

## Polarization dependence of transient photoconductivity in *trans*-polyacetylene

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(Received 20 April 1987)

We present the results of a series of measurements of the polarization dependence of the transient photoconductive response in both oriented and nonoriented *trans*-polyacetylene. Our results indicate that in nonoriented samples, the short-time photoconductivity is dominated by intrachain absorption and intrachain transport, while in oriented samples both interchain and intrachain photogeneration (with different absorption depths) of charge carriers are important. In oriented samples the photoconduction due to interchain excitation is slightly larger than that due to intrachain excitation.

### I. INTRODUCTION

The one-dimensional nature of organic semiconducting polymers renders their optical properties highly anisotropic. In particular, it is expected that the absorption coefficient for light polarized parallel to the chain direction will be much larger than that for the perpendicular direction. For the case of *trans*-(CH)<sub>x</sub> this has been verified by numerous experiments on oriented samples, including polarized reflectivity measurements.<sup>1-3</sup> Another consequence of the quasi-one-dimensionality of such polymers is that the primary photoexcitations also tend to be self-localized with motion principally along individual chains and relatively weak interchain hopping. In *trans*-(CH)<sub>x</sub> this is implied by polarized photoinduced-absorption measurements<sup>1</sup> and demonstrated through the photoconductivity results presented in this paper.

The combination of these two features in polyacetylene allows examination of the photoexcitations of this system in ways which would be otherwise impossible. For example, by performing polarized pump-and-probe photoinduced bleaching experiments on nonoriented samples of *trans*-(CH)<sub>x</sub>, Vardeny *et al.*<sup>4</sup> were able to estimate the diffusion coefficient of the photoexcitations. In this experiment the direction of the polarization of the probe beam was varied with respect to that of the pump. It was found that when the polarization directions coincided the photoinduced bleaching was initially twice as large as when they were orthogonal. This photoinduced dichroism decays and by measuring the decay time constant they were able to estimate the diffusion coefficient.

In the pump-and-probe experiment of Rothberg *et al.*,<sup>5</sup> the energy of the probe beam was chosen to coincide with midgap absorption. This transition has been shown to be due to the presence of photoinduced charged solitons. Again it was found that with parallel pump and probe polarizations, the photoinduced absorption is initially twice as large as when the polarizations are orthogonal. This has been interpreted as evidence for intrachain creation of charged solitons as the initial photoexcitation. It was also found that (in certain samples at low temperature) another

peak appears in the photoinduced absorption which is delayed by approximately 40 ps relative to the initial peak. This peak is larger when the pump and probe polarizations are orthogonal than when they are parallel. This has been interpreted as evidence for charged-soliton formation by a secondary process<sup>6</sup> in which the initial excitations are polarons created through interchain absorption.

Both of these experiments take advantage of the fact that even though the samples are macroscopically isotropic, they are microscopically anisotropic. When an electron-hole pair is generated via photon absorption, the excitation rapidly self-localizes (i.e., forms a soliton or polaron).<sup>7</sup> Thus, for short times, the excitation retains a memory of the chain segment on which it was created.

This paper presents the results of a series of transient photoconductivity measurements which probe the anisotropy of photocarrier generation and transport in *trans*-(CH)<sub>x</sub>. The first section will deal with experiments performed on nonoriented samples. The results of these measurements show that photogeneration proceeds primarily through intrachain processes and (at short times) transport is along the chain. The second section is devoted to oriented samples. Again, transport is along the chain; however, in this case it is possible to have interchain generation with relatively high quantum efficiency. The final section will address the origin of this apparent difference between the two types of samples.

### II. PHOTOGENERATION AND TRANSPORT IN NONORIENTED SAMPLES

Polarized fast transient photoconductivity in nonoriented samples of *trans*-(CH)<sub>x</sub> can loosely be viewed as pump-and-probe experiments in which the probe is the dc bias field. This field defines a unique direction along the sample, and the direction of the polarization of the optical field can be varied with respect to this direction. The measured photocurrent is the component of the current flow along the direction of the static field.

In order to analyze the photoconduction process we will make several simplifying assumptions. First, we will

assume that the absorption coefficient for light polarized parallel to the chain direction is much larger than that for light polarized in the perpendicular direction. Numerous experiments<sup>1,2</sup> and calculations<sup>8</sup> have verified that this is a reasonable assumption. Second, we will assume that (at short times) transport occurs primarily along the chain direction. The validity of this assumption will be discussed further below, but it is, at least initially, justified by the large anisotropy in the overlap integrals ( $t_{\parallel} \gg t_{\perp}$ ).<sup>8</sup>

Given these assumptions, we will proceed to analyze the polarization dependence of the photoconductive response. Our procedure is to calculate the response for chains with a given orientation with respect to the static and optical fields, and then to average over all chain directions in the plane of the substrate.

