

PHOTOEXCITATIONS AND PHOTOCONDUCTIVE RESPONSE IN HIGHLY ORIENTED TRANS  
POLYACETYLENE

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ABSTRACT

The results of a combined study of Resonant Raman Scattering, near infrared photoinduced absorption and photoconductive response of an highly oriented form of trans polyacetylene are presented and discussed. Raman spectra have been obtained for all the four different scattering configurations. Photoinduced spectra have been studied for various polarizations of the laser beam with respect to the stretching direction.  $I_{ph} - V$  curves of the photoconductive response have been studied as a function of both the polarization of the beam and the direction of the current flow with respect to the stretching direction. The results are interpreted in terms of the anisotropy of the vibrational, optical and transport properties peculiar of the polymeric structure.

INTRODUCTION

Aim of this short note is to review the status of our ongoing research on the vibrational, optical and transport properties of an highly oriented form of trans polyacetylene.

The motivation of such studies is the need for a better understanding of the conduction mechanism and of the properties and the nature of the photogenerated charge carriers in conjugated polymers. In fact most of the experimental investigations carried out on trans polyacetylene have used isotropic Shirakawa films which are unsuitable to detect the highly anisotropic behaviour of the optical and transport properties which should characterize a synthetic, quasi one-dimensional metal.

Trans polyacetylene synthesized according to the traditional Shirakawa procedure (1) consists of an insoluble fleece of loosely tangled fibrils with diame-

ter of  $\sim 20$  nm, randomly oriented. Two synthetic routes to obtain a fully oriented material have been so far reported: one which proceeds via the preparation of a stretchable prepolymer (2) which yields polyacetylene by pyrolysis; the other (3) which adopts the Ziegler-Natta polymerization procedure and uses a Ti-based catalyst, yields films 20-40 nm thick, which can be stretched up to 7-8 times their original length. This latter form of polyacetylene, which has been investigated in the present study, exhibits a typical fibrillar morphology with an almost perfect alignment of the fibrils along the stretching direction.

#### RESONANT RAMAN SCATTERING

Fig. 1 shows the uncorrected Raman spectra of oriented polyacetylene obtained in the four possible scattering configurations namely X(ZZ)Y, X(ZX)Y, X(YZ)Y and X(YX)Y (Z stretching axis) obtained using the  $\lambda = 609.6$  nm exciting frequency. Because of the high anisotropy of the optical properties of the sample (4) it is expected that large correcting factors due to reflectivity and absorption should be applied to the observed intensities. A simple model to roughly account for these effects has been worked out (5,6), yielding the following values for the corrected integrated intensity ratios:

$$I_{X(ZX)Y}/I_{X(ZZ)Y} = I_{X(YZ)Y}/I_{X(ZZ)Y} = 0.03; \quad I_{X(YX)Y}/I_{X(ZZ)Y} = 0.01 \quad (1)$$

An exhaustive presentation and discussion of the experimental results is beyond the scope of this note and is discussed elsewhere (5,6). We present here only the relevant conclusions reached.

- i) The corrected data appear to rule out that the intensities of the X(ZX)Y, X(YZ)Y and X(YX)Y configurations originate entirely from the amorphous part of the sample. Indeed in this case one would expect the same intensities in all these configurations (7) which is not what is observed.
- ii) One can assume that the configuration exhibiting the lowest intensity X(YX)Y reflects only the scattering from randomly oriented molecules. If this is the case one has to conclude that  $\alpha_{zy}$  and  $\alpha_{yz}$  components of the molecular polarizability tensor are non zero. The change in shape of the Raman bands, namely an increase of the relative intensity of their high frequency parts in the X(YX)Y configuration is then indicative of the fact that most of the short conjugated segments are contained in the amorphous fraction of the sample.
- iii) Conversely one can assume that no amorphous part (i.e. randomly oriented fibrils) is present in the film. If this is the case the corrected intensity ratios imply that also the  $\alpha_{yy}$  component is non vanishing and that  $\alpha_{zz} \gg \alpha_{zy} (\alpha_{yz}) > \alpha_{yy}$ . This could be indicative of a slight misalignment of the transition moment of the  $\pi \rightarrow \pi^*$  electronic transition with respect to the chain

axis. It is reasonable to assume that this misalignment increases with the decrease of the electronic delocalization (8) thus accounting for the change in the observed bandshape previously discussed.

