PHYSICAL REVIEW B VOLUME 43, NUMBER 9 15 MARCH 1991-II

Anisotropy of the picosecond photocurrent in stretched *trans*-polyacetylene for above- and below-gap excitation

A. D. Walser and R. Dorsinville
Institute for Ultrafast Spectroscopy and Lasers and Center for Analysis of Structure and Interfaces and Electrical Engineering Department, The City College of New York, New York, New York 10031

R. Tubino
Istituto di Fisica dell'Universita', Via Vienna 2, Sassari, Italy
and Istituto di Chimica delle Macromolecole, Consiglio Nazionale delle Recherche, Italy

R. R. Alfano
Institute for Ultrafast Spectroscopy and Lasers and Center for Analysis of Structure and Interfaces and Electrical Engineering Department, The City College of New York, New York, New York 10031

(Received 22 October 1990)

The temperature dependence of the picosecond photocurrent with below-gap excitation (1.06 μm) was measured for a highly oriented form of *trans*-polyacetylene. The one-dimensional (1D) picosecond photocurrent was found to be independent of temperature, while the 3D picosecond photocurrent was found to be temperature dependent with an activation energy of 63 meV. In addition, the anisotropy of the photoresponse of *trans*-polyacetylene for both above- (0.53-μm) and below-gap (1.06-μm) excitation was studied. The anisotropy ratio for below-gap excitation was independent of intensity, while the anisotropy ratio of the photoresponse for above-gap excitation decreased as the intensity increased. It was found that the picosecond photoconductive response was greatest with below-gap excitation. These results demonstrate the photoproduction of nonlinear charged carriers (solitons and polarons) at energies that are below the principal interband absorption edge and are explained qualitatively using the bimolecular recombination model.

INTRODUCTION

Over the years the one-dimensional structure of the highly oriented polymer stretched *trans*-polyacetylene [*trans*-(PA)] has received considerable experimental[1–3] and theoretical[4,5] attention. *trans*-(PA) has a twofold-degenerate ground state that is believed to lead to mobile topological chain distortions or kinks called solitons, which are responsible for many of the interesting properties of the polymer.[6–9] According to the Su, Schrieffer, and Heeger (SSH) model, solitons can be photogenerated in *trans*-(PA) when an incident photon excites an electron-hole pair, and the lattice then distorts around the photogenerated charged carriers leading to soliton-antisoliton (S^+S^-) pairs. This model stimulated a host of experiments to challenge or prove the existence of solitons.[10–21] The results of photoinduced experiments and simultaneous electrical conductivity and electron-spin-resonance (ESR) measurements confirmed the predictions of Su and Schrieffer and also established the reversed spin-charge relation of the soliton model.[10,11]

Photoconductive and photoinduced absorption measurements in aligned *trans*-(PA) samples[22–26] using polarized excitation can help to unravel the nature and characteristics of its mobile charge carriers. Bleier *et al.* studied the anisotropy of the picosecond photoconductive response of highly oriented Durham-Graz–type polyacetylene and found that the picosecond photocurrent with an excitation energy of 2.6 eV (above-gap excitation) was about four times larger when the light is polarized perpendicular to the chains (after correcting for reflection losses the ratio reduced to 1.7). Bleir *et al.* also claimed that the anisotropy ratio (1.7) is independent of both the excitation energy (from 1.7 to 3.2 eV) and the intensity of the incident light. Most photoconductive experiments to date were performed with above-gap ($\hbar\omega > 2\Delta$) excitation where the charged soliton pairs are generated indirectly via electron-hole pairs. However, theoretical calculations using the SSH or Takayama *et al.* (TLM) models have shown that the energy to create a soliton at rest (E_s) is less than one-half the single-particle gap (2Δ). By studying the excitation profile well below the principal interband absorption edge using photoinduced absorption as a direct measure of the excitation density, Blanchet *et al.*[19] were able to demonstrate that direct photogeneration of charged soliton-antisoliton pairs is possible. In this paper, we present the results of a series of picosecond photoconductive measurements[25] that examines the anisotropy for both above- and below-gap excitation and the temperature and intensity dependence of the photogenerated charged carriers in *trans*-(PA) for below-gap excitation. We present evidence that under certain conditions the photoconductive anisotropy is strongly intensity dependent and compare the above- and below-gap responses in an effort to determine the nature and transport properties of the photoexcited charged carriers.