Consider the situation depicted in Fig. 1. Here the chain makes an angle  $\Theta$  with the bias field while the polarization of the optical field makes an angle  $\Phi$  with the bias field. The probability of photocarrier generation can be written as the sum of two terms, one describing intrachain generation and the other describing interchain generation. Then, the number of photocarriers is proportional to

$$N \propto \alpha_{\parallel} \eta_{\parallel} \cos^2(\Theta - \Phi) + \alpha_{\perp} \eta_{\perp} \sin^2(\Theta - \Phi), \quad (1)$$

where  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the absorption coefficients for parallel and perpendicular processes,  $\eta_{\parallel}$  and  $\eta_{\perp}$  are the quantum efficiencies for charge carrier generation, and  $(\Theta - \Phi)$  is the angle between the optical field and the chain direction. Once a carrier is created it can move along the chain and carry current. For a field strength  $E$ , the drift velocity of the carrier along the chain is

$$v_{\parallel} \propto \cos(\Theta) \quad (2)$$

and the component of this velocity along the bias field is

$$v_E \propto \cos^2(\Theta). \quad (3)$$

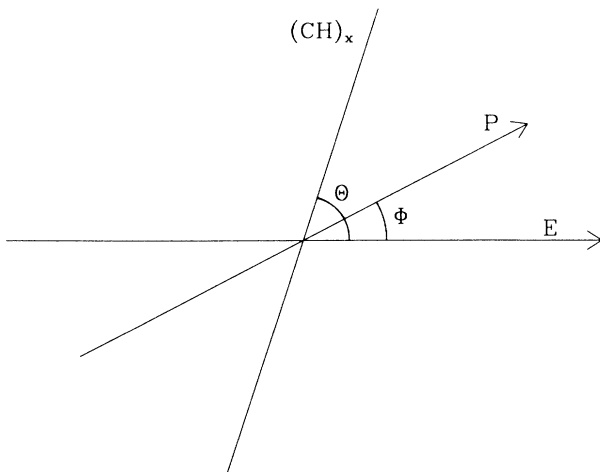


FIG. 1. Schematic diagram showing relative orientations of a typical  $trans\text{-(CH)}_x$  chain, the polarization of the incident light, and the dc electric field.

Thus the photocurrent due to chains with this orientation may be written as

$$I_P \propto [\alpha_{\parallel} \eta_{\parallel} \cos^2(\Theta - \Phi) + \alpha_{\perp} \eta_{\perp} \sin^2(\Theta - \Phi)] \cos^2(\Theta). \quad (4)$$

Note that those chains which are oriented parallel to the bias field will be the most effective for carrying current. If intrachain photogeneration dominates, then light polarized parallel to the static field will favor creation of carriers on these chains, and if interchain photogeneration dominates then light polarized perpendicular to the static field will dominate creation of carriers on these chains.

The above analysis is not expected to apply for all of the  $trans\text{-(CH)}_x$  chains since structural studies indicate that approximately 80% of the material is crystalline and the remaining fraction is amorphous. The contribution of the amorphous regions to the photoconductivity is expected to be isotropic and will tend to decrease the overall anisotropy. Assuming the photoconductivity due to the amorphous regions is equivalent to that of the crystalline portions, Eq. (4) becomes

$$I_P \propto (1-f)[\alpha_{\parallel} \eta_{\parallel} \cos^2(\Theta - \Phi) + \alpha_{\perp} \eta_{\perp} \sin^2(\Theta - \Phi)] \cos^2(\Theta) + \alpha_a f, \quad (5)$$

where  $f$  is the amorphous fraction and  $\alpha_a$  is the absorption coefficient of the amorphous material. Averaging over all orientations in the plane then yields

$$I_P(\Phi) \propto \frac{1}{8}(1-f)\{\alpha_{\parallel} \eta_{\parallel} [1 + 2 \cos^2(\Phi)] + \alpha_{\perp} \eta_{\perp} [1 + 2 \sin^2(\Phi)]\} + \alpha_a f \quad (6)$$

and the ratio of the photocurrent for polarization parallel to the field to that for polarization perpendicular to the field is

$$\frac{I_P(0^\circ)}{I_P(90^\circ)} = \frac{(1-f)(3\alpha_{\parallel} \eta_{\parallel} + \alpha_{\perp} \eta_{\perp}) + 8\alpha_a f}{(1-f)(\alpha_{\parallel} \eta_{\parallel} + 3\alpha_{\perp} \eta_{\perp}) + 8\alpha_a f}. \quad (7)$$

The simple formulas derived above for the polarized photoconductivity experiment are identical to those describing polarized pump and probe photoinduced absorption. This is a consequence of the one-dimensional nature of the photoexcitations and of the assumption that the excitations only move along the chain.

