted line). Arrows indicate excitation wavelengths used in this study.

EXPERIMENTAL RESULTS

The transient absorption dynamics of *m*-LPPP films with an Al layer of different thicknesses or without it was investigated under excitation by different wavelengths and different intensity laser pulses. With excitation at 470 nm, *m*-LPPP film covered with a 150 nm Al layer shows positive or negative transient absorption, depending on the probe wavelength [see Fig. 1(a)]. The observed transient absorption signals correlate well with the transient absorption spectrum of photogenerated excitons reported in Ref. 14. The relaxation kinetics at all probe wavelengths in Fig. 1(a) are qualitatively similar; the initial decay may be characterized by an ~25 ps time constant, while starting from about 50 ps, the decay slows down and may be characterized by an ~200 ps time constant. The initial part may be slightly affected by the exciton-exciton annihilation, which often causes nonexponential decays; however, its influence on the relaxation kinetics at the used excitation intensity should be weak.[22] Therefore, the nonexponential kinetics should be mainly related to material inhomogeneity and/or exciton quenching. A weak, long-lived induced absorption relaxation component is also observed in kinetics measured at 640 nm. Polarons have strong absorption at this probe wavelength [23]; therefore, this component can be assigned to a low concentration of photogenerated polarons, evidently Coulomb bound polaron pairs.

The relaxation kinetics in a film without the protective Al layer are significantly different and exhibit a much larger polaron pair absorption contribution. Figure 1(b) shows kinetics measured under excitation at 470 nm and probed at several different wavelengths, showing varying contributions from excitons and polaron pairs. Kinetics probed at 490 nm is similar to that observed in film covered with a 150 nm Al layer and decays to zero within ~200 ps, showing that this wavelength monitors exciton decay and that other excited species with longer lifetimes do not contribute significantly to the transient absorption. The transient absorption kinetics at 620 and 720 nm carries contributions from both excitons and polaron pairs.[14,23] At 720 nm excitons dominate the response, but there is also a significant polaron pair component with an ~0.8 ns time constant. At 620 nm on the other hand, polaron pairs are dominating the response (close to the absorption maximum of polarons[22]) and the relaxation kinetics has a dominating slow decay component related to polaron pair decay, in addition to the exciton decay. The slow decay may be approximated by a biexponential function with 0.8 and ~15 ns time constants. The probe wavelength of 590 nm is close to the isobestic point between exciton and ground state absorptions.[14] Exciton absorption is low at this probe wavelength and its decay is compensated by the polaron absorption. The kinetics measured in a film covered with a thin semitransparent 24 nm Al layer is almost identical to that measured in uncovered film, showing that this thickness of the overcoat does not prevent penetration of air gases into the polymer film.

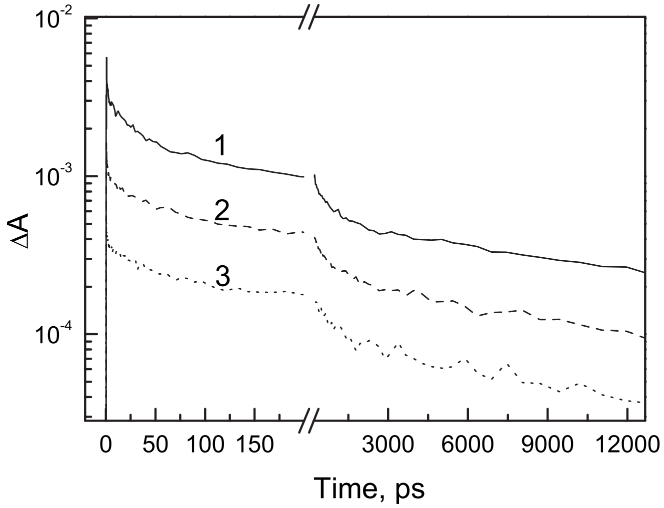

FIG. 2. Transient absorption kinetics of *m*-LPPP film without Al layer as a function of excitation pulse energy, excited at 470 nm and probed at 650 nm. (1) 0.2 mJ/cm^2, (2) 0.05 mJ/cm^2, and (3) 0.02 mJ/cm^2.