METHOD

The anisotropy of the optical, vibrational, and transport properties of polyacetylene can only be studied in samples possessing a high degree of orientational order. Polyacetylene synthesized according to the procedures indicated by Shirakawa *et al.*[26] consist of fibrils that are randomly oriented. Within the fibrils the individual polyenic chains are arranged in a three-dimensional lattice of high regularity. The lack of preferential orientation of the fibers makes polyacetylene an essentially isotropic material. Our oriented samples were prepared using the Ziegler-Natta polymerization procedure. This method uses a Ti-based catalyst[27] to yield films of *cis*-polyacetylene 10–40 μm thick, which can be stretched up to seven or eight times their original length. Highly oriented *trans*-(PA) can be obtained by thermal isomerization of the pristine polymer. The material studied in our work is characterized by a relatively large density (1.0–1.1 g/cm^3) approaching that of the theoretical[28] crystallographic (1.15 g/cm^3). X-ray diffraction patterns of similarly prepared samples have shown a very high degree of preferred orientation of the crystallites with the chain axis parallel to the stretching directions.[29] The highly stretched *trans*-(PA) film was attached by pressure to the copper electrodes of a microstrip line optical switch constructed from a sheet of dielectric material sandwiched between two sheets of copper. The details of the construction have been published elsewhere.[30] For temperature measurements, the sample was mounted on the cold finger of a nitrogen Dewar. Copper-Constantan thermocouples were used to monitor the temperature. The above-gap photoexcitation was produced by 0.53-μm (2.4-eV), 25-ps pulses from a frequency-doubled yttrium-aluminum-garnet (YAG) laser. For below-gap photoexcitation, the fundamental frequency 1.06 μm (1.17 eV) of the YAG laser was used. The maximum photon flux used in any experiment was approximately 6×10^{15} cm^{-2} (per pulse). A half-wave plate suited for each frequency was used to rotate the polarization of the optical pulses with respect to the stretching direction of the polymer. The optical switch was biased by a 400 V source, which is well within its Ohmic range. The peak photocurrent was signal averaged for approximately 100 shots using a boxcar integrator.

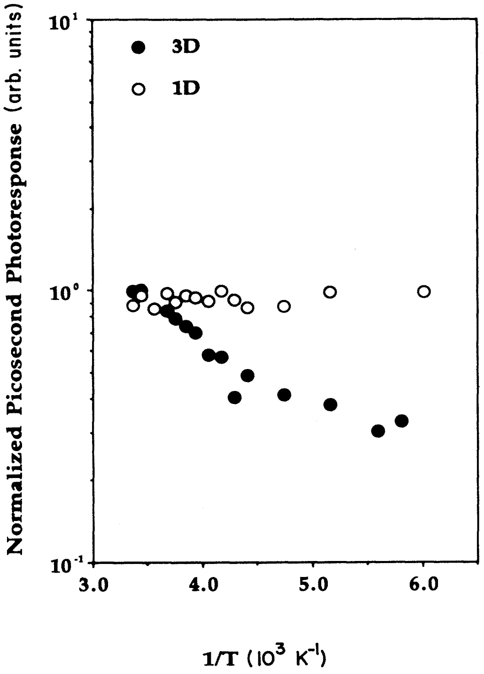

FIG. 1. Semilogarithmic plot of the temperature dependence of the 1D and 3D picosecond photoconductive response of *trans*-(PA) with below-gap excitation.

RESULTS

Figure 1 shows a semilogarithmic plot of the picosecond photoconductive response as a function of temperature for the 1D (applied electric field parallel to the polymer chain direction) and 3D (applied electric field perpendicular to the polymer chain direction) configurations at a laser intensity of approximately 31.2 MW/cm^2. The polarization of the excitation pulse was perpendicular to the stretching direction for both cases to keep the penetration depths identical and to obtain the strongest possible signal. In the 1D configuration, the photocurrent is practically independent of the temperature between 300 and 160 K. In the 3D configuration, the photocurrent decays with temperature between 300 and 200 K. The activation energy (E_a) in this region is approximately 0.063 eV. These results are very similar to those we obtained for above-gap excitation.[14] Below 200 K there is a change of slope where the temperature-dependence levels off. This may be explained by assuming that the phonon-activated hopping becomes relatively inefficient at low temperature and that tunneling through the barrier becomes the main mechanism for charge transfer between neighboring chains. Another possible reason for the change in the slope is the effect caused by misaligned chains, which is characteristic of the fibrous Shirakawa (PA) polymers, where contributions of the temperature-independent 1D photocurrent to the temperature-dependent 3D photocurrent become more pronounced as the temperature decreases.

