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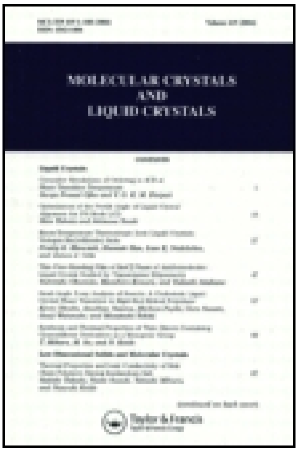

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Short-Lived Photoinduced Excitations in Trans-Polyacetylene

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Version of record first published: 04 Oct 2006.

To cite this article: Lewis Rothberg, Thomas M. Jedju, Paul D. Townsend, Shahab Etemad & Gregory L. Baker (1991): Short-Lived Photoinduced Excitations in Trans-Polyacetylene, Molecular Crystals and Liquid Crystals, 194:1, 1-12

To link to this article: http://dx.doi.org/10.1080/00268949108041145

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Mol. Cryst. Liq. Cryst., 1991, vol. 194, pp. 1–12
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SHORT-LIVED PHOTOINDUCED EXCITATIONS IN *TRANS*-POLYACETYLENE

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Abstract We report subpicosecond studies of the photoinduced transient midgap absorption in oriented *trans*-polyacetylene. Measurements of the response following above bandgap excitation are made with pump polarizations both parallel and perpendicular to the chain direction. We observe rapid formation and decay of charged soliton pairs in each of these configurations. When photoexciting perpendicular to the chains, however, we also observe long-lived absorption in the gap which we ascribe to polarons. These data can explain the observed behavior of the photoconductivity in *trans*-polyacetylene.

Keywords: Solitons, polarons, nonlinear optics, transport, picosecond spectroscopy

INTRODUCTION

Recent developments in synthetic methods have revitalized interest in polyacetylene[1]. In particular, the ability to make samples with well aligned polymer chains has produced material with very high nonlinear susceptibilities[2] and nearly metallic values of dopant induced conductivity[3]. The flexibility of the conjugated polymer chains results in a strong electron phonon coupling which leads to a dressing of charge carriers by the lattice. These transport and nonlinear optical properties need to be understood in terms of these lattice stabilized quasiparticles.

The simple structure of *trans*-polyacetylene has made it the prototype for theoretical work on quasi-one-

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dimensional organic semiconductors[4,5]. The chains consist of carbons with alternating single and double bonds between them. If we arbitrarily numbered the carbons along the chain, these bonds could be phased such that the double bonds all occur "to the right" of even numbered carbons or, alternatively, "to the left". Of course, these configurations are energetically equivalent but they are distinguishable when they both occur on the same chain and there is an interruption of bond phasing between them. These interruptions or domain boundaries have been called solitons because they are shape preserving distortions of the lattice which obey a nonlinear wave equation. Dopant induced midgap absorption[6,7] as predicted by the Su, Schrieffer and Heeger picture of polyacetylene[8] ($(CH)_x$) verified the existence of charged solitons since it was shown to be associated with spinless quasiparticles.

Su and Schrieffer exploited the structural simplicity of $(CH)_x$ to model the chain deformations after photoexcitation of electron hole pairs[9]. They predicted that intrachain pairs would evolve into a pair of charge carrying domain walls between the degenerate bond alternation phases[5] of *trans*-$(CH)_x$. The Su-Schrieffer prediction of directly photogenerated charged solitons has been verified by picosecond transient measurements on the midgap absorption characteristic of charged solitons in our laboratory[10]. That work and other experiments[11-13] have also shown that the analogous millisecond photoinduced absorption experiments observe charged solitons which are created indirectly following interchain excitation of electron hole pairs. For interchain excitation, the Su and Schrieffer simulations predict formation of polarons rather than solitons and most explanations of the millisecond photoinduced absorption are predicated on the assumption that polarons eventually react to form charged solitons[14,15].

