

Femtosecond transient absorption study of oriented poly(9,9-dioctylfluorene) film: Hot carriers, excitons, and charged polarons

S. Xu, V. I. Klimov, B. Kraabel, H. Wang, and D. W. McBranch

Chemical Science and Technology Division, CST-6, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We present a transient absorption spectroscopy study of oriented poly(9,9-dioctylfluorene) film. By comparing the spectral features and dynamics at different wavelengths using different probe polarizations, we conclude that three species are generated after the photoexcitation: hot carriers, excitons, and charged polarons. The charged polaron spectrum is measured with the probe beam polarized perpendicular to the polymer chains, and two bands are recognized. In addition, a new band in mid-IR regime is observed that decays faster than excitons, and whose peak shifts in time. This feature is assigned to hot carriers.

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Conjugated polymers have emerged as a promising class of optoelectronic materials, due to their low manufacturing costs and the wide range over which their optical and electronic properties may be chemically tuned by altering the side-groups on the polymers. Conjugated polymers have been used in devices such as light-emitting diodes,^{1,2} light-emitting electrochemical cells,³ photodiodes,⁴ and lasers.⁵ However, the quantum efficiency of the devices made from conjugated polymers is generally low, and the photophysics of these materials is still not well understood.^{6,7} A deeper understanding of the photophysics is vital in order to improve device performance.

Although many groups have been studying the photophysics of conjugated polymers over the past two decades, many questions remain.⁸ For example, it is still subject to debate whether the initial photoexcitation is band-like (free carriers) as in semiconductors⁹ or excitonic in nature as in molecular solids.¹⁰ It is generally accepted that photoluminescence is generated by intrachain excitons and that the formation of secondary interchain species (nonradiative excitations) occurs in varying degree depending on the molecular morphology of the polymer chains within the film.^{6,7,11,12} The interchain species have been studied in detail in a number of PPV derivatives,¹³⁻¹⁵ but there is still no consensus regarding its fundamental description. Understanding its nature and formation mechanism is important for improving the quantum efficiency of conjugated polymers.

In this paper, we present a femtosecond transient absorption study of oriented Poly(9,9-dioctylfluorene)(PFO) film, from 400 to 2700 nm, and with the probe polarized both parallel and perpendicular to the polymer chain. For the first time, we observe two bands in mid-IR regime. In addition to fully resolving the exciton band previously reported as an incomplete band due to the limited spectral range of prior measurements,¹⁶ we observed a new band that decays faster than the exciton and whose peak shifts in time towards the exciton peak. Furthermore, by probing with the polarization perpendicular to the polymer chains, we separate the spectrum of nonradiative excitons from that of radiative intrachain excitons, and observe two photoinduced absorption bands in visible spectral regime. The dichroic ratio of these two photoinduced absorption bands rules out the assignment of these two bands to the interchain exciton.

The femtosecond (fs) transient absorption (TA) experimental setup has been described in detail in an earlier publication.¹⁷ Briefly, we used an amplified Ti:sapphire laser (Clark-MXR) with an optical parametric amplifier (OPA) to generate tunable visible to mid-IR pulses. The samples are photoexcited at 400 nm. A half-wave plate and polarizer are used in both pump and probe beams to change the polarization of pump beam and probe beam separately. Chirp-correction is performed¹⁷ to ensure that the transient absorption signals at different wavelengths correspond to the same time delay. The oriented PFO film is seated in a cryostat at liquid nitrogen temperature and kept under vacuum (5×10^{-6} Torr) to reduce photodegradation. By analyzing linear absorption spectra measured under different polarizations, we find that the anisotropy of our oriented PFO sample is between 0.5 and 0.6. The TA signals of four polarization combinations are measured: (1) both pump polarization and probe polarization parallel to the sample orientation; (2) both perpendicular to the sample orientation; (3) pump polarization parallel but probe polarization perpendicular to the sample orientation; and (4) pump polarization perpendicular but probe polarization parallel to the sample orientation. The results with the pump beam polarized perpendicularly to the sample orientation (combinations 2 and 4) are the same as those with the pump polarization parallel to the sample orientation (combinations 1 and 3), except that the signals were about four times smaller. This matches the linear absorption anisotropy, indicating that the decrease of the signal is simply due to decreased absorption. Therefore, the results presented in this paper are only those with the pump polarization parallel to the sample orientation (combinations 1 and 3). In addition, we measured TA spectra and dynamics under different pump intensities and found that the results, especially the dynamics at most of the wavelengths, are strongly dependent on the excitation density. The results and discussions were published in our previous paper.¹² The data presented in the current paper are measured in the same day and under the same pump fluence, 0.38 mJ/cm^2 , far below the photochemical damage threshold, $\sim 160 \text{ mJ/cm}^2$.