Figure 2 shows the relaxation kinetics at 650 nm in the uncovered film measured under different excitation intensities. The shape of the kinetics is independent of excitation intensity, except of the initial (<10 ps) relaxation, which becomes faster and more pronounced at higher excitation intensity; this fast intensity dependent relaxation can be related to exciton-exciton annihilation.[22] The polaron absorption decay is insensitive to the excitation intensity, showing that the polaron pair recombination does not depend on their concentration and thus may be assigned to a geminate process.

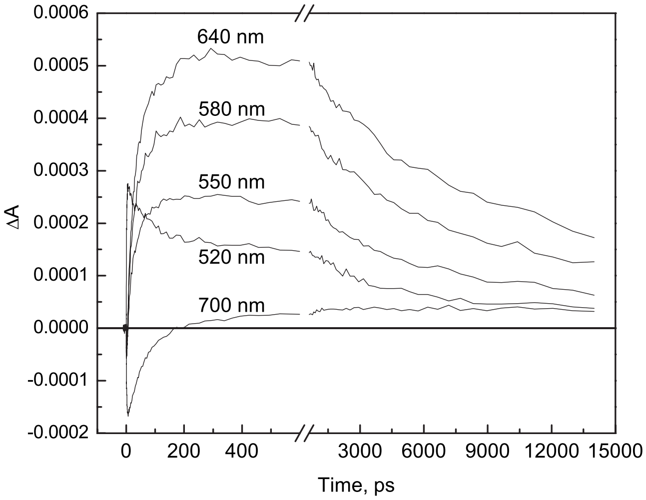

FIG. 3. EDA kinetics of *m*-LPPP film with 150 nm Al layer at different probe wavelengths. Excitation wavelength was 470 nm.

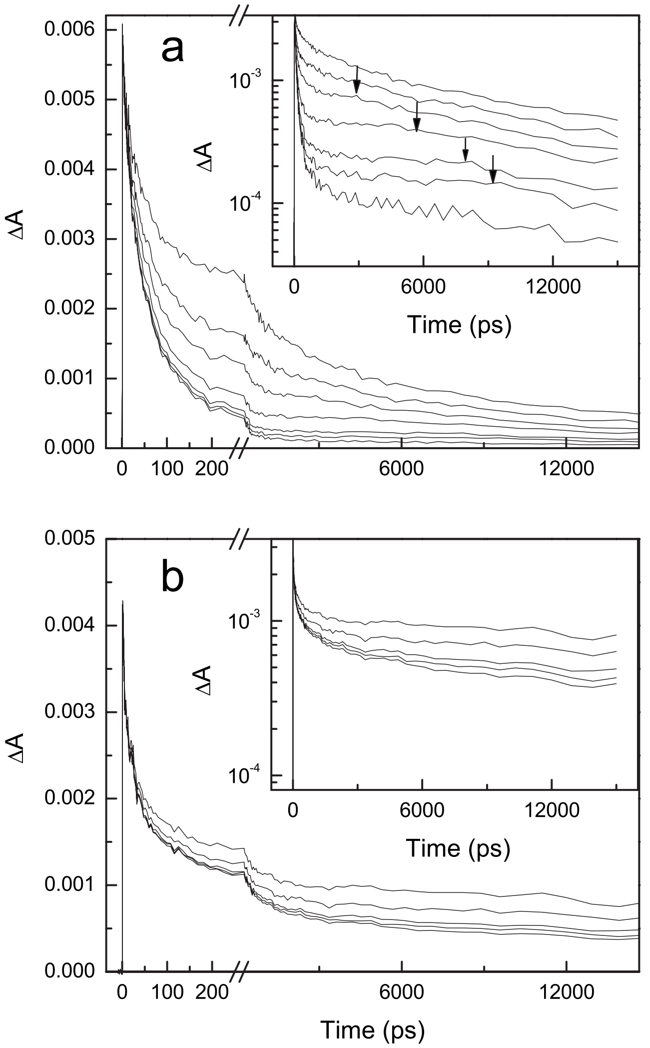

FIG. 4. (a) Transient absorption kinetics excited at 387 nm and probed at 650 nm in the film covered with a 150 nm Al layer at applied voltages of 0, 4, 6, 11, 15, 18, and 22 V (from bottom up) and (b) in the film covered with a 24 nm Al layer at applied voltages of 0, 5, 7, 11, and 15 V (from bottom up). The insets show the same kinetics on a logarithmic scale. Arrows in (a) indicate the time positions when faster decay starts.