Nevertheless, polarons have not yet been

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conclusively shown to exist in *trans*-$(CH)_x$. Recent theoretical work, in fact, casts doubt on whether they are thermally stable in $(CH)_x$[16,17]. Polarons are, however, expected to have midgap absorptions in the mid-infrared[18]. With the advent of oriented polyacetylene, we have undertaken polarized time-resolved absorption experiments to directly investigate the manifestations of interchain excitation. We observe transient absorption that we believe is due to polarons, measure their approximate quantum yield and are able to formulate a picture which explains the grossly different behavior of fast (ps) and slow (ms) photoconductivity in $(CH)_x$.

EXPERIMENTAL

The samples are grown by the Durham route and oriented by stretching them during polymerization[19]. Their thickness is approximately 5μm and they are sandwiched between two BaF_2 plates. The stretch ratio is 12:1 and X-ray measurements show the chains to be aligned to better than ±2.5 degrees[20]. Polarized Fourier transform infrared (FTIR) spectroscopy indicates that this alignment is preserved over the entire sample. There is no observable contamination of the polarized FTIR due to regions with misaligned chain segments. The sample thickness is large enough that, except for reflected light, all of the pump light at 575 nm is absorbed regardless of polarization even though the absorption depth is known to be 25 times smaller for light at this wavelength polarized parallel to the chain direction.

A schematic of the transient infrared absorption apparatus[21] is displayed in Figure 1. A synchronously pumped rhodamine dye laser is amplified at 10 Hz repetition rate by a frequency doubled Q-switched Nd:YAG laser to obtain mJ pulses of 350 fs duration. Part of these pulses is used as a pump to photoexcite electron hole pairs in the polyacetylene which has about a 1.4 eV

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bandgap. The remainder is used to generate a synchronized