As a measure of TA, we use $(-\Delta T/T)$, which is defined as $-(T - T_0)/T_0$, where T and T_0 are the transmission of the probe beam in the presence and absence of the pump beam,

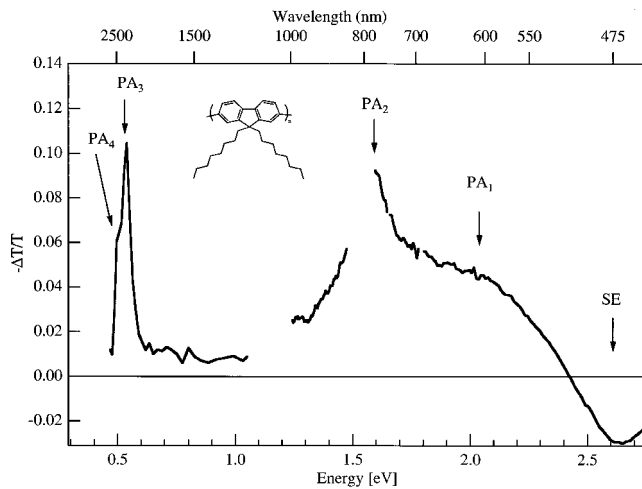


FIG. 1. Transient absorption spectrum of PFO measured with probe beam parallel to the sample orientation (polymer chain direction). SE stands for stimulated emission; PA for photoinduced absorption. The inset shows the chemical structure of PFO.

respectively. A positive TA signal ($-\Delta T/T > 0$) implies the absorption increases following photoexcitation, and is termed photoinduced absorption (PA). A negative TA signal ($-\Delta T/T < 0$) may be caused by either bleaching or stimulated emission. The absorption decrease due to either increasing the population of the upper state or decreasing the population of the lower state (for a given electron transition), or both, is called bleaching (BL). An increase in transmission caused by the amplification of the probe light due to population inversion of an emissive state is called stimulated emission (SE).

The TA spectrum at zero time-delay with the probe polarization parallel to the sample orientation is shown in Fig. 1. Four PA peaks and one SE peak can be distinguished. The four PA peaks are centered at 600 nm (PA_1), 780 nm (PA_2), 2300 nm (PA_3), and 2500 nm (PA_4); and the SE peak is centered at 475 nm (SE). The dynamics of each feature measured under the same pump fluence (0.38 mJ/cm^2) are shown in Fig. 2. The similar dynamics of SE, PA_2 , and PA_4 imply that they originate from the same species. Since only intrachain excitons can generate stimulated emission, it is concluded that these three features are from excited state transitions of excitons. Comparing the dynamics in Fig. 2, we infer that two other species are present, in addition to excitons. One is longer lived than the excitons and has an absorption band around 600 nm (PA_1). The other decays more quickly than excitons and is responsible for the spectral feature around 2300 nm (PA_3).

When the probe polarization is perpendicular to the sample orientation, the transient absorption spectrum in the visible regime changes dramatically [see Figure 3(a)]. Only two photoinduced absorption bands are observed. One is centered at 600 nm and matches the spectral position of PA_1 . The second PA band (labeled PA_5) is below 500 nm in the spectral region where the stimulated emission band (SE) is observed under the parallel probing conditions. The absence of stimulated emission under perpendicular probing conditions can be explained by the dipole orientation of excitons.