Photoconductive measurements as a function of polarization (the angle between the optical electric field and the polymer chain) were carried out in the 1D configuration. The maximum signal is obtained in this configuration, for it hs been shown by several groups that transport occurs primarily along the chain. The dependence of the photocurrent on the polarization direction for the 1.06- and 0.53-μm excitation pulses is shown in Fig. 2. The incident photon flux density for the 1.06- and 0.53-μm excitations are 36 and 43 MW/cm^2, respectively.

The above-gap excitation (0.53-μm) curve in Fig. 2 has been normalized (to the number of absorbed photons) and corrected for any anisotropy that is due to reflectivity. Because of the sample thickness (approximately 20 μm),

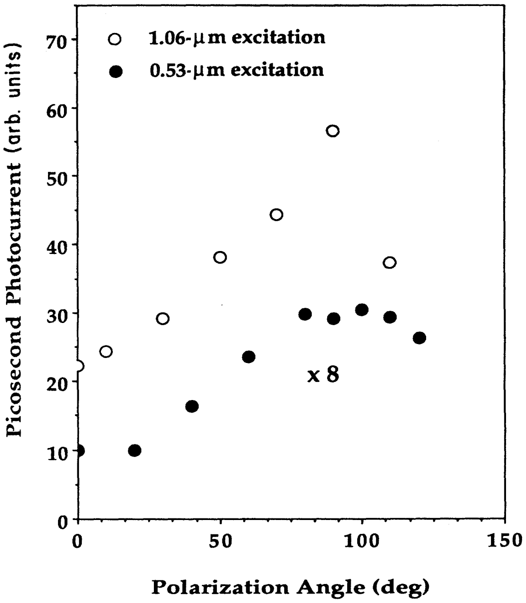

FIG. 2. Anisotropy of the corrected 1D picosecond photoconductive response with respect to the polarization of the incident excitation above (2.34 eV) and below-gap (1.17 eV). Notice, for proper scaling, that 8× the above-gap photoresponse is plotted.

it is reasonable to assume that all incident photons that are not reflected are absorbed for above-gap excitation. This was verified by measuring the transmission of the sample which proved to be opaque. However, for below-gap excitation (1.06 μm) some of the incident photons are transmitted as well as reflected. Thus, the 1.06-μm curve in Fig. 2 was normalized and corrected for reflection and transmission. The angle θ is defined as the angle that the polarization of the optical field makes with the polymer chain (i.e., the optical field is parallel to the polymer chain at $\theta=0°$ and perpendicular at $\theta=90°$). The ratio of the corrected photocurrent at $\theta=90°$ to that at $\theta=0°$ for below-gap excitation (1.06 μm) is approximately 2.4. The ratio for above-gap excitation (0.53 μm) is approximately 4.5. Any shifts of the minima or maxima from $\theta=0°$ or 90°, respectively, in Fig. 2 is probably due to misalignment of the polymer chains with respect to the switch electrodes during the mounting of the sample. Note that the picosecond photoconductive response is maximum for perpendicular polarization for both the above- and below-gap excitations.

In Fig. 3 the intensity dependence of the ratio of the photocurrent when the optical electric field is perpendicular to the chain to that of the photocurrent when the optical electric field is parallel to the chain is shown. Each curve has been corrected for the difference is absorbed photons, due to the polarization and frequency dependence of the reflectivity and transmission. There is a clear intensity dependence of the ratio for above-gap excitation, with a change from 7.4 to 4.5. Note that the ratio decreases as the intensity increases. The ratio shown in Fig. 3 for below-gap excitation is nearly independent of intensity at a value of approximately 2.4, in contrast to the above-gap response. The intensity dependence of the picosecond photocurrent for below- and above-gap perpendicular excitation is shown in Fig. 4. Similarly, shown in Fig. 5 is the intensity dependence of the picosecond photocurrent for below- and above-gap parallel excitation. In each figure the picosecond photocurrent