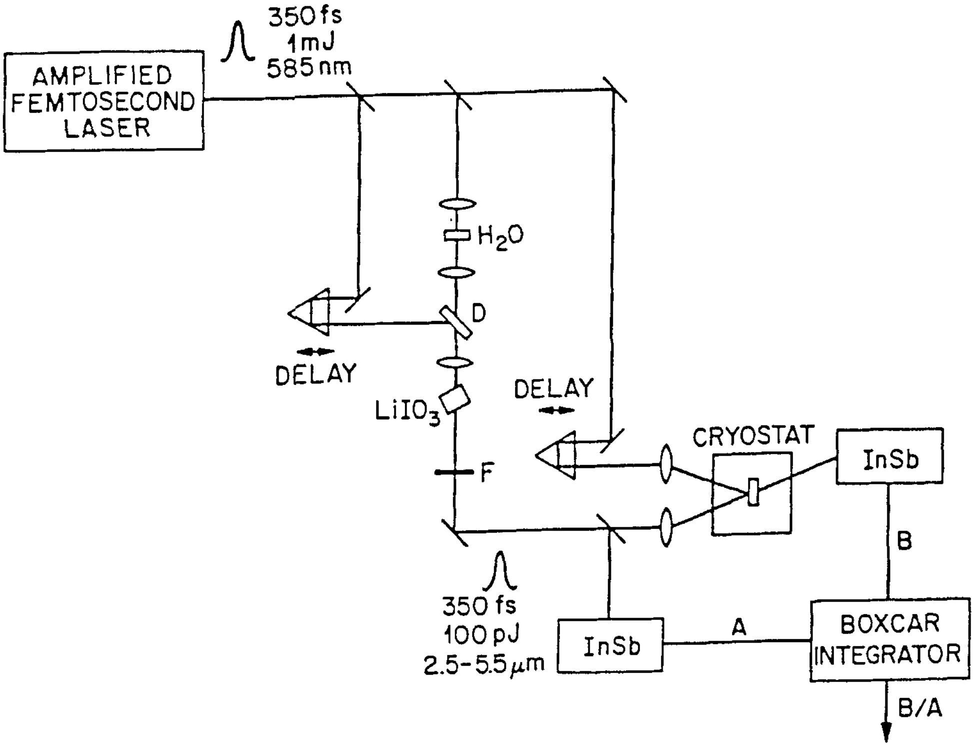

FIGURE 1 Block diagram of the laser apparatus

tunable infrared probe in a spectral region (2.5-5.5μm) where charged solitons (and probably polarons) are known to absorb. This probe pulses are formed by difference frequency mixing of the 575 nm pulses with white light continuum generated in water as shown in the Figure. Wavelength tuning of the probe is then easily accomplished by angle tuning the $LiIO_3$ mixing crystal to phase match different components from the white light continuum. At a fixed crystal angle, the spectral width of the infrared pulses is approximately 30-50 meV.

The pump and probe pulses are overlapped on the sample with variable pathlength delay to permit us to study the temporal evolution of the transient absorption induced by the pump. The samples are placed in a cryostat with CaF_2 windows but all of the studies we report here

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are at room temperature. We note in passing that one of the reasons for this is that heating of the sample by the pump is substantial (of order 100K) on the picosecond timescale and we believe that temperature dependence studies in pulsed laser experiments on $(CH)_x$ can easily be influenced by this effect. One InSb detector is used to measure transmission through the sample and a second is used to correct for pulse to pulse energy fluctuations in the probe intensity. The ratio is measured by a boxcar integrator and compared with pump on and off to ascertain transmission changes $\Delta T/T$ induced by the pump. Experiments on photoexcited free carrier absorption in Si verify our experimental resolution to be about 0.5 ps.

RESULTS AND INTERPRETATION

Figure 2 presents the transient absorption dynamics for a 0.45 eV probe with the pump polarized either parallel (squares) or perpendicular (circles) to the chain axes.

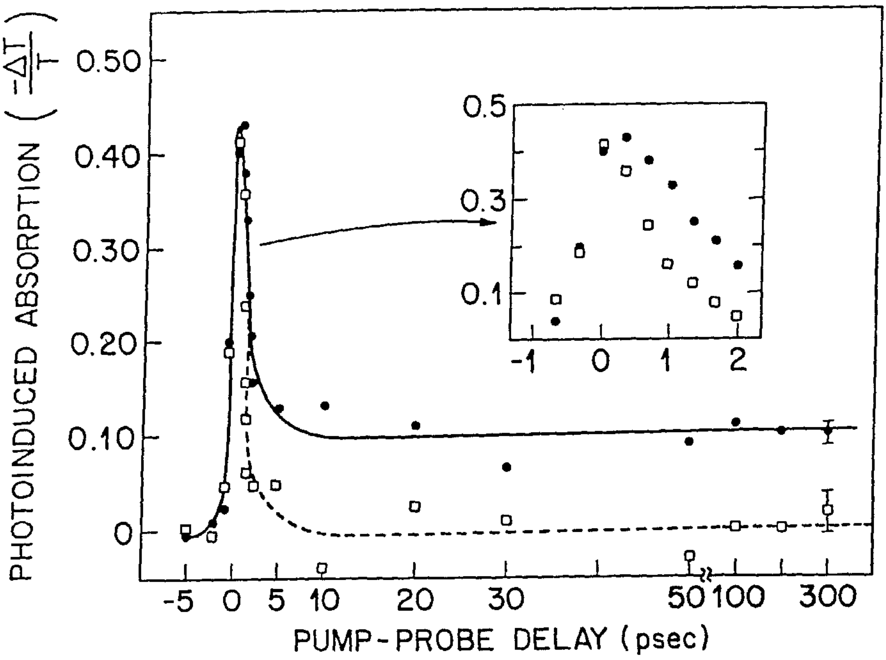

FIGURE 2 Transient absorption dynamics at 0.45eV for parallel (□) and perpendicular (●) pump.