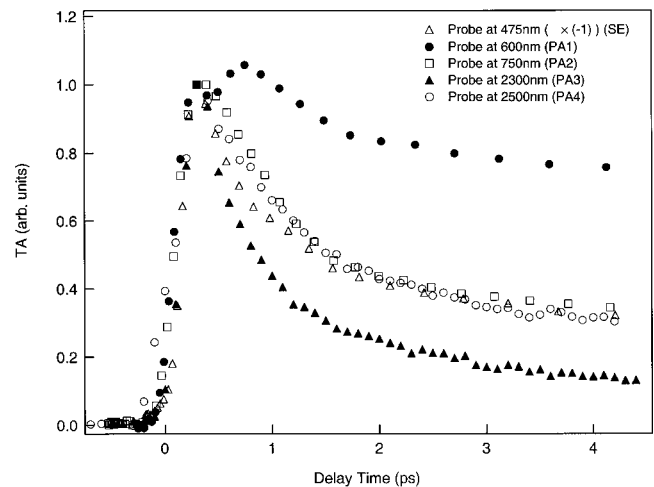


FIG. 2. Decay dynamics of transient absorption signals (after normalization) under the same pump fluence (0.38 mJ/cm^2) but at different wavelengths: (○) 2500 nm; (▲) 2300 nm; (□) 750 nm; (●) 600 nm; and (△) 475 nm [$\times(-1)$]. Both the pump and probe polarization are parallel to the sample orientation (polymer chain direction).

Since the electron and hole of intrachain excitons are situated on the same polymer chain, the dipole moment of intrachain excitons is along the chain, and therefore has a negligible interaction with probe light polarized perpendicular to the chain. The photoinduced absorption bands at 600 nm (PA_1) and 450 nm (PA_5), observed with the probe light polarized perpendicular to the chain, indicate the presence of species having a dipole moment at least partially perpendicular to the chain. However, the magnitude of the PA_1 signal along the chain is still ten times greater than that perpendicular to the chain. This rules out an assignment of this feature to an interchain exciton, i.e., an electron and hole separated onto neighboring chains, with dipole moment across the chains. Both charged polarons and excimers might be expected to have wave functions polarized primarily along the chain, but with an off-axis component greater than that of the intrachain exciton. The single polaron is a localized state with an ellipsoidal wave function slightly extended along the polymer chain,¹⁸ and consequently can have transition dipole moments both parallel and perpendicular to the chain. The excimer is a superposition of the wave functions of excited states of individual chains, and is expected to have a transition dipole moment primarily along the chains, but with an off-axis component depending on the degree of charge separation across the chains. Both polarons and excimers are expected to be longer-lived than excitons, as observed for PA_1 . However, transient absorption studies on DP6-PPV show that the PA_1 signal increases upon doping with C_{60} ,¹² which cannot be explained by the excimer model. Since the TA features for PFO and DP6-PPV are similar,¹² we assign the PA_1 band observed in PFO to polaron absorption.

It is apparent from Fig. 2 that the peak of the TA time scan at 600 nm is shifted to a longer delay time, while its coherent spike is at the same time delay as other decay curves. This implies that charged polarons are not the primary excitations. Upon subtraction of the coherent spike