If all perpendicular photogeneration process can be ignored then the ratio of parallel to perpendicular photocurrents is expected to be

$$\frac{I_P(0^\circ)}{I_P(90^\circ)} = \frac{3(1-f) + 4f}{(1-f) + 4f}. \quad (8)$$

In Eq. (8) we have assumed a random planar average for  $\alpha_a$ ;  $\alpha_a \approx \alpha_{\parallel}/2$ . As perpendicular processes become more important this ratio will tend to decrease. Note that having a larger absorption probability parallel to the chain does not guarantee that parallel processes will dominate the photoconduction since it is possible that a large absorption coefficient is accompanied by a small quantum efficiency and vice versa.

Details of the photoconductivity apparatus and sample preparation have been given elsewhere.<sup>9</sup> In addition, the laser was linearly polarized with a piece of polaroid film, and a half-wave plate was used to rotate the polarization

at the sample. Photon energies of 2.1 and 2.2 eV were used, and photon fluxes were in the range of  $10^{13}$ – $10^{14}$   $\text{cm}^{-2}$  (per pulse).

In order to be certain that there was no net alignment of the chains in the samples used, the reflectivity as a function of polarization was measured. It was found that the samples were optically isotropic, indicating that corrections to the photocurrent due to anisotropic optical properties were unnecessary.

For the polarization-dependence data, the boxcar was arranged so that the sample point coincided with the peak of the photocurrent pulse. The half-wave plate was adjusted to yield the desired polarization direction and the peak photocurrent was signal averaged for  $\sim 100$  shots. Within experimental error, the shape of the photocurrent waveform was independent of the polarization direction.

The dependence of the peak photocurrent on polarization direction for a typical sample is shown in Fig. 2. The angle between the bias field and the polarization of the optical field is  $\Phi$ . The solid line is a fit to the functional form

$$I_p(\Phi) \propto A[1 + B \cos^2(\Phi + C)], \quad (9)$$

where the values of the coefficients  $A$ ,  $B$ , and  $C$  are 0.5, 0.9, and  $-2^\circ$ , respectively. Using these values, the anisotropy ratio (defined as the ratio of the peak photocurrent with polarization parallel to the bias field, to that with polarization perpendicular to the bias field) for this sample is  $[I_p(0^\circ)/I_p(90^\circ)] = 1.9$ . This value varied slightly from sample to sample but (for all thin samples) was in the range  $[I_p(0^\circ)/I_p(90^\circ)] = 1.8 \pm 0.1$ . For samples which were obviously thicker this ratio was somewhat smaller.

Using a cw light source and a chopper, the cw photoconductive response was also measured on the same samples. In contrast to the transient response, the cw photocurrent was isotropic to within 5%. Thus at later times the excitations have "forgotten" their initial polarization.

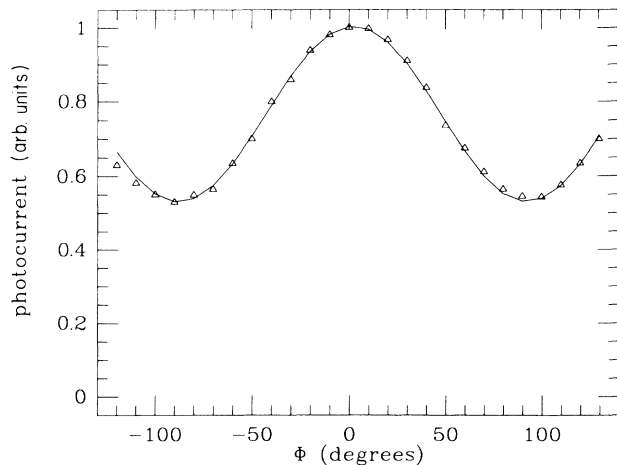


FIG. 2. Dependence of the peak photocurrent on polarization direction for a nonoriented (isotropic) sample.

This is in agreement with the decay of photoinduced dichroism at times beyond a few nanoseconds.

