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Time-resolved spectroscopy of infrared active vibrations in 2,5-dioctyloxy poly(phenylene vinylene) films

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Abstract

We report on picosecond time resolved spectroscopy of photogenerated infrared active vibrations in thin films of 2,5-dioctyloxy poly(phenylene vinylene). We excited the films by ≃4 ps long pulses of 565 nm laser light with 2×10^{13} photons/cm^2 per pulse and repetition rate of 76 MHz. We then followed the temporal evolution of the infrared active vibrational (IRAV) spectrum using a subsequent, variably delayed, weak tunable IR probe pulses of similar temporal duration. Under these conditions, we show clear spectroscopic evidence for photogenerated infrared active vibrations at times which are shorter than our temporal resolution (<4 ps). We suggest that the transient IRAV absorption is due to secondary polarons formation following exciton dissociation.

Keywords: Infrared active vibrations; Polymer photophysics; Pico-second spectroscopy

1. Introduction

Separate charges in π-conjugated polymers are usually accompanied by a local chemical bond rearrangement and form either charged solitons (in degenerate ground state systems) [1] or polarons (in non-degenerate ground state systems) [2]. These charge defects have a unique signature in the form of strong infrared active vibrational (IRAV) mode absorption in the mid-IR range. The IRAV spectrum is due to the eigen-modes of the polymer chain, for which the oscillator strength is enormously enhanced by the small kinetic mass of the localized charged defect [3]. Furthermore, in neutral defects with similar kinetic masses, such as coherently bound pair of positive and negative solitons [4], the localized modes due to the defect are not IR active, hence no IRAV absorption appears. Photon absorption by either doping induced or photoinduced IRAV has been routinely used to determine the charge state of the defects generated in a variety of polymers, such as polyacetylene [5–8], substituted polyacetylene [9], poly-thiophenes [10], poly-phenylene vinelyne derivatives [11], and pyridine-based polymers [12].

In previous studies we reported picosecond time resolved photoinduced absorption (PIA) by IRAV in poly[2-methoxy-5-(2-ethyl-hexyloxy)-*p*-phenylene-vinylene] (MEH-PPV) and MEH-PPV mixed with C_{60} [13,14]. Using pulsed excitations applied at 76 MHz repetition rate with 2×10^{13} cm^{-2} photons per pulse, we observed the IRAV spectra of polarons within ≃4 ps [14]. Subsequent studies of transient excited state absorption in the IRAV regime under various excitation conditions were reported by several groups. Under very intense pulses at moderately low repetition rate excitation conditions, IRAV absorption spectra were observed within 0.1 ps following the excitation pulse in PPV and PPV derivatives [15–17]. No spectral evolution of the IRAV absorption was observed. Under similar excitation conditions Sakamoto et al. [18] observed evolution of the IRAV spectrum in the 1–10 ps time interval in PPV films. Frolov et al., on the contrary, have shown that by using a very low excitation power and high sensitivity (relative transmission changes $|\Delta T/T| < 10^{-4}$) no IRAV spectrum was observed at room temperature [19] on a ≃5 ps time scale in 2,5-dioctyloxy poly(phenylene vinylene) (DOO-PPV) films. Thus it appears that polaron photogeneration probably depends on the excitation conditions and sample purity, indicating extrinsic charge separation mechanisms.

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In the present work we report on $\simeq 4$ ps time resolved high spectral resolution ($\simeq 1$ meV) [14] PIA spectroscopy in pristine DOO-PPV films at $\simeq 10$ K. We show that the IRAV spectrum is instantaneously (to within our temporal resolution) developed and it decays on a time scale of few hundred ps. We compare our ps IRAV results with recent studies of photoexcitations in the pecosecond and sub-pecosecond time domains and conjecture that the photogeneration of polarons is a secondary process enhanced by the large pump photon density and/or by external defects.

2. Experimental

The time resolved infrared PIA set-up consists of three dye lasers that are synchronously pumped by the same frequency-doubled cw mode-locked Nd/YAG laser (Fig. 1). The pulses from two dye-lasers are difference frequency mixed within a silver thiogallate crystal to produce $\simeq 3$ ps tunable mid-IR (6–12 μm) probe pulses, while the third laser is used to produce the pump pulses. The pump can be independently tuned from the UV through the visible spectral range by using various dyes and second harmonic generation. For the present study, a pulsed R6G dye laser at 565 nm was used for the pump. The system was operated at a repetition rate of 76 MHz and excitation fluence of $\simeq 2\times10^{13}$ photons/cm^2 per pulse, of which approximately half was absorbed by the polymer film. An overall temporal resolution of $\simeq 4$ ps was achieved with this set-up [20].