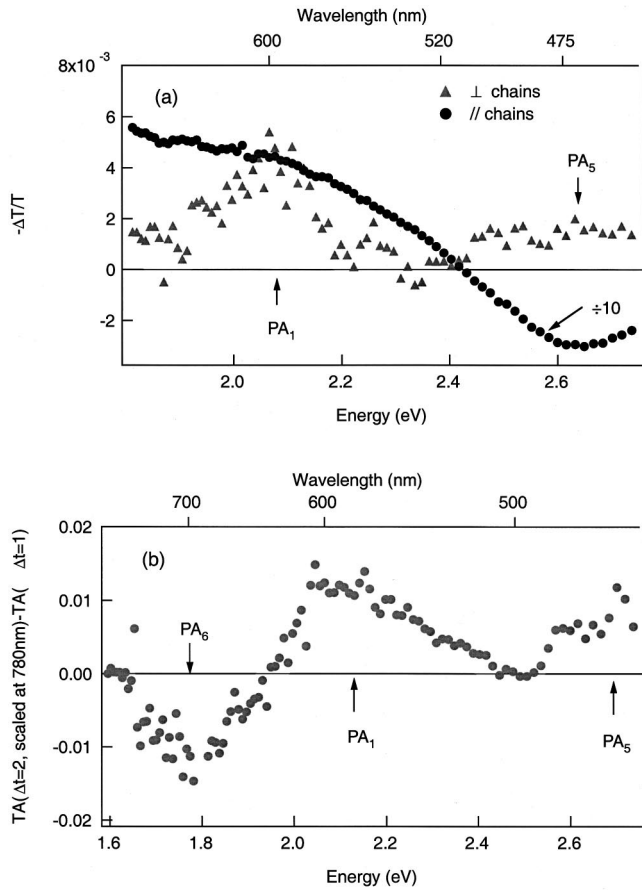


FIG. 3. (a) Transient absorption spectra with probe polarization perpendicular to polymer chains (\blacktriangle) and parallel to polymer chains (\bullet). SE stands for the stimulated emission and PA for photoinduced absorption. (b) The differential spectrum, which is the result of scaling the 2 ps spectrum so that it matches the 1 ps spectrum at 750 nm (the photoinduced absorption given by excitons), and then subtracting it from the 1 ps spectrum. Both the 1 and 2 ps spectra are taken with probe polarization parallel to polymer chains.

(which is due to an instrument artifact¹⁹) using the laser autocorrelation curve, the growth rate of time scan at 600 nm can be fit to a time constant of 350 ± 50 fs.

If we scale the parallel-probe transient absorption spectrum at the delay time of 2 ps so that the intensity of PA_2 (due to the excitonic transitions) matches the spectrum at 1 ps, then subtract it from the spectrum at 1 ps, we obtain a differential spectrum [Fig. 3(b)]. In this differential TA spectrum, the positive peaks are caused by excitations that decay slower than excitons, while the negative peaks are from excitations decaying faster than the excitons. There are two positive bands in Fig. 3(b): one at 600 nm, the other below 500 nm. They match the two bands in the spectrum probed with polarization perpendicular to the chain [Fig. 3(a)]. The equivalent amplitude of these two bands in differential TA spectrum [Fig. 3(b)] demonstrates that they have similar decay dynamics, and suggests they are due to the same species. In addition, we observed a negative band around 700 nm (PA_6) in the differential spectrum [Fig. 3(b)]. The negative sign means the species responsible for this band decays faster than excitons. This band cannot be seen in the TA

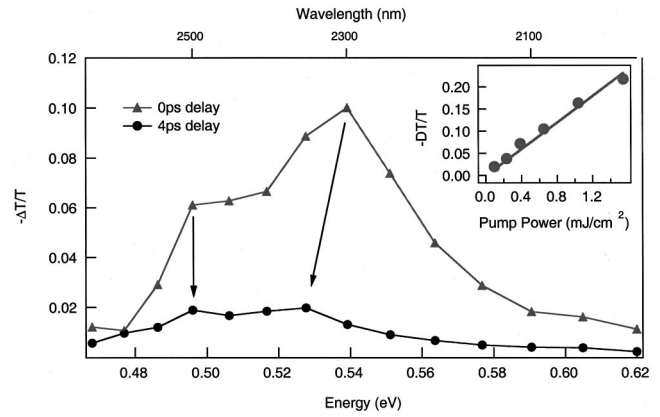


FIG. 4. Transient absorption spectra between 2000 and 2650 nm at 0 ps time delay (\blacktriangle) and 4 ps time delay (\bullet). The probe polarization is parallel to the sample orientation (polymer chain direction). The inset shows the pump intensity dependence of the TA signal at 2300 nm.

spectrum shown in Fig. 1, since it is buried by the strong exciton absorption band around 750 nm. The existence of this short-lived nascent species is more clearly seen in the transient absorption spectrum in mid-IR regime.