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The parallel pump case is expected to be dominated by creation of intrachain electron hole pairs and the recovery dynamics are the same as what we observed previously in unoriented Shirakawa polyacetylene[22]. Based upon the spectrum (Figure 3) and its similarity to millisecond spectra of charged solitons[12], we ascribe this absorption to charged soliton pairs formed by the Su-Schrieffer mechanism. They are formed in less than 500 fs and subsequently decay in about 1.5 ps by geminate recombination. Fewer than 5% of the photogenerated solitons remain 10 ps after the pump pulse.

The case of perpendicular polarized pump is quite obviously different in that there is a long lived absorption. The rapidly decaying component is, however, extremely similar in both its dynamics (see inset to Figure 2) and its spectrum (Figure 3). These similarities lead us to conclude that this component also represents charged solitons formed by the Su-Schrieffer mechanism.

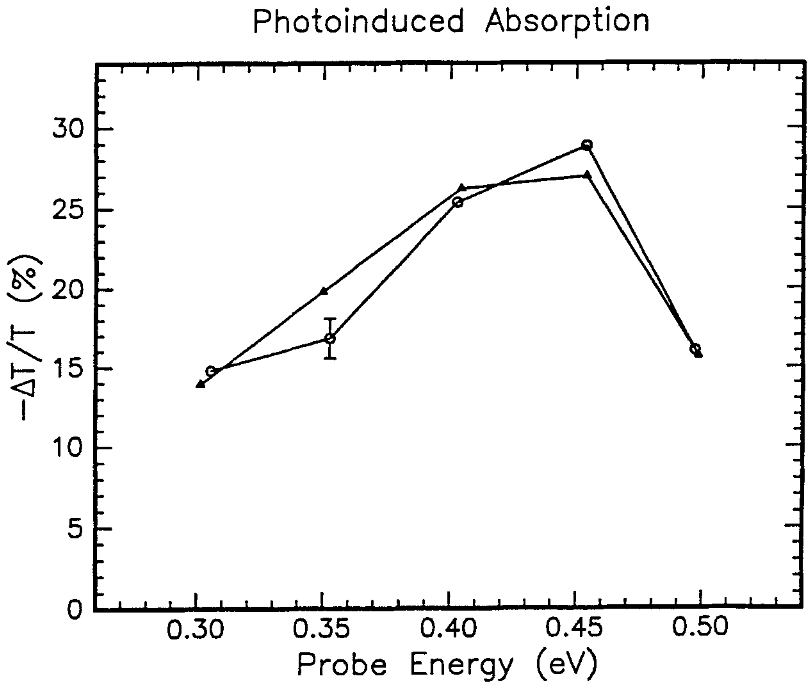

FIGURE 3 Induced absorption spectrum at 0.5 ps delay for parallel (○) and perpendicular (▲) pump.

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Because the long lived absorption only occurs in the case of pumping perpendicular to the polymer chains, it is natural to associate it with an interchain absorption process. Figure 4 presents evidence to support the idea that it is not also a manifestation of intrachain charged soliton creation. The Figure illustrates that the spectra obtained at long pump-probe delays in this configuration are not the same as the charged soliton spectra. They have substantially more absorption to the red around 0.3 eV (2.0±0.3 times as much) than would solitons with equivalent absorption at 0.45 eV. We therefore assign this absorption to polarons formed in less than 500 fs by interchain excitation and having lifetime of at least 1 ns.