We also investigated the influence of an applied electric field on the polaron generation and recombination kinetics by measuring the electric field induced changes of the transient absorption. Free polarons are evidently also generated under applied field; however, transient absorption gives no possibility to distinguish between free polarons and bound pairs. Figure 3 shows the EDA kinetics at different wavelengths in the film covered with a 150 nm Al layer at 18 V of applied voltage. The electric field splits excitons into polaron pairs,[14,23] which leads to exciton quenching and polaron generation. A positive EDA signal observed in the 520–640 nm region, where polarons have strong absorption, shows that the electric field increases their number. The exciton quenching component (700 nm) contributes to the EDA signal only during the exciton lifetime of several hundred picoseconds and gives information about the polaron pair generation dynamics.[14] At later times, only polaron species contribute to the observed EDA signal, and the EDA signal relaxation on a nanosecond time scale reflects the polaron decay. Figure 4(a) shows the transient absorption kinetics at 650 nm in the film covered with a 150 nm Al layer under different applied voltages. (The built-in voltage of about 0.6 V related to different work functions of Al and ITO electrodes was not accounted.)

The long time scale corresponds to polaron dynamics when excitons are already absent and polaron pair generation is already finished. This part of the kinetics experiences complex changes with increase in the applied voltage. At 4–11 V of applied voltage, the electric field slows down the relaxation kinetics, but by further increasing the applied voltage, the relaxation becomes faster again. This behavior is more clearly expressed in the inset where the same kinetics is shown on a logarithmic scale. The field influence on the transient absorption kinetics in a film covered with a thin 24 nm Al layer is simpler [see Fig. 4(b)]. The applied voltage only slows down the relaxation rate and no faster relaxation is observed, even at the highest applied voltages. (It should be noted that very high voltage could not be applied in this case because of the sample degradation.)

DISCUSSION

There are controversial data in the literature regarding polaron pair photogeneration in *m*-LPPP films at zero applied field. Graupner *et al.*[11] observed a relatively strong long living induced absorption with the typical polaron spectrum induced by 400 nm excitation. Muller *et al.* observed 10% yield of bound polaron pairs,[13] whereas our investigations performed at similar experimental conditions showed negligible polaron absorption without applied field.[14,20] Comparison of the relaxation kinetics in films covered with thick and thin Al layers, or without it, gives a possible explanation of the discrepancies in the literature data—the field-free generation of polaron pairs is related to impurities such as oxygen and/or water molecules adsorbed from the ambient air. A thick (150 nm) aluminum layer deposited on top of the polymer film partly protects the polymer from air and keeps the level of impurities in the sample lower. These polymer films therefore showed much lower photoinduced zero-field polaron absorption than the unprotected films. The decay kinetics of polaron pairs generated under field-free conditions in uncovered and covered films are, however, very similar, implying that polaron pairs in both films are generated by the same mechanism, i.e., by charge separation at impurities. The only difference between protected and unprotected films appears to be the impurity concentration and consequently the generation efficiency. The polaron pair generation efficiency at zero field may be estimated from comparison of the exciton and polaron absorptions. With the help of known exciton and polaron cross sections[14] and by comparing the transient absorption intensity at 650 nm at zero delay time when the exciton absorption dominates with that at 1 ns when polaron absorption dominates, we obtain a polaron pair yield of about 20% in the film without Al cover, and about 3% in the film covered with a thick Al layer. In a pristine polymer film free of impurities, zero-field polaron pair formation would be probably negligible.

Other authors have also made observations of impurity-induced polaron pair formation. Thus, Graupner *et al.* noticed that oxidation of the *m*-LPPP polymer, which takes place upon irradiation with visible light in the presence of oxygen, enhances the film photoconductivity by an order of magnitude.[24,25] Enhancement of photoinduced polaron absorption due to electron transfer to electrophilic carbonyl groups created by polymer oxidation was also reported.[26] Air humidity was also shown to enhance the dark conductivity of π-conjugated polymers by several orders of magnitude.[27,28]

The data in Figs. 3 and 4(a) and previous results[11,14,20] show that applying an external electric field to the polymer film generates additional polarons as compared to field-free conditions. Thus, our results highlight two mechanisms of polaron photogeneration in *m*-LPPP films: (1) formation of polaron pairs induced by impurities, requiring no applied field or excess energy, and (2) breaking of strongly bound polymer excitons in pristine polymer films, requiring a strong applied external electric field or excess vibrational energy.[14,20] It should be noted that the second mechanism does not exclude defect role in charge generation. As it was shown in Ref. 29, the polaron generation in conjugated polymers always occurs on some defect sites; however, properties of these defect sites are different than those created by air gases. We will now examine to what extent the two modes of polaron generation, field-free and field induced, are similar or different in various aspects, and how they are related.