#### PHOTOINDUCED ABSORPTION

The intensity of the photoinduced band (9) at 0.49 eV has been investigated as a function of the angle  $\theta$  formed by the direction of the electric vector and the stretching direction (10). It is observed (Fig. 2) that the intensity of the photoinduced absorption is reduced when the polarization of the laser beam is changed from perpendicular to parallel to the stretching direction. Since the sample used is thick ( $t \gg 1/\alpha$ ) all the impinging radiation is absorbed (and therefore the same number of excess carriers is created) regardless the light

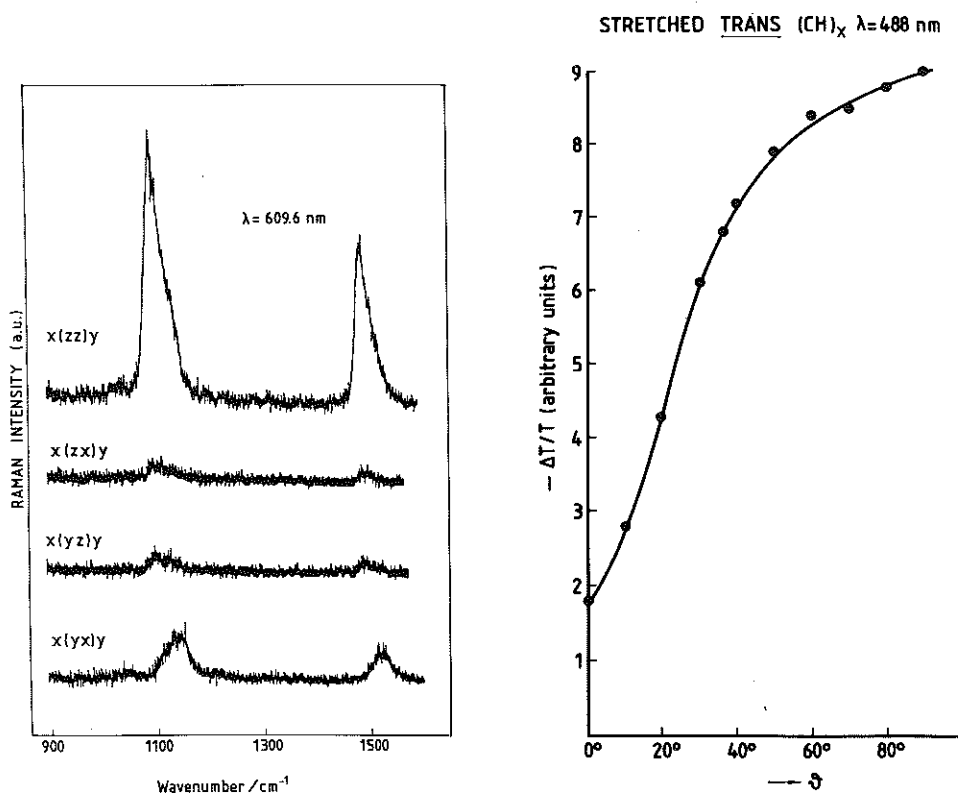


Fig. 1. Observed Raman intensities of trans  $(\text{CH})_x$  for the four different scattering configurations. Power on the sample: 13 mw.