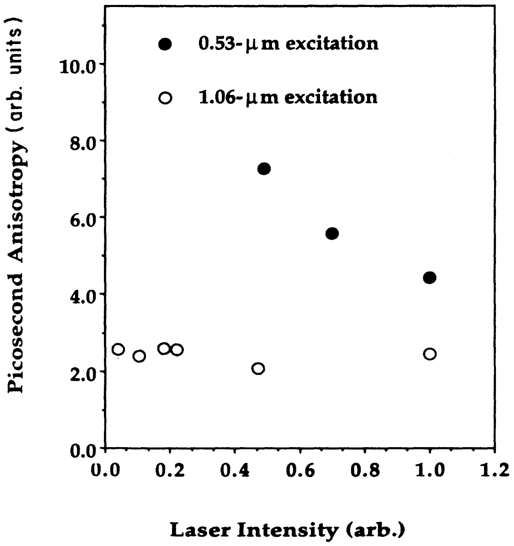

FIG. 3. Intensity dependence of the ratio of the photocurrent when the optical electric field is perpendicular to the chain to that of the photocurrent when the optical electric field is parallel to the chain with a maximum laser intensity of 36.4 MW/cm^2 and 43.3 MW/cm^2, respectively. Each curve hs been corrected for reflection and/or transmission.

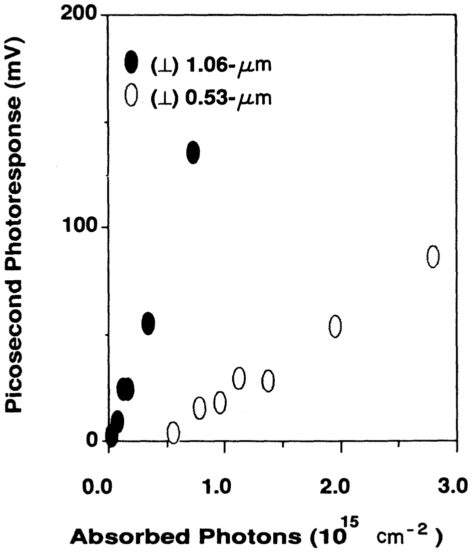

FIG. 4. 1D picosecond photocurrent with respect to the number of absorbed photons with perpendicular polarization of the above- and below-gap excitations.

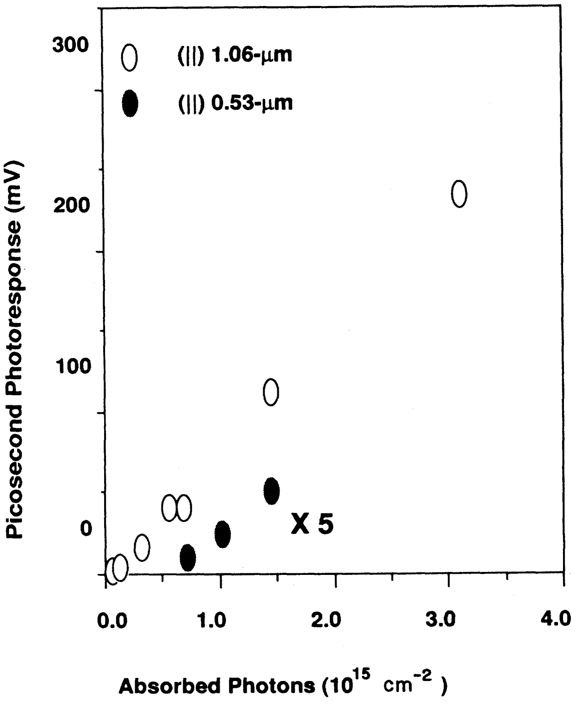

FIG. 5. 1D picosecond photocurrent with respect to the number of absorbed photons with parallel polarization of the above- and below-gap excitations. Notice, for proper scaling, that 5× the above-gap photoresponse is plotted.

is plotted with respect to the number of absorbed photons/cm^2. In Figs. 4 and 5, the photocurrent is directly proportional to the laser intensity at each excitation wavelength and optical field polarization. In each case the photoconductive response is greater for below-gap excitation. This point is dramatically illustrated in Fig. 5, where the actual photoconductive response for above-gap parallel excitation has been multiplied by a factor of 5 and plotted.

