

Assignment of the picosecond photoinduced absorption in phenylene vinylene polymers

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 (Received 1 September 1993)

We report results of time-resolved photoinduced absorption experiments on oriented poly(2-methoxy-1,4-phenylene vinylene) films using probe energies from 0.2 to 2.3 eV. We observe two photoinduced absorption bands centered near 0.5 and 1.5 eV which form within our time resolution (< 1 ps) and decay with a fast (ps) and a slow (ns) component. The relaxation dynamics for the two bands are *identical*, indicating they are from the same excited species. On the basis of the spectra, the dynamics, and the pump intensity and polarization dependences, we conclude that these absorption features are due to bound polaron pairs and not to singlet or triplet excitons as previously suggested.

Conjugated polymers hold promise as quasi-one-dimensional semiconductors with chemically tunable optical and electronic properties.^{1,2} One of the most exciting examples is the development of electroluminescent devices based on poly(para-phenylene vinylene)s (PPVs).³ A thorough understanding of the photogeneration and charge transport processes is needed in order to further advance PPV-based light emitting devices. Although a substantial amount of experimental⁴⁻¹⁰ and theoretical¹¹ work has been reported for PPVs, a consistent picture for the overall electronic excitation processes has yet to emerge. In this paper, we report results of time-resolved photoinduced absorption (PA) experiments on oriented poly(2-methoxy-1,4-phenylene vinylene) (M-PPV) films, emphasizing the relaxation dynamics of neutral excitations in the ps regime. Well-aligned samples allow us to study the anisotropic behavior of the photoexcitation dynamics, which is useful for comparison with other oriented conjugated polymer systems.

Because of the luminescent characteristics of PPVs, many experiments have been performed to study photoluminescence (PL) dynamics.⁴ However, these measurements probe only the luminescent excited species, which are usually a small fraction of all the excited species created by photoexcitation. Studying PA in the ps regime, a complementary experiment to PL, enables us to minimize the importance of extrinsic effects and to address the nature of photogenerated species immediately upon excitation as well as subsequent relaxation dynamics. Millisecond PA (Ref. 5) and PA detected magnetic-resonance studies⁶ have identified long-lived triplet excitons and bipolarons in PPVs. Recently, ps PA results on unoriented PPV derivatives in the 1.0–2.5 eV spectral range have been reported.^{7,8} A single photogenerated absorption band at ~ 1.5 eV was observed and ascribed to triplet and/or single exciton absorption.^{7,8} In this paper, we report a new transient PA band in the mid-infrared (~ 0.5 eV) which has dynamics identical to those of the 1.5-eV PA band. The observation of this mid-infrared PA band casts doubt on the previous interpretation of the

ps PA. We assign the origin of these PA bands to photo-generated polaron pairs,^{9,10} which are formed with a large quantum yield. The anisotropy data show that these polaron pairs are created in greater quantity for excitation with light polarization orthogonal to the polymer chains.

The samples are fully converted M-PPV films; synthesis via polymerization of 2-methoxy-*p*-xylylene bis(tetrahydrathiophenium chloride) has been described elsewhere.¹² The time-resolved photoinduced absorption experiment was performed on oriented, free standing films, about 5 μm thick with an 8:1 stretch ratio, sandwiched between two CaF_2 plates. The data were obtained using an amplified synchronously pumped dye laser that produced 300-fs pulses of “white light continuum” to be used as a broadband probe. For the mid-infrared probe pulses, this white light was difference frequency mixed with 605-nm pulses in LiIO_3 to obtain tunable radiation from 0.2 to 0.5 eV. PA, or the change in transmission ($\Delta T/T$), was measured using two photodiodes to detect both the probe and, for normalization, a reference pulse which did not pass through the sample. The samples were excited with 300-fs pulses at 605 nm (2.05 eV) or 100-ps pulses at 532 nm (2.33 eV). The probe polarization was fixed parallel to the chain direction, while the pump polarization was varied with a half-wave plate. The maximum energy of the excitation light was 5–10 μJ per pulse over an $\sim 1\text{-mm}^2$ beam spot. When performing experiments on pump intensity dependence, the excitation beam was attenuated and its intensity was measured at the sample position prior to introducing the sample.