The fact that the photocurrent is almost twice as large when the light is polarized parallel to the static field suggests two possibilities for the photoconduction. Either the photoexcitations are produced as a result of intrachain absorption and transport occurs primarily along the chain or they are produced as a result of interchain excitation and transport occurs primarily perpendicular to the chains. The second possibility is ruled out since the photoconductive response has been shown to be at least 50 times larger when the static field is parallel to the chain.<sup>10</sup> Further, the close agreement between the photoconductivity anisotropy ratio and the anisotropy ratio measured in the midgap photoinduced-absorption experiments<sup>5</sup> indicates that both experiments are looking at the same excitation, the soliton. Thus, the origin of photoconduction in *trans*-(CH)<sub>x</sub> is intrachain photogeneration of charged solitons and subsequent transport of these solitons along the chain.

The anisotropy ratio of  $\sim 2$  measured in both the photoconductivity and photoinduced-absorption experiments indicates that the amorphous regions are significant. Using Eq. (8) we can estimate the size of the amorphous fraction as  $f \approx 0.2$ . Although this value is identical to that measured in x-ray experiments, the agreement is perhaps fortuitous since the mobility is probably lower in the amorphous regions than in the crystalline regions. Moreover, Eq. (8) completely ignores interchain generation and transport processes.

### III. ORIENTED SAMPLES

In this portion of the experiment we used stretch-oriented *trans*-(CH)<sub>x</sub> samples prepared via the Durham route. The stretch ratio was approximately 20. X-ray studies<sup>11</sup> of this type of film have shown that the chains are parallel to the stretch direction to within a few degrees. Since these samples are free-standing films, they are mounted somewhat differently than the thin nonoriented Shirakawa films. Gold microstrip electrodes are first evaporated on a small ( $1 \times 2$  mm<sup>2</sup>) piece of film, which is then attached to the usual alumina microstrip by means of silver paint. The electrodes are oriented on the sample so that the bias field is parallel to the chain direction.

Figure 3 shows the dependence of the peak photocurrent on the polarization direction of the optical field. In contrast to the results for the nonoriented material, the photocurrent is now seen to be largest when the optical polarization is perpendicular to the chain direction. Fitting to the functional form of Eq. (7) yields  $A = 0.39$ ,  $B = 1.51$ , and  $C = 84^\circ$ . The small angular offset is due to the uncertainties associated with mounting the sample such that the chains are parallel to the static field. Thus, in this case the anisotropy ratio is 0.4.

This is a somewhat misleading result since the reflectivity of the sample is also a strong function of the polarization direction.<sup>2</sup> With light polarized parallel to the chain direction the reflectivity is  $R_{\parallel} \sim 0.5$  while the reflectivity for light polarized perpendicular to the chain is

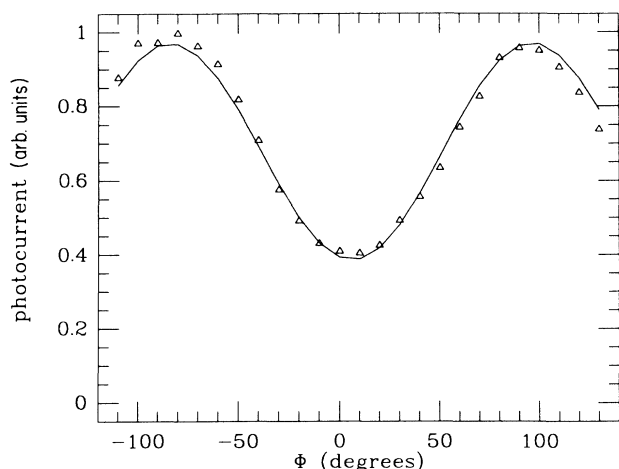


FIG. 3. Dependence of the peak photocurrent on the polarization for an oriented sample, for  $\Phi=0$ , the polarization is parallel to the applied field (and parallel to the chain direction).

approximately  $R_{\perp} \sim 0.05$ . Thus, corrections must be made for the number of absorbed photons. Since the sample is optically thick for both polarizations the correction factor is

$$\frac{(1-R_{\perp})}{(1-R_{\parallel})} \approx 2. \quad (10)$$

After these corrections are made there is very little anisotropy left in the transient photocurrent. The anisotropy which remains after correcting for reflectivity still favors perpendicular polarization. It must also be remembered that the absorption depths for the two different polarizations are very difficult. This means that (all other things being equal) the density of photoexcited carriers will be much greater within the optical-absorption depth for the parallel polarization. Thus, any bimolecular recombination processes will be more important for the parallel case.

As in the nonoriented case, the shape of the wave forms was independent of the polarization direction. Also, both polarizations have the same intensity dependence (linear). We are left with the conclusion that there is very little difference between the photocurrents due to the two different polarization states.