Looking in detail at the transient absorption spectrum (Fig. 1) in the mid-IR region, one may discern two closely-spaced spectral features: a peak at 2300 nm with a shoulder at 2500 nm. Interestingly, the decay dynamics at 2300 nm are quite different from that at 2500 nm [see Fig. 2(a)]. The decay of the photoinduced absorption at 2500 nm matches that of the stimulated emission at 475 nm and the photoinduced absorption at 750 nm, implying that it is another excited-state transition of the intrachain excitons, in agreement with reports for PPV.²⁰ However, the decay of the photoinduced absorption at 2300 nm is much faster than that of the intrachain excitons (Fig. 2). The mid-IR photoinduced absorption spectra at different time delays (see Fig. 4) also indicate that there are two species contributing to the transient absorption spectrum in this regime. At zero time delay, there is a strong peak at 2300 nm and a shoulder at 2500 nm. After 4 ps, the peak at 2300 nm dramatically decreases and the peak position shifts towards 2500 nm, while the signal at 2500 nm decreases less and the peak position does not change (Fig. 4). This suggests that there is a nascent species at early time immediately after the photoexcitation, and the shift of the peak position of its spectrum suggests a transient energy relaxation of this state. The linear intensity dependence of the peak intensity at 2300 nm (inset of Fig. 4) indicates that the generation of this species is a single-photon process. In order to subtract the overlapped signal generated from the exciton and get the dynamics of this nascent species, the time-scan at 2500 nm was scaled at longer time delay so as to match that at 2300 nm and then subtracted from the time-scan at 2300 nm. Single exponential fitting of this differential time-scan shows that the lifetime of the nascent species is 150 ± 50 fs.²¹ This matches typical hot carrier relaxation times.²² The spectral shift is also an expected feature of hot carrier relaxation. Thus we propose that the nascent excitations responsible for the photoinduced absorp-

tion at 2300 nm are hot carriers.

The physical picture of the initial photoexcitation process can be described using the Born–Oppenheimer principle. The ground state of conjugated polymers is like a one-dimensional semiconductor. The π electrons are delocalized and the π wave function is uniformly distributed within the conjugation length. When a π electron is excited to the π^* state, this configuration is no longer the most stable one. According to the SSH model,²³ the equilibrium positions of certain atoms shift, which changes the configuration of the polymer backbone and creates a localized phonon field. The excited electron becomes trapped in this local phonon field and forms the polaron. However, the formation of the polaron involves nuclear movement, which is much slower than the electronic transition according to the Born–Oppenheimer principle.²⁴ Hence the initial excitation should have the same configuration as the ground state. As a result, the excited state is initially delocalized and the electron and hole are loosely bound. If the polymer chain does not distort, the excitations are one-dimensional free carriers, just like those in inorganic semiconductors. We call them hot carriers because they resemble carriers in semiconductors and the lattice (the polymer backbone) has not reached its stable equilibrium configuration. However, in some respect, they are

also like Wannier excitons due to finite conjugation length. Hence, the term “hot carriers” we employ here has the same connotation as the term “hot excitons” used in other papers.^{6,25} Here, we observe it experimentally for the first time.

In summary, our results provide a detailed picture of the spectral dynamics in an oriented PFO film. The TA spectra and dynamics obtained with different probe polarizations show there are three species generated after photoexcitation: hot carriers, excitons, and charged polarons. The initial photoexcitation is the hot carrier. It gives rise to the photoinduced absorption at 2300 and 700 nm. The exciton gives the stimulated emission at 475 nm and photoinduced absorption at 750 and 2500 nm. The third species, which we attribute to charged polarons, has two photoinduced absorption bands (600 and 450 nm).

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