DISCUSSION

It is widely accepted that for above-gap excitation in conducting polymers, excess charge carriers created by doping or photon absorption strongly interact with the lattice (electron-phonon interaction), giving rise to charged excitations that carry along a chain distortion. In the case of one-dimensional chain polymer with a degenerate ground state, such as *trans*-(PA), the localization of the carrier is predicted[4] to give rise to topological highly mobile solitons. These charged carriers are believed to determine the electrical transport properties of this polymeric semiconductor. Since this kind of excitation can only exist in pairs, the bond alternation kink cannot be carried along when the electron is transferred to a neighboring chain, and a polaron is formed in this case.[31] Therefore, both solitons and polarons can be available to participate as photocarriers in *trans*-(PA).

TEMPERATURE DEPENDENCE OF THE PICOSECOND PHOTOCURRENT WITH BELOW-GAP EXCITATION

With oriented samples we are able to separate the contribution of the charged carriers moving along the polymer chains (1D configuration) from those that are moving across them (3D configuration). The temperature dependence of the transient picosecond photoconductive response of *trans*-(PA) in the 1D and 3D configurations for below-gap excitation shown in Fig. 1 is very similar to our previously reported measurements for above-gap excitation.[14] The similarity of these two measurements implies that they arise from the same mechanism (solitons and polarons). For above-gap excitation, the photogeneration of the charged soliton paris occurs indirectly via an electron-hole pair. In the case of below-gap excitation, the photogeneration of the charged carriers is direct. The energy gap (E_g) for *trans*-(PA) is approximately 1.8 eV. With an excitation energy of 1.17 eV (1.06 μm) one would expect, assuming that *trans*-(PA) behaves like a typical three-dimensional inorganic semiconductor, that the photoconductive response would not occur except as a result of two-photon absorption or through band tailing. However, measurements of the photoconductivity under pressure have shown that the absorption edge for *trans*-(PA) does not arise from static disorder or associated band-tailing effects known in amorphous semiconductors.[21] Also, earlier experimental results, such as the observation of a threshold near the soliton pair creation energy, strongly suggest that the photocurrent at 1.17 eV is due to direct excitation of the charged carriers.[32] The linear dependence of the photocurrent with respect to the laser intensity of the below-gap excitation shown in both Figs. 4 and 5 further substantiates that direct excitation is the main photogenerating process occurring here.[33]

We previously reported that with above-gap excitation ($\hbar\omega > 2\Delta$) the picosecond photocurrent of *trans*-(PA) was temperature independent in the 1D configuration and temperature dependent in the 3D configuration.[14] The temperature independence of the transient photocurrent in the 1D configuration violates both band and hopping conduction since both are strongly dependent on temperature. Therefore, it seems reasonable to assume that the photogenerated charged carriers have unusual properties that are maintained only when traveling along the chain. Conwell and Jeyadev have shown through theoretical analysis that the mobility of solitons should not depend much on temperature between 70 and 300 K.[34]

In the 3D configuration for carriers produced on the chain, the first step of their random walk motion would take place by phonon-assisted hopping, giving rise to a perpendicular hopping conductivity. In this case the charged carriers should be polarons since a simultaneous jump of a soliton-antisoliton pair is highly unlikely. Thus one is led to conclude that the 63-meV activation energy (E_a), observed for the 3D picosecond photocurrent in Fig. 1, represents the activation energy for a polaron to hop between neighboring chains. The activation energy (E_a) in the 3D configuration for below-gap ($E_a = 63$

meV) and above-gap ($E_a = 43$ meV) excitations are of the same order of magnitude. The similar values of the activation energies strongly suggest that the charged carriers for both cases are one in the same. The difference between the two may be due to heating effects, which are more critical for above-gap excitation because of the greater absorbtion and smaller penetration depth.