Figure 1 shows the steady-state fluorescence spectrum and the PA spectrum [the change in optical density, $\Delta \text{O.D.} \equiv -\log_{10}(1 + \Delta T/T)$] from 0.2 to 2.5 eV at 200 ps delay acquired with parallel excitation at 2.05 eV and parallel probe polarization. The absorption edge of M-PPV occurs at 2.2 eV, red shifted ~ 0.25 eV with respect to that of unsubstituted PPV. Vibronic structure which has been associated with backbone carbon stretching

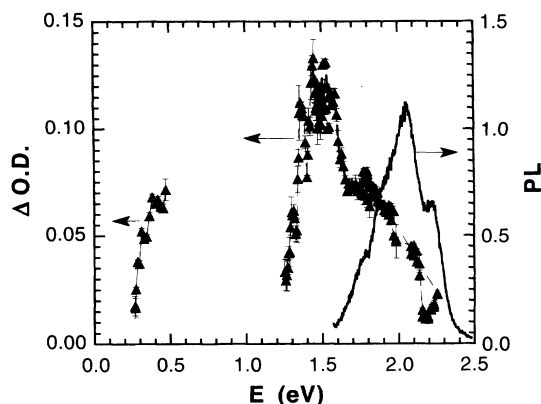


FIG. 1. Steady-state PL spectrum, using 3 eV excitation energy with polarization parallel to the chains, and PA spectra taken at 200 ps delay with 2.05-eV parallel excitation. PA clearly shows two bands centered around 0.5 and 1.5 eV.

modes in PPV (Ref. 13) is also visible in the M-PPV emission spectrum. It appears that methoxy substitution on the phenyl ring shifts the absorption and emission energies rigidly without affecting the vibronic features or the excited state geometry. PA is strongly polarized along the polymer chain direction. When probing with perpendicularly polarized light, the PA signal is at least one order of magnitude smaller than that obtained with parallel probe light. The PA spectra consist of two bands, one at ~ 1.5 eV and one at ~ 0.5 eV, apparently peaking just out of our experimental reach. The PA peak at 1.5 eV is similar to previously reported ps PA results on other PPVs,^{7,8} but the mid-infrared band at 0.5 eV has not been reported before to our knowledge.

Figure 2 shows the 1.5-eV PA band with both parallel and perpendicular polarized excitation at 2.33 eV and probing at 200 ps delay. The sharp feature at 1.6 eV is an experimental artifact due to stimulated Raman scattering in the water used to generate a white light continuum, causing photodiode saturation. The dip at 2.2 eV is intrinsic to M-PPV and coincides with the absorption edge of the parallel direction. Since the probe light is parallel to the chain direction, it is strongly absorbed by the sample at this energy. Therefore, the PA signal at this energy

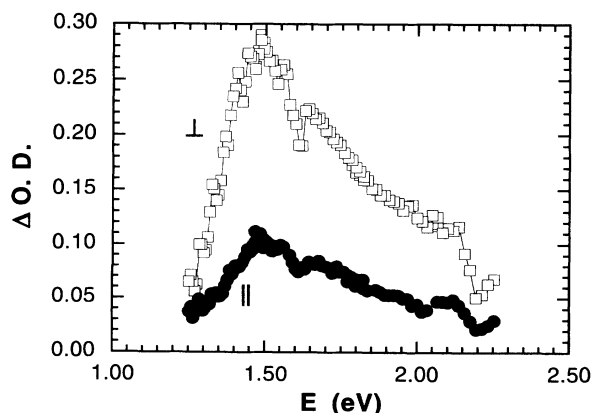


FIG. 2. PA spectra taken at 200 ps delay with 2.33-eV excitation parallel and perpendicular to the stretch direction.

is a combination of excited-state absorption and depletion of ground-state population (bleaching). It should be pointed out that when exciting with 2.33-eV light, pump light of either polarization is absorbed completely by the M-PPV film. However, the perpendicular polarization pump generates an ~ 3 times larger PA signal than the parallel (Fig. 2). Apart from this magnitude difference, the two spectra are identical, indicating that the excited species responsible for the PA signal is independent of the pump polarization. Furthermore, varying the pump energy from 2.05 eV to 2.33 eV does not affect the PA spectra (Figs. 1 and 2).

Figure 3(a) shows the PA dynamics with 1.55-eV (800 nm) and 0.29-eV (4.3 μm) probes from -100 to 500 ps. Remarkably, *the dynamics of the visible and the infrared PA features are identical, clearly indicating that they are due to the same excited species.* The PA signal appears within the resolution of our experimental apparatus (~ 1 ps) with no detectable rise time. The PA decay dynamics consist of a fast and a slow component for all probe wavelengths we have studied. The solid line in Fig. 3(a) is a biexponential fit with a short-time constant, ~ 10 ps, and a long-time constant, ~ 1.2 ns. The two-rate fit is not to suggest two underlying processes, nor to rule out other functional forms. We merely emphasize that the PA decay is not a single exponential function. The PA spectrum at zero time is very similar to that shown in Fig. 2, with slightly more weight in the blue. For comparison, Fig. 3(b) depicts the PL decay dynamics with 2.5-eV (500 nm) excitation for M-PPV as measured by a streak camera with ~ 20 -ps resolution.