Fig. 2. Photoinduced absorption intensity of the 0.49 eV band of trans  $(\text{CH})_x$  as a function of  $\theta$  (see text).  $\lambda = 488$  nm,  $T = 77$  K. Power on the sample: 100 mw.

polarization. Therefore apart from the correction for the reflectivity anisotropy ( $1-R_{||}/1-R_{\perp} \sim 0.7$ ) the intensity of the photoinduced absorption should be independent of  $\theta$ . Our data can be therefore interpreted as an evidence for the direct bimolecular recombination of the oppositely charged carriers, taking place because of the relatively high photon flux ( $10^{17}$  photons/s  $\text{cm}^2$ ). In fact because of the anisotropy in the optical constants, the penetration depth  $\delta$  for polarization parallel to the stretching direction is about one order of magnitude lower than the depth for perpendicular polarization ( $\delta_{||}/\delta_{\perp} = \alpha_{\perp}/\alpha_{||}$ ). Therefore in the parallel configuration the greater confinement of the photogenerated carriers is responsible for their higher recombination rate which results in a lower intensity of the photoinduced absorption.

The polarization properties of the two photoinduced absorptions at 0.49 and 0.17 eV have been also determined. Both these bands exhibit a very high dichroic ratio  $\alpha_{||}/\alpha_{\perp}$  with respect to the polarization of the IR probe indicating that they are both strongly polarized along the chain axis. This behaviour is quite similar to the one exhibited by the corresponding IR bands induced by chemical doping (11) thus giving further support to the hypothesis that chemical "doping" and photoexcitations across the gap result in similar perturbations of the electronic and vibrational energies.

#### PHOTOCONDUCTIVE RESPONSE

Electrical transport measurements with injection of the carriers by light should help to avoid the complexity of the interpretation of the data of "doped" samples where excess charge carriers are likely to be bound to the dopant counterion. In order to detect the dimensionality of the charge transport we have studied the photoconductive response of the highly oriented polyacetylene for both current flow parallel and perpendicular to the stretching direction. A brief account of our results (which will be exhaustively presented in a forthcoming publication) is given here. Fig.3 shows the  $I_{\text{ph}}-V$  characteristic curves for electric field applied along ( $E_{||}$ ) and across ( $E_{\perp}$ ) the chain direction respectively. The interpretation of these data can be attempted on the basis of the Onsager theory (12) following a similar analysis performed by Siddiqui (13) on the photoconductive response of polydiacetylene. For high light intensities the photocurrent  $I_{\text{ph}}$  of a thick ( $t \gg 1/\alpha$ ) sample is given by

$$I_{\text{ph}} = (2ew) \left( \frac{\eta I}{\alpha \beta} \right)^{\frac{1}{2}} \mu (\Phi(E))^{-\frac{1}{2}} E \quad (2)$$

where  $\mu$  is the carrier mobility,  $\beta$  the bimolecular recombination constant,  $\alpha$  the absorption coefficient,  $E$  the applied electric field,  $\eta$  the quantum efficiency,  $I$  the laser intensity,  $w$  the width of the electrodes and  $\Phi(E)$  the probability for a photogenerated e/h pair of escaping geminate recombination.

When a photon ( $\hbar\omega > E_g$ ) is absorbed a bound e/h pair is created with quantum efficiency close to 1. The bound pair has then a probability  $\Phi(E)$  of avoiding geminate recombination. The probability dependence on the electric field  $E$ , temperature  $T$ , wavelength excitation  $\lambda$  is dependent on the dimensionality of the charge transport reflecting the very nature of the random walk process (14) involved. The following brief comments on the data displayed in Fig.3 can be made:

a) The photoconductive response along the stretching direction is about one order of magnitude higher than in the perpendicular direction.

b) The photoconductive response decreases by increasing  $\lambda$ . This can be due to the fact that the Coulomb radius (and therefore the probability of escaping recombination) of the photogenerated carriers increases with the photon energy, since the thermalization of initially hot carriers is achieved by dissipating the excess kinetic energy over the local potential by phonon emission. Moreover