COMPARISON OF THE PICOSECOND PHOTOCURRENT ANISOTROPY FOR ABOVE- AND BELOW-GAP EXCITATION

The anisotropic character of charge transport in conjugated polymers arises from the large differences between intrachain and interchain overlap integrals. The large overlap between atomic wave functions along the chain gives rise to the formation of strong π covalent bonds, while small overlap between adjacent chains is responsible for the weak van der Waals bonding. This electronic structure is responsible for the electrical anisotropy (i.e., the ratio of the 1D photocurrent to the 3D photocurrent) of polyacetylene. However, as previously discussed, *trans*-polyacetylene exhibits a so-called "pump anisotropy" for a given orientation of the applied dc electric field. The photoconductive response increases as the light polarization is changed from parallel to perpendicular with respect to the chain direction. This phenomenon, which has been observed by various groups,[15,18,24] has received two different explanations. One school of thought is the bimolecular recombination of the photocarriers related to their topological nature (Dorsinville *et al.* and Blanchet *et al.*).[17] In their model the polarization anisotropy is due to the difference in the nonlinear recombination for the two configurations (1D and 3D). The perpendicular and parallel absorption coefficients are 4×10^4 and 6×10^5 cm^{-1}, respectively at 2.4 eV, with corresponding penetration depths of 25 and 1.7 μm. Therefore, the penetration depth is much smaller and the charge density much greater for parallel excitation. Hence, nonlinear bimolecular recombination is more likely to occur for this polarization of the laser, reducing the number of charged carriers that participate in photoconduction. The opposite occurs with perpendicular excitation, where the charged carrier density is less, thus allowing a greater number of the initially photogenerated charged carriers to contribute to the photocurrent.

The other model is related to the difference in geminate recombination rates between interchain and intrachain carriers in *trans*-(PA).[35] Carriers created on different chains escape geminate recombination. With perpendicular polarization of the laser, more long-lived interchain carriers can be directly photogenerated (Townsend and Friend and Bleir *et al.*).[37,36] The observation by Bleir *et al.* that the rate of decay of the slow photocurrent component is intensity independent seems to favor this interpretation. However, it is well known that only a small percentage of the initially photogenerated charged carriers contribute to the slow component. Nonlinear bimolecular recombination may be affecting only the first stage of the dynamics of the charged carriers in *trans*-(PA). The slow component dynamics is mostly controlled by impurities and defects in the sample.

The present data add the salient information that (1) for above-gap excitation the pump anisotropy depends on the intensity, (2) the below-gap anisotropy is significantly smaller than the above-gap anisotropy and is independent of the intensity, and (3) the photocurrent is greatest for below-gap excitation. These results can be accounted for by using the bimolecular recombination model as follows: As the above-gap excitation intensity increases, the charge density increases more rapidly for the perpendicular polarization of the laser than for the parallel polarization, reducing the above-gap anisotropy ratio. The probability of generating free-electron–hole pairs is greatly reduced with below-gap excitation. Since fewer photons are absorbed as well, this reduces the charged carrier density and the bimolecular recombination rate for all polarizations. Hence, as the laser intensity increases, the relationship between the charge density for the perpendicular and parallel polarizations remains the same, and in turn, the below-gap anisotropy ratio is constant. This also explains why the below-gap anisotropy is smaller than the above-gap anisotropy. The role bimolecular recombination plays in reducing the number of charged carriers that participate in the picosecond photocurrent is made clear in Figs. 4 and 5. Hence one can see that regardless of the polarization of the optical field (perpendicular or parallel) the photocurrent is always greatest for the case of below-gap excitation, where the bimolecular recombination rate is lowest.

The intensity dependence of the above-gap anisotropy is possibly influenced by heating effects following the laser pulse. A temperature increase is expected following illumination with above-gap photons polarized along the polymer chains. Under these conditions the penetration depth is minimum [$d = 1/\alpha = (6\times10^5)^{-1}$]. Moreover, as we are considering short (25 ps) laser pulses, heat diffusion beyond the illumination volume can be neglected to a first-order approximation. The temperature increase following a pulse is given by

$$\Delta T = N\varepsilon / lc\rho ,$$

where N is the number of absorbed photons per cm^2 per pulse, l is the penetration depth, c is the specific heat, ρ is the density, and ε is the photon energy. Assuming $N = 10^{15}$ photons/cm^2, $\rho = 1.1$ g/cm^3, $c = 1$ J/K, and $\varepsilon = 2.34$ eV we get $\Delta T = 263$ K for parallel polarization. This heating following the pulse is large enough to increase the hopping conduction, which has an activation energy of 0.05 eV. This could effectively reduce the above-gap anisotropy as the laser intensity increases.