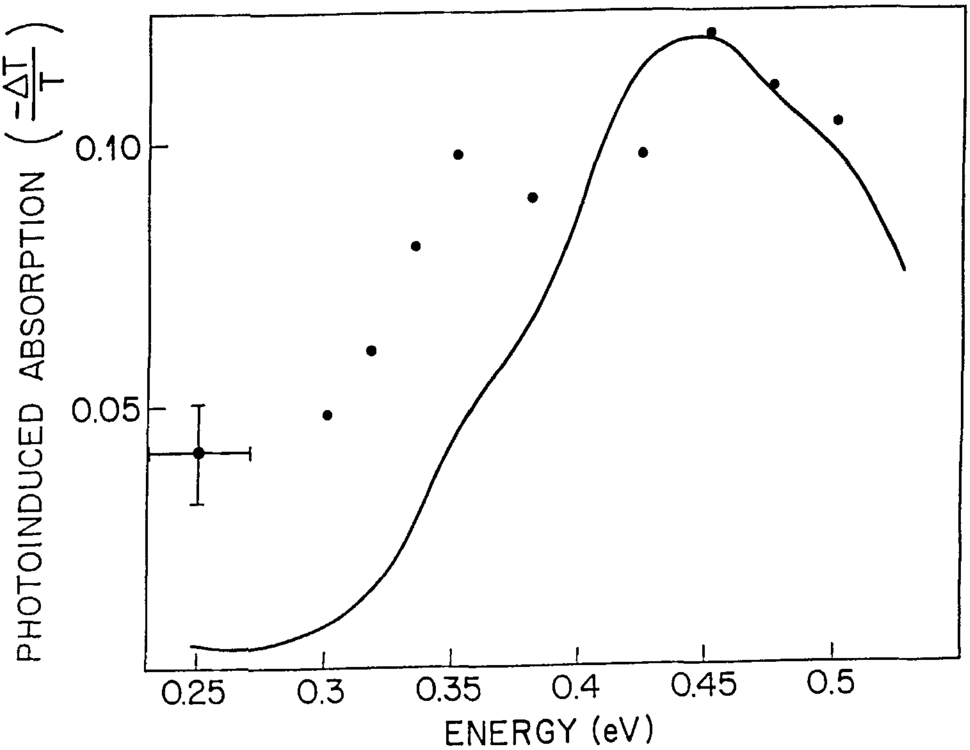

FIGURE 4 Absorption spectrum for perpendicular pump at 10 ps delay. Solid line is the rescaled ms spectrum from reference 26 for comparison.

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Interpreting the perpendicular photoinduced absorption as two components has the added benefit of explaining a curious feature of the dynamics which is illustrated by the inset to Figure 2. Note that the maximum transient absorption occurs several hundred femtoseconds later in the perpendicular case. This would be a natural consequence of superposing the charged soliton decay dynamics (i.e. the parallel case) with a long lived absorption which grows in as it "integrates through the pump pulse".

In the context of this picture, a comparison of the fast components in the parallel and perpendicular cases should give us the relative quantum yield for solitons. It turns out, however, that the relative size of these signals is intensity dependent and one additional set of measurements is necessary to extract this information. Figure 5 presents the intensity dependence of the photoinduced midgap absorption at the temporal peak of the fast component. The data are corrected for reflectivity so that the horizontal axis can be taken directly as absorbed fluence. While the signal in the perpendicular case is nearly linear with absorbed energy, the signal in the parallel case is strongly saturated. We have showed previously[14] that this saturation occurs when the entire absorption depth of the material becomes filled with charged solitons and that one can account quantitatively for the magnitude of the resonant nonlinear susceptibility $\chi^{(3)''}(-\omega,\omega,\omega,-\omega)$ with this picture. The implication, of course, is that at high fluence the material continues to absorb the light in its usual absorption length but that the electron hole pairs formed do not fully evolve into charged solitons before recombining.