Polymer films were obtained by dissolving DOO-PPV in chloroform solution and subsequently drop casting onto a specially prepared reference semiconducting superlattice (SL) grown on $\simeq 0.5$ mm thick InP substrate. The polarized photoinduced intersubband absorption of the SL served as a reference signal for calibration and for optimization of the pump-probe overlap [13]. The negative relative differential transmission through the polymer-substrate assembly, $-\Delta T/T$, was used to obtain the PIA of the sample film. The sample was held in a cold-finger cryostat at ambient temperature of $\simeq 10$ K.

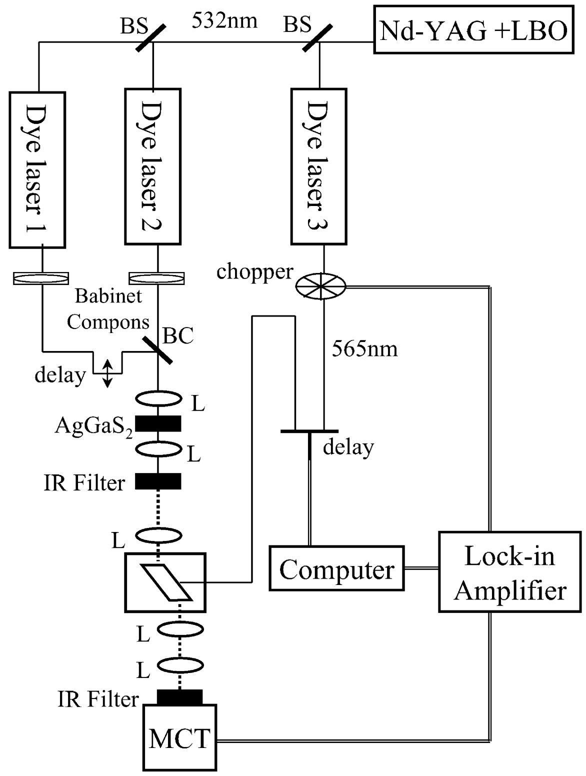

Fig. 1. The picosecond visible-pump/mid-IR-probe experimental set-up. The pulse repetition rate is 76 MHz, and the pulse duration, both visible and mid-IR, is 3–5 ps. The probe energy resolution is better than 1 meV in the 6–12 μm wavelength range.

3. Experimental results

Fig. 2 shows the transient PIA spectra of pristine DOO-PPV in the spectral range of 100–200 meV and time domain of 1–700 ps. The values of $(-\Delta T/T)$, in Fig. 2, are given by the gray color scale bar. Three spectral lines, marked as SL, A and B are clearly observed. The reference SL line at $\simeq 160$ meV is identified from our previous measurements [21]. The other two PIA bands are due to the photoinduced IRAV in the polymer: a relatively narrow line (A) at $\simeq 185$ meV and a much broader line (B) peaking at $\simeq 120$ meV. Similar IRAV lines were observed under steady state excitation conditions, and identified as due to photogenerated polarons [11,13]. All PIA features are instantaneous to within our temporal resolution.

Fig. 3 shows several PIA spectra at selected delay times as marked in the figure. Again, the spectra show the photoinduced SL, A and B absorption bands. It is readily seen that already at a delay time of 3 ps all three PIA bands are resolved. The PIA bands decay with characteristic

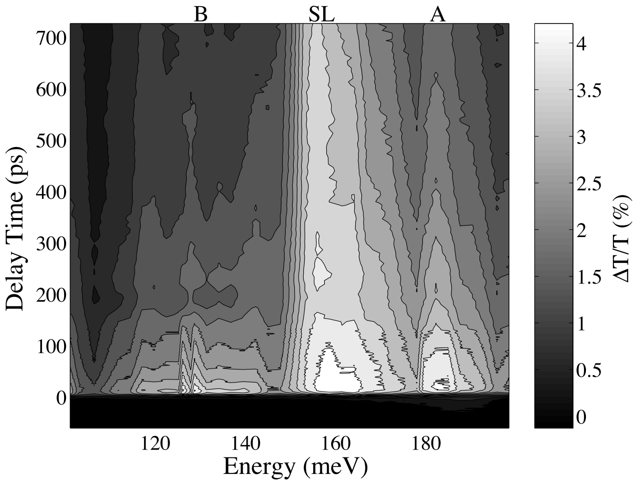

Fig. 2. Picosecond PIA as a function of probe photon energy and delay time for DOO-PPV film at 10 K. The PIA magnitude is given by the gray color scale bar on the right. SL marks the photoinduced SL inter-subband absorption, A and B mark the polymer photoinduced IRAV lines.