The two modes of polaron formation have quite different dependence on impurity concentration. For unprotected films with high impurity level [Fig. 4(b)], we can estimate that only ~25% of polarons are generated by electric field assistance at an applied voltage of 15 V, while 75% are generated by the field-free charge separation mechanism at impurities. In the protected film with low impurity concentration [Fig. 4(a)], about 70% of polarons are created by field-stimulated polaron generation at the same applied voltage. Analysis of EDA kinetics also shows that the field-induced polaron generation efficiency in a film covered with a thick aluminum layer is more than two times higher than that in a film with a thin Al layer (data not shown). From this, it is clear that the two polaron generation processes compete with each other; impurities, causing field-free polaron generation, reduce the efficiency of field-induced polaron generation.

Time dependence of polaron generation is intimately connected to the mechanism of formation. Previous studies as well as the data in Fig. 3 show that field induced polaron pair generation in pristine *m*-LPPP with little excess energy is relatively slow and occurs on the tens of picosecond time scale. Additional information about the polaron pair formation dynamics can be obtained by comparing polaron and exciton absorption anisotropy decays. Figure 5 shows the transient absorption relaxation kinetics measured at 520 nm related to stimulated emission of excitons and at 590 nm where polarons absorb. Exciton depolarization under 470 nm excitation occurs during several picoseconds; the anisotropy decays to approximately half its initial value within ~1 ps. Exciton depolarization under 387 nm excitation (not shown) is even slightly faster. Depolarization of the transient absorption at 590 nm contains fast (~2 ps) and slow (~100 ps) components. The fast component is similar to that related to excitons therefore should be attributed to the exciton absorption at this probe wavelength. The slow component should be unambiguously related to polarons since excitons are completely depolarized on hundreds of picosecond time scale. The polaron anisotropy decay occurs on the time scale of tens and hundreds of picoseconds, much slower than the de-

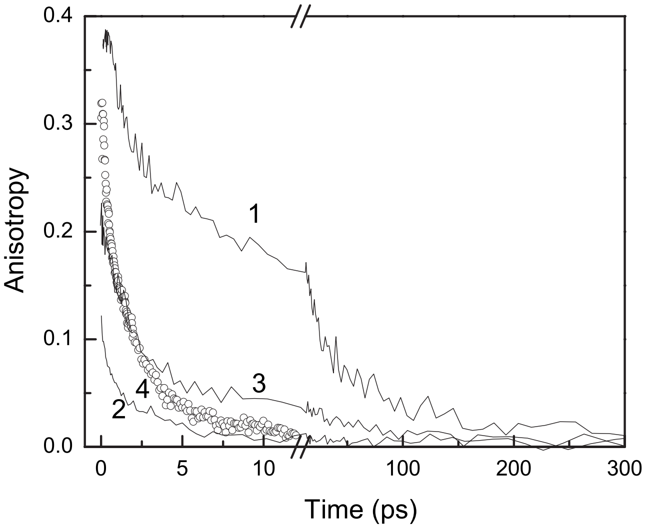

FIG. 5. Absorption anisotropy related to polarons generated at zero applied field and probed at 590 nm in film covered with a 24 nm Al layer with 470 nm excitation (curve 1) and with 387 nm excitation (curve 2). Curve (3) shows absorption anisotropy related to polarons generated at 15 V of applied voltage in film covered with a 150 nm Al layer and measured at 590 nm with 470 nm excitation. Curve (4) shows absorption anisotropy related to excitons measured in a film covered with a 150 nm Al layer measured at 520 nm with 470 nm excitation.

cay of exciton polarization memory, and shows that polaron diffusion is much slower than exciton diffusion.

There is a significant difference between polaron absorption anisotropy values measured at different conditions. The polaron absorption is almost depolarized under 387 nm excitation. 387 nm excitation creates high energy "blue" excitons which very rapidly (few hundred femtoseconds) transfer their energy to lower energy excitons and therefore loose the polarization memory.[30] This sets the time scale of field-free polaron formation in *m*-LPPP with blue-wing excitation to at least a few hundred femtoseconds. Thus, when the main absorption of the polymer is excited a few energy transfer steps are required to reach the impurities where polaron formation occurs. This picture is somewhat reminiscent of the dissociation site model developed for a polythiophene polymer[31] to describe exciton dissociation at sites having very low exciton binding energy. However, the concentration of dissociation sites in the polythiophene polymer was very low and energy transfer slower, resulting in the slower overall polaron formation (tens of picoseconds).