To assess the relative yield of photogenerated Su-Schrieffer solitons for parallel and perpendicular excitation, then, we compare the slopes at low intensity in Figure 5. After a small correction to subtract the

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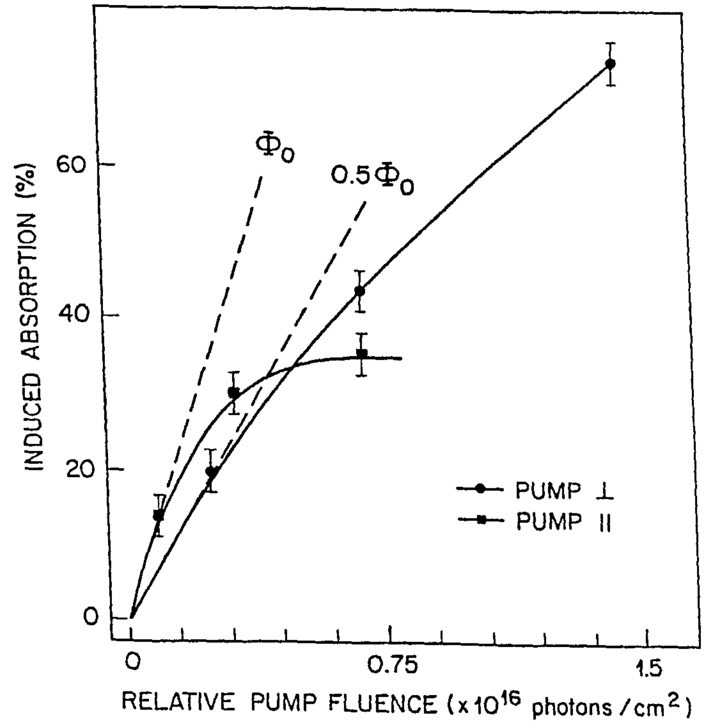

FIGURE 5 Absorbed fluence dependence of the photoinduced absorption at 0.5 ps delay and 0.45eV. Dashed lines are asymptotes to low intensity slope.

part of the perpendicular signal that is due to the component we have assigned to polarons, a relative quantum yield of $\Phi_\perp/\Phi_\parallel \approx 0.6 \pm 0.3$ is obtained. If we assume that the low intensity yield for soliton pairs is unity and that polarons are the only other excitation, then the yield for polarons is ~ 0.4±0.3. Baeriswyl and Maki have calculated interchain excitation probabilities[23] and they also conclude that creation of intrachain electron hole pairs will be the dominant process even in the perpendicular excitation geometry. It will be interesting to study the wavelength dependence of this branching ratio and compare with theory.

Our results suggest a resolution to the anomalous observations of "fast" and "slow" photoconductivity in *trans*-$(CH)_x$. In particular, they explain how it can be that the millisecond photoconductivity[14] is highly anisotropic and temperature dependent while the picosecond photoconductivity[24] is nearly isotropic and temperature independent. This is reminiscent of our data where the slow component is highly anisotropic and temperature dependent[14] and the fast component is neither. It is reasonable to conclude that a small fraction of escaped charged solitons ($<10^{-2}$) are responsible for the fast photoconductivity and that the polarons and resulting secondary charged solitons[14] are responsible for the slow photoconductivity. This picture predicts that there will be an intensity dependence as in Figure 5 to the anisotropy of the fast photoconductivity and this has recently been observed by Walser et.al.[25].

In summary, we have done femtosecond time-resolved studies of the photoinduced midgap absorption of oriented Durham *trans*-polyacetylene. When the pump field is polarized along the chain axes, we observe direct photogeneration of charged soliton pairs in < 500 fs as predicted by Su and Schrieffer. Over 95% of these recombine geminately in about 2 ps. Volume filling of the lattice by these excitations explains the optical saturation behavior of the material. We have also performed experiments with orthogonally polarized pump fields designed to isolate the contribution of interchain excitation of charge carriers. In this case, most of the absorbed light still goes into generating intrachain electron hole pairs and Su-Schrieffer solitons. There is, however, an additional long lived absorption with a somewhat redder spectrum which we assign to polarons. Our results bear a striking similarity to photoconductivity results which suggests and explanation for the qualitative differences between millisecond and picosecond photoconductivity.

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