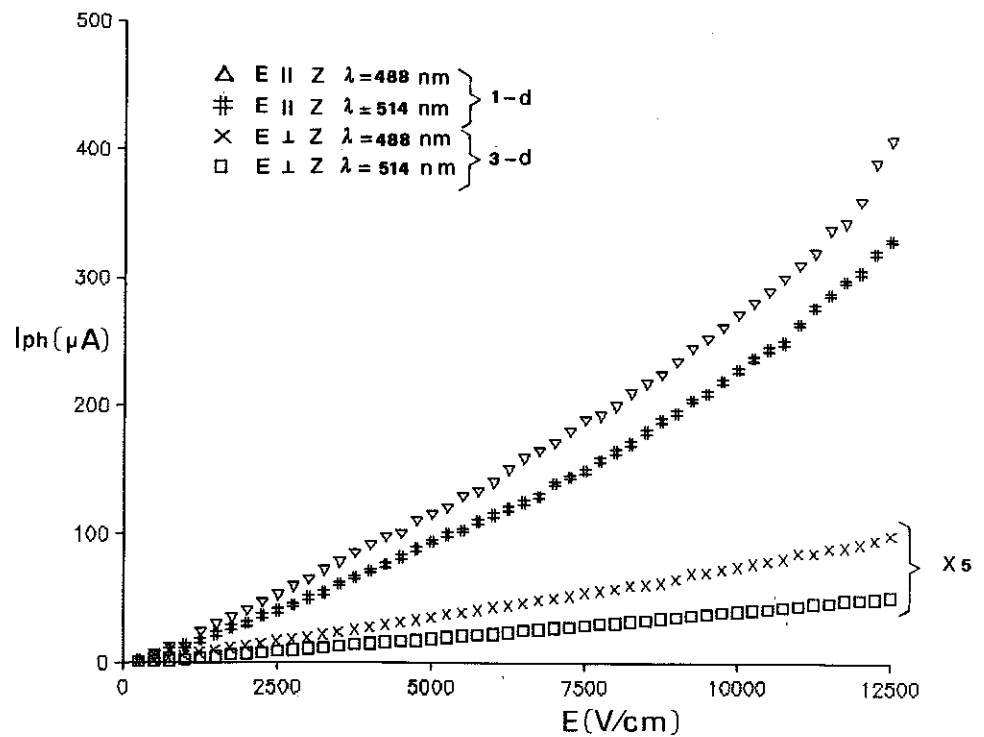


Fig. 3. Photoconduction of trans (CH)<sub>x</sub> for E||Z and E $\perp$ Z (Z stretching direction). Electrode separation 0.4 mm. Power on the sample: 45 mw. Load resistor: 220 kohm.

as  $\alpha(488 \text{ nm}) < \alpha(514 \text{ nm})$  a slightly greater confinement (which again implies greater recombination) of the carriers occur for the higher wavelength.

c) The observed photoconductive response for  $E_{\perp}$  and  $E_{\parallel}$  is clearly indicative of the effects of the dimensionality on the charge transport. In fact while the  $I_{\text{ph}}-V$  curve for  $E_{\perp}$  (quasi 3-d case) exhibits a linear behaviour over the entire range of  $V$  the  $I_{\text{ph}}-V$  dependence for  $E_{\parallel}$  (quasi 1-d case) is clearly non linear. This reflects the field dependence  $\Phi(E)$  of the escape probability predicted by the Onsager model applied to the 3-d ( $\Phi_3(E)$ ) and the 1-d ( $\Phi_1(E)$ ) cases. In fact while  $\Phi_3(E)$  is essentially independent of  $E$  within a large range of  $E$ ,  $\Phi_1(E)$  exhibits approximatively a linear dependence on  $E$  (15).

Since in the high laser intensity regime the photocurrent is proportional to  $\Phi(E)^{\frac{1}{2}}$  (Eq. 2) one then expects an  $I_{\text{ph}} \propto E^{3/2}$  dependence in the 1-d case as indeed observed. The deviation from such behaviour observed at low  $E$  are indicative of a changeover from an  $E$  controlled drift, to a  $T$  controlled diffusive motion of the charge carriers.

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