Observation of the high polaron absorption anisotropy under 470 nm excitation is only possible if the field-free polaron formation time, is much, shorter than the exciton depolarization time, i.e., much shorter than 1 ps. This suggests that polaron generation occurs directly at the optically excited polymer segments that are in contact with the electron accepting impurities, perhaps through charge transfer states formed by polymer-impurity interaction. The long-wavelength absorption "tail" appearing in aged *m*-LPPP samples (see inset in Fig. 1) with high concentrations of impurities is another indication of the presence of such states and their role in field-free polaron pair generation.

The field-induced polaron generation leads to much lower polaron absorption anisotropy. As it was already discussed, this generation mechanism is in competition with the generation on impurities. The main contribution to the field-induced polaron generation comes from mobile excitons, which split into polaron pairs dominantly after depolarization on a picosecond time scale, in agreement with the polaron generation model developed in Refs. 8, 11, 13, and 14

Electron-hole recombination and its electric field dependence is another important aspect of the polaron dynamics. Figure 2 shows that the recombination rate is independent of polaron concentration, suggesting that the recombination is a geminate. A similar conclusion was reached by Muller *et al.*[13] on the basis of transient photocurrent measurements. This implies that the majority of the generated polarons remains within the Coulomb attraction field of the counterion. From Fig. 2, we also see that the polaron concentration decays in a nonexponential process and as it was discussed above, the decay may be fitted by a biexponential function. However, considering the disordered nature of the polymer film, it may be physically more appropriate to use a stretched exponential function $\exp(t^{-\alpha})$ for the fit, which gives also a good agreement with experimental data. Thus, a distribution of charge separation geometries of the polymer chain and impurity results in a variation of the lifetime of the charge pairs from 0.8 ns to tens of microseconds.[16,17] As Fig. 1(b) shows, the excited species with the 0.8 ns lifetime is observed at 720 nm, where "normal" polaron absorption is absent.[11,14] Evidently, the species with the shortest lifetime has a distinct redshifted spectrum; this species can hardly be attributed to some other excited state, such as singlet or triplet excitons, because the lifetime is too long for singlet excitons and too short for triplet excitons, the latter having lifetimes of the order of milliseconds and a yield of only 0.2%.[32–34] Moreover, the 0.8 ns species was observed only in polymer films with high impurity concentration. A redshifted absorption spectrum and fast relaxation can be understood to be consequences of a tightly bound polaron pair—a short distance between the positive and negative ions of the polaron pair is expected to give rise to a modified spectrum as compared to a more loosely bound polaron pair as well as fast recombination. Tightly bound polaron pairs with a broader absorption spectrum were also observed and attributed to interchain pairs formed by electron transfer to a neighboring oxidized chain.[25] Excited species with similar lifetime observed by time resolved fluorescence were also attributed to aggregate states[35] or to on-chain chemical defects.[36]

Although the 15 ns time window used in the present measurements only captures the initial part of the recombination dynamics, in total extending into the microsecond time range,[17] we can obtain useful information about the recombination and charge transport through the film. Comparison of the electric field influence on the polaron decay kinetics in films covered with thick and thin Al layers reveals different contributions to the field dependent dynamics. In samples with the thin aluminum layer possessing high defect density, the electric field slows down the polaron decay. The inset in Fig. 4(b) shows that the polaron decay rate decreases by