It is reasonable to assume that parallel polarization favors intrachain excitation of electron-hole pairs (and subsequently soliton pairs), while perpendicular polarization leads to the generation of interchain electron-hole pairs (and subsequently polarons). If this assumption is correct, our results then indicate that one of two situations must be occurring: either the photoconductivity-related properties (e.g., mobility along the chain) of solitons and polarons are similar, or one type of excitation is rapidly converted to the other (i.e., polarons rapidly recombine to form solitons). However, with these results alone it is not possible to determine which of these is more important.

The properties which have the largest effect on the photoconductivity are the free-carrier lifetime, the mobility,

and the probability to escape geminate recombination. Since a polaron may be viewed as a bound soliton pair<sup>12</sup> it is not totally unexpected that solitons and polarons might be similar with respect to these properties. It is also known that two like polarons are unstable against the formation of charged soliton pairs<sup>12</sup> since this process lowers the total energy of the excitation pair. This process will occur when the two polarons happen to drift close to each other and would lead to a photocurrent which is non-linear in excitation intensity (i.e., it is a bimolecular process). Since only linear-intensity dependences are observed it can be concluded that this process does not dominate the charge-carrier generation.

#### IV. COMPARISON OF THE TWO MATERIALS

One of the implications of the averaging procedure outlined in Sec. II is that the photoconductivity of the aligned material should be larger by a factor of approximately

$$G = \frac{1}{\frac{3}{8}(1-f) + \frac{1}{2}f} \quad (11)$$

than the photoconductivity of the nonoriented material (since no averaging is necessary for the aligned material). Using  $f \approx 0.2$  yields  $G \approx 3$ . Although precise comparison of the photoconductive response of the two materials is made difficult by the uncertainties in calibrating the incident light flux, the measured ratio of the two materials is  $G_{\text{expt}} \approx 2-5$ , in good agreement with the theoretical result.

Upon first inspection, the results for the anisotropy ratio for the two materials seem contradictory. In the nonoriented material the anisotropy favors polarization in the direction of the static field, while for the aligned material the opposite is true. Of course there is no contradiction, the two different types of behavior are simply due to the large anisotropy in the absorption coefficient and the high degree of alignment of the Durham samples.

The anisotropy ratio of the absorption coefficient in *trans*-(CH)<sub>x</sub> has been estimated<sup>2</sup> as  $\alpha_{\parallel}/\alpha_{\perp} \approx 25$ . Thus, while samples of thickness  $\sim 1000$  Å may be relatively thick for light polarized parallel to the chain they are still thin for light polarized perpendicular to the chain. When light propagates through such a sample of nonoriented polyacetylene, any chains which are oriented with an angle less than  $\cos^{-1}(0.2) \approx 80^{\circ}$  to the polarization direction will have a greater probability of absorbing a photon through intrachain absorption than interchain absorption. The result is that a very small fraction of the photons are absorbed due to interchain processes. In fact the ratio of the number of photons absorbed via intrachain processes to that for interchain processes is (assuming the chains orientations are randomly distributed in two dimensions) given by the ratio of the absorption coefficients. As a consequence, experiments on nonoriented *trans*-(CH)<sub>x</sub> are dominated by intrachain absorption consistent with the results obtained in the photoconductivity experiment.

In contrast, the high degree of alignment in stretch oriented Durham polyacetylene allows one to overcome the large anisotropy in the absorption coefficients and

“force” the photons to be absorbed via interchain absorption. With these materials it should be possible to compare the behavior of solitons and polarons. The differences between these two excitations, as they relate to photoconductivity, appear to be very small. The slight anisotropy which exists indicates that interchain absorption is more efficient for producing photoconductivity.

## V. CONCLUSIONS

In conclusion, we have measured the polarization dependence of the photoconductive response in both nonoriented and oriented *trans*-(CH)<sub>x</sub> samples. Our results indicate that as a consequence of the large anisotropy in the absorption coefficient, photoconduction in nonoriented samples is dominated by intrachain excitation and transport. For oriented samples it is possible to generate interchain excitations as well as intrachain excita-

tions. The differences in the photoconductivity due to the two types of excitations are small, but interchain-generated excitations give slightly higher values. This indicates that either the properties of solitons and polarons are similar, or that polarons are rapidly converted to solitons. We also conclude that experiments on nonoriented samples are relatively insensitive to interchain absorption and that experimental efforts to study the effects of photo-generated polarons (i.e., photoinduced absorption) should concentrate on the aligned material.

## ACKNOWLEDGMENTS

We thank D. C. Bott for useful discussions and C. S. Brown for preparation of the stretch-oriented polyacetylene samples used in this work. Supported by the Office of Naval Research.

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