Figure 4 shows the dependence of Δ O.D. on pump intensity at 200 ps delay for parallel excitations with pump

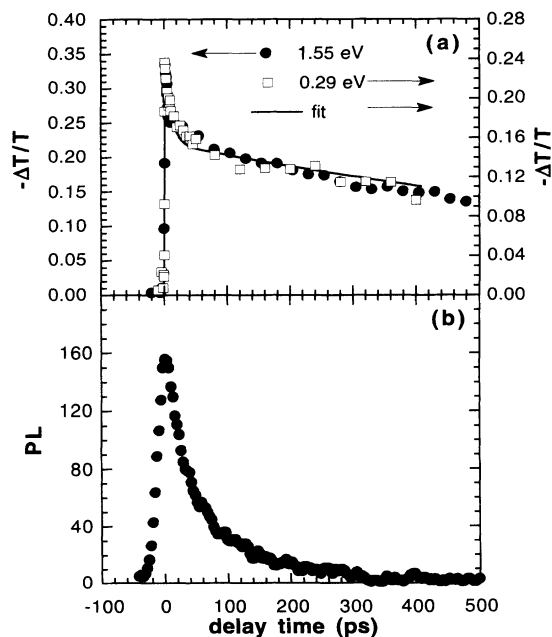


FIG. 3. (a) PA dynamics at 1.55 eV probe energy (solid circle) compared to those at 0.29 eV probe energy (open square). The solid line is a biexponential fit to the 0.29-eV dynamics with $\tau_1 \sim 10$ ps and $\tau_2 \sim 1.2$ ns. (b) PL dynamics taken with a streak camera is shown for comparison with PA dynamics in (a).

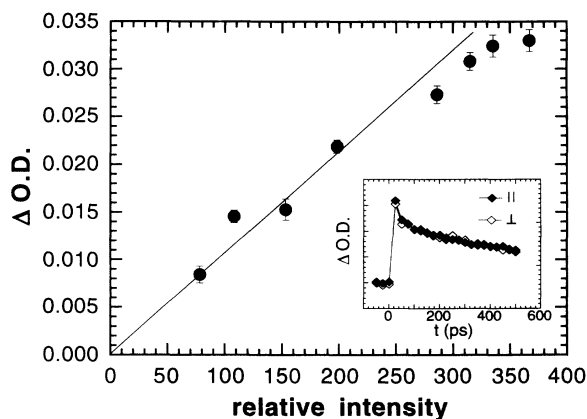


FIG. 4. PA signal at 0.29 eV probe energy as a function of excitation intensity (parallel polarization). The line is a guide to the eye for a linear intensity dependence. The intensity dependence for 1.55 eV probe energy is similar. The inset shows the PA dynamics with 2.05-eV parallel and perpendicular excitation and 1.55-eV probe.

energy of 2.05 eV and probe energy of 0.3 eV. It clearly shows a linear dependence at low intensities ($\leq 10^{15}$ photons/cm²) and becomes sublinear at high intensities. Superlinear pump intensity dependence was never observed in our study. The inset to Fig. 4 depicts identical PA dynamics for parallel and perpendicular excitation.

The similarity between the spectrum of the ps PA band at 1.5 eV and that of the millisecond transient absorption at 1.5 eV, which is known to be triplet exciton absorption,⁵ has led Sinclair *et al.* to assign the ps PA to the same transition of triplet exciton absorption.⁷ Samuel *et al.* observed considerably more spectral dynamics and assigned the 1.5-eV PA to a combination of singlet and triplet excitons.⁸ In light of our data, we believe that these interpretations of the PA are incorrect and discuss the reasoning and alternative explanation below. First, we believe that triplet excitons can be ruled out as an explanation of the 1.5-eV PA on the basis of the concomitant mid-infrared (0.5 eV) band which is not a feature of the triplet excitons observed in PA detected magnetic-resonance experiments in PPVs.⁶ Second, the immediate (sub-ps) appearance of the PA band is too fast for spin-forbidden intersystem crossing. Such rapid intersystem crossing is unprecedented in organic systems. To rationalize the rapid appearance of the triplet exciton absorption, Sinclair *et al.*⁷ and Samuel *et al.*⁸ have compared the PPV PA dynamics to those of polydiacetylene where the triplet PA signal was observed within 3 ps after excitation.¹⁴ This fast formation of triplet excitons has been explained by the creation and recombination of free electron-hole pairs¹⁵ or, alternatively, by spin-conserving fission of a highly excited singlet exciton into two triplet excitons.¹⁶ In either case, it is necessary to excite far above the absorption edge, e.g., using 3.94-eV excitation or two-photon (at 1.97 eV) excitation in polydiacetylene-toluene-sulfonate (PDA-pTS). Contrary to PDA-pTS, M-PPV shows linear to sublinear PA dependence on the excitation intensity (Fig. 4). This rules out any photoexcitation processes due to two-photon absorption. Our ex-

citation energy (2.05–2.33 eV) is too low to create two triplet excitons by singlet fission. Moreover, the explanation of free electron-hole pairs is unlikely for M-PPV given the subpicosecond appearance of the PA. Therefore, we feel that the picosecond PA cannot be due to triplet excitons.