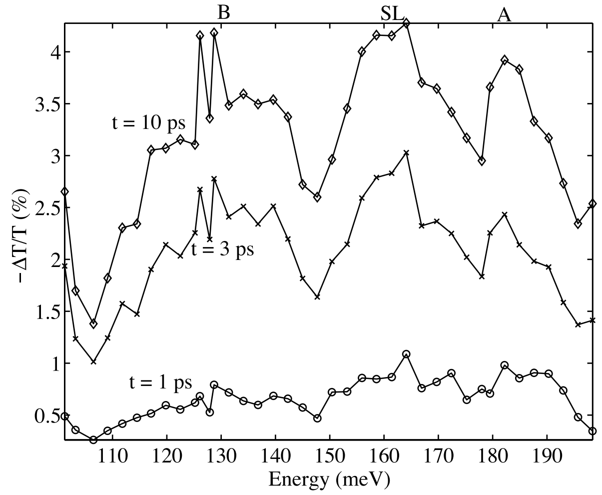

Fig. 3. Picosecond PIA spectra at selected probe delay times for DOO-PPV films at 10 K.

lifetimes which are shorter than the time interval between two consecutive pulses (≃12 ns), as can be seen from their reduced intensity in the negative delay time spectrum (the −1 ps curve).

Fig. 4 shows the temporal evolution of the PIA bands on a 1–160 ps time interval. As expected, the SL reference line shows a decay time of the order of 1 ns [20]. The IRAV bands, decay on a somewhat shorter time scale, where line B appears to decay somewhat faster than line A.

4. Discussion

In π-conjugated polymers charged excitations, such as polarons, locally convert the symmetrical Raman active modes into IR active vibrations [3]. On the other hand, neutral excitations such as a pair of positively and negatively charged solitons [4] or excitons [22], do not lead to such a conversion and consequently do not show IRAV. IR absorption is possible once the wavefunctions of the species that constitute the pair become ‘incoherent’ and the charges can be considered as separated. Photoinduced or doping induced IRAV absorption serves, therefore, as a unique evidence for the photogenerated charged excitations.

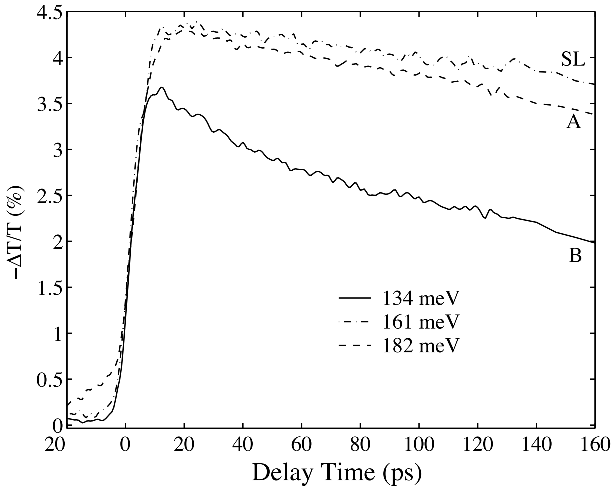

Fig. 4. Picosecond transient PIA probed at the peaks of the A, B and SL bands, shown in Fig. 2.

In this respect, the data presented here give an unambiguous evidence for the presence of separated polarons in DOO-PPV on a time scale of less than 4 ps following pulsed excitation. The data, however, do not give any clue as to the sequence of events prior to that time scale.

The efficiency at which polarons are produced following pulsed photoexcitation may depend on various factors, such as the excitation photon fluence, the presence of charge traps and ambient temperature. Ultrafast charge generation may occur either via direct charge separation of the excitons via static quenching at existing defects or by sequential transitions to highly excited state which dissociate quickly [23]. Recent studies in the sub-ps time domain [24] indicated that such effects are already operative at exciton densities as low as 10^{18} cm^{-3}. In addition, in the presence of impurities, high density of long lived photogenerated trapped polarons and triplet excitons may be created at low temperatures by the intense excitation. These long-lived species may serve as exciton quenchers, thereby giving rise to fast polaron formation.

The time resolved PIA measurement presented here for DOO-PPV were performed at 10 K with moderately intense pulses at a repetition rate of 76 MHz. Using the SL absorption as a calibration for the photon fluence through the polymer and the magnitude of the measured $\Delta T/T$, we estimate the polaron density to be $\simeq 10^{18}$ cm^{-3} per pulse. Under these conditions, it is plausible that the observed IRAV absorption is due to secondary photogenerated polarons that are the result of the high fluence induced exciton disintegration.

Finally, our results differ from those reported in Ref. [19], in which no IRAV spectrum was observed within ≃5 ps after the photoexcitation of similar films of DOO-PPV at room temperature. In addition, in our sample we do not observe any spectral evolution of the IRAV absorption, as reported in Ref. [18], where temporal evolution of the IRAV spectrum of PPV films took place during 1–10 ps after the excitation. These differences in the experimental results may indicate that polaron formation following photoexcitation of conjugated polymers is a secondary process that may depend on sample and excitation conditions.

5. Summary

We used picosecond time resolved PIA spectroscopy to measure transient infrared active vibrations in pristine films of DOO-PPV. We found evidence for polaron formation already within the 4 ps duration of the excitation pulse.

These charge carrying polarons are possibly formed by a fast disintegration of the initially photoexcited excitons.

Acknowledgements

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