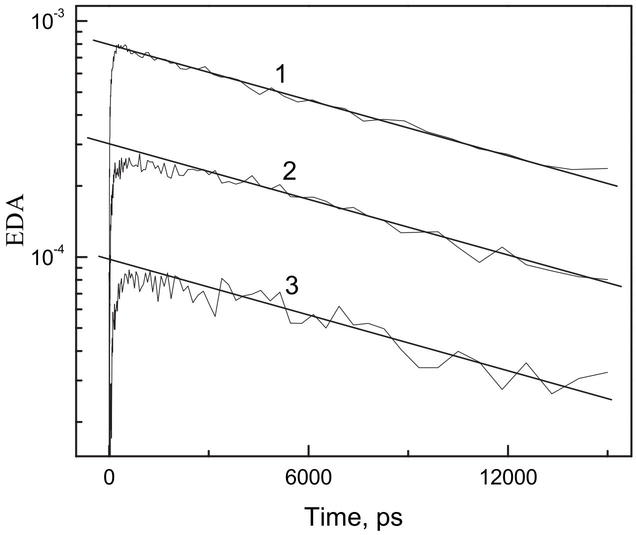

FIG. 6. EDA kinetics at different excitation intensities of a film with a 150 nm Al layer at 15 V applied voltage. (1) 0.3 mJ/cm^2, (2) 0.1 mJ/cm^2, and (3) 0.03 mJ/cm^2.

increasing applied voltage, suggesting that the electric field separates polaron pairs and prevents them from recombining. Thus, the main electric field influence on the photoconductivity in films with high impurity concentration is manifested by prolongation of the polaron lifetime rather than by field induced polaron generation.

In the sample with the thick Al layer, the field influence on the polaron decay is more complex [see Fig. 4(a)]. At low applied voltage, the electric field slows down the polaron decay, while at high voltage the polaron decay rate increases again. By comparing the kinetics of Figs. 4(a) and 4(b), we see that the slowing down of polaron recombination at low electric field (<10 V) is more pronounced for the polarons formed through field assistance, as compared to polarons formed via the field free mechanism. This is an understandable result since polaron pairs generated by field assistance are initially aligned along the electric field, while pairs generated on impurities have random orientations.

Two processes may be responsible for the faster decay at very strong applied field for electric-field generated polarons in pristine film: nongeminate polaron pair recombination and charge extraction from the sample. We can eliminate the first process because the decay rate, as Fig. 6 shows, does not depend on the excitation intensity and thus on the polaron concentration. The polaron decay rate observed at very high voltages suggests their extraction time being of the order of several nanoseconds. This estimation is in good agreement with the hole mobility of about 10^{-3} cm^2/V s in *m*-LPPP polymer.[37] We do not observe fast polaron density decay related to their extraction in samples with high defect density. This may be due to two reasons. First, the presence of defects reduces the charge carrier mobility. Indeed, about ten times lower mobility was determined from dynamic Stark shift measurements in samples kept in ambient atmosphere for several months.[38] Second, the created on impurities polaron pairs, which dominate observed polaron absorption in the samples with high defect density, are strongly bound and do not produce free mobile polarons. The later explanation is in line with the conclusion made in Ref. 35 that emissive aggregate states do not contribute to photocurrent.

CONCLUSIONS

Polaron generation and recombination dynamics on the subpicosecond to tens of nanosecond time scale was investigated in *m*-LPPP polymer films by means of ultrafast electromodulated transient absorption spectroscopy. From the present studies and previous studies,[14,20] the following characteristics were identified.

(1) There are two modes of polaron formation with distinct behavior, impurity induced in the absence of an external electric field and electric field induced in pristine film.

(2) The efficiency of impurity induced polaron pair generation is up to 20%.

(3) The efficiency of field induced polaron pair generation depends on the strength of the applied electric field.

(4) Impurity induced charge formation at zero applied field competes with field induced charge generation.

(5) Field induced charge generation is relatively slow, occurring throughout the excited state lifetime,[14,20] while impurity induced charge generation occurs on the subpicosecond time scale. Light absorption in the red wing of the absorption spectrum excites impurity induced charge transfer states, which form polarons in the absence of an applied electric field within the time resolution of the experiment, <100 fs. Impurity induced charge formation following main band excitation occurs on the few hundred femtosecond time scales after a few energy transfer steps.

(6) Polaron decay through geminate electron-hole recombination occurs with widely distributed lifetimes, from ~0.8 ns to microseconds; the polarons characterized by the shortest decay time have a redshifted absorption spectrum (as compared to more long-lived polarons) and are attributed to tightly bound polarons.

(7) Polaron decay acceleration observed on a nanosecond time scale at strong electric field should be related to the charge carrier extraction from the film with the rate consistent with a hole mobility of approx. 10^{-3} cm^2/V s.

ACKNOWLEDGMENTS

The work was supported by the Agency for International Science and Technology Development Programmes in Lithuania, Swedish Energy Administration, the Swedish Research Council, the Crafoord Foundation, and EU LASERLAB Europe access program Contract No. RII3-CT-2003-506350.

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