Singlet excitons can also be ruled out as an explanation for the PA. The first supporting evidence is that the PA decay dynamics are distinctly different from the PL decay which measures the disappearance of singlet excitons (Fig. 3). Moreover, when cooling to 77 K, the PA decay is virtually unchanged while PL decay is significantly slower with increased luminescence (singlet exciton) yields. In addition, we observe no signature of a contribution from stimulated emission in our measurements even though the PL spectrum overlapped with the blue portion of the 1.5-eV PA band. Evidently, the PA in the ps regime is not due to singlet excitons and is probably from a species created with a higher quantum yield.

Bipolarons in PPV exhibit millisecond PA bands at 0.6 and 1.6 eV. However, the linear intensity dependence and the immediate formation time of the PA signal strongly argue against assigning these picosecond PA features to bipolarons. Experimental work by Bassler *et al.* on negatively charged phenylenevinylene oligomers also found bands at 0.6 and 1.6 eV, presumably due to singly-charged species (polarons).¹⁷ If PA were from individual polarons, the decay dynamics would be bimolecular because it takes two polarons to recombine and return to ground state. The PA dynamics for both parallel and perpendicular excitation are identical (cf. inset to Fig. 4) even though the excitation densities differ by over an order of magnitude, ruling out bimolecular recombination kinetics. In addition, Frankevich *et al.*⁹ have shown that the number of photogenerated carriers is thermally activated and therefore could not occur so rapidly or with such a high yield, in contradiction with PA being due to polarons.

Having ruled out other explanations for the instantaneously photoexcited species, we propose that the observed ps PA is due to polaron pairs.^{9,10} A polaron pair consists of a positively and a negatively charged polaron which reside on separation conjugation segments but do not act independently because they are still close enough to interact with each other. Upon photoexcitation, both singlet excitons and polaron pairs are formed immediately, with branching ratios depending on the excitation energy. The existence of polaron pairs has been proposed by two groups^{9,10} to understand charged excitations in PPV and related polymers. Presumably, these polarons are separated by barriers so that the positive- and negative-charge parts of the wave functions do not overlap and the probability of emission is small. One possibility for the microscopic origin of such a barrier is a conjugation interruption, e.g., a photoinduced partial ring twist. Such inclusions have been proposed to stabilize similar photogenerated charged pairs in polyanilines.¹⁸ The Coulomb binding force between the charges must be sufficiently strong so that nearly all polaron pairs geminately recombine, resulting in the linear intensity dependence of the PA. We presume that the recombination of

the polaron pairs is mostly nonradiative. We have, however, observed a small amount of exciton luminescence [unobservable on the scale of Fig. 3(b)] lasting to > 50 ns which is linear in pump intensity.¹⁹ This small delayed luminescence could be due to singlet excitons which derive from polaron pairs.

Little is known, either experimentally or theoretically, about the exact energy positions of the absorption features for polaron pairs. The position of the first even-parity excited state (S_2) of PPV has been determined to lie 0.5 eV above the lowest singlet excited state (S_1) based on two-photon fluorescence experiments.²⁰ Since polaron pairs are bound electron-hole pairs analogous to excitons but with less overlap between the electron and hole wave functions, it may be that the excited-state manifolds of singlet excitons and polaron pairs are similar, with the 0.5-eV absorption analogous to the S_1 to S_2 transition. We also do not know whether the correlation of the picosecond PA bands with bipolaron⁵ and isolated negative polaron spectra is fortuitous.

In summary, picosecond transient absorption spectroscopy in the mid-infrared as well as in the visible-infrared

has provided new insight into the nature of the excited species formed by photoexcitation of PPVs. We observed immediate appearance (≤ 1 ps) of PA bands at 0.5 and 1.5 eV. The decay dynamics are identical at both energies and consist of a fast (≤ 10 ps) and a slow (≥ 1 ns) component. Transient dynamics, spectra, and pump intensity dependence rule out triplet excitons and bipolarons as an explanation for the ps PA. Due to the lack of gain and the dissimilar PL and PA decay dynamics, we attribute the ps PA to polaron pairs and not luminescent singlet excitons. The polaron pairs are created with a large quantum yield and decay primarily on a subnanosecond time scale via geminate nonradiative recombination. No evidence of substantial triplet exciton or bipolaron formation was observed in the first 500 ps after photoexcitation.

The authors wish to thank Professor R. Alfano for lending us the streak camera for PL dynamics measurements. We also acknowledge helpful discussions with H. Antoniadis, E. Conwell, Z. Soos, I. Sokolik, V. Vardeny, and W. Wilson.

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