CONCLUSION

We have shown that for below-gap excitation, the picosecond photoconductive response of *trans*-(PA) is temperature dependent in the 3D configuration with an activation energy of 63 meV and temperature independent in the 1D configuration. From these measurements we infer that solitons and polarons are probably the principal charged carriers in *trans*-(PA) and that these carriers can be generated directly with below-gap excitation. We have also shown that the ratio of the photocurrent when the optical electric field is perpendicular to the chain to that of the photocurrent when the optical electric field is parallel to the chain decreases with laser intensity (from 7.4 to 4.5) for above-gap excitation and is independent of intensity for below-gap excitation. In addition, we find that the picosecond photocurrent is greatest for below-gap excitation independent of the optical field polarization. These results are well accounted for by the bimolecular recombination model and the effects of laser heating.

ACKNOWLEDGMENTS

This work is supported in part by NASA Grant No. 449521 and National Science Foundation Grant No. RII-88-02964.

---

[1] P. Piaggio, G. Dellepiane, L. Piseri, R. Tubino, G. Zannoni, G. Zerbi, and G. Lugli, J. Mol. Struct. **115**, 193 (1984).

[2] P. Piaggio, G. Dellepiane, L. Piseri, R. Tubino, and C. Taliani, Solid State Commun. **50**, 947 (1984).

[3] M. Galtier, M. Charbonnel, A. Montaner, and J. L. Ribeb, Polymer **25**, 1253 (1984).

[4] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1968 (1979).

[5] W. P. Su and J. R. Schrieffer, Proc. Natl. Acad. Sci. USA **77**, 5626 (1980).

[6] S. Etemad, A. J. Heeger, and A. G. MacDiarmid, Annu. Rev. Phys. Chem. **33**, 443 (1982).

[7] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).

[8] M. J. Rice, Phys. Lett. **71A**, 152 (1979).

[9] H. Takayama, Y. R. Lin-Lin, and K. Maki, Phys. Rev. B **21**, 2388 (1980).

[10] J. Orenstein and G. Baker, Phys. Rev. Lett. **49**, 1043 (1982).

[11] Z. Vardeny, J. Strait, D. Moses, T. T. Chung, and A. J. Heeger, Phys. Rev. Lett. **49**, 1657 (1982).

[12] C. V. Shank, R. L. Fork, J. Orenstein, and G. L. Baker, Phys. Rev. Lett. **49**, 1660 (1982).

[13] Graciela B. Blanchet, C. R. Fincher, T. C. Chung, and A. J. Heeger, Phys. Rev. Lett. **50**, 1938 (1983).

[14] A. Walser, A. Seas, R. Dorsinville, R. R. Alfano, and R. Tubino, Solid State Commun. **67**, 333 (1988).

[15] R. Dorsinville, S. Krimchansky, R. R. Alfano, J. L. Birman, R. Tubino, and G. Dellepiane, Solid State Commun. **56**, 857 (1985).

[16] R. Dorsinville, M. Szalkiewicz, R. Tubino, J. L. Birman, and R. R. Alfano, Synth. Met. **17**, 509 (1987).

[17] R. Tubino, R. Dorsinville, A. Seas, J. Birman, and R. R. Alfano, Phys. Rev. B **38**, 8318 (1988).

[18] M. Sinclair, D. Moses, R. H. Friend, and A. J. Heeger, Phys. Rev. B **36**, 4296 (1987).

[19] Graciela B. Blanchet, C. R. Fincher, and A. J. Heeger, Phys. Rev. **51**, 2132 (1983).

[20] L. Rothberg, T. M. Jedju, and G. L. Baker, IEEE J. Quantum. Electron. **QE-24**, 311 (1988).

[21] D. Moses, A. Feldblum, E. Ehrenfreund, and A. J. Heeger, Phys. Rev. **26**, 3361 (1982).

[22] R. Dorsinville, S. Krimchansky, R. R. Alfano, J. L. Birman, R. Tubino, and G. Dellepiane, Solid State Commun. **56**, 857 (1980).

[23] M. Sinclair, D. Moses, and A. J. Heeger, Solid State Commun. **59**, 6 (1986).

[24] H. Bleir, S. Roth, H. Lobentanzer, and G. Leising, Europhys. Lett. **4**(12), 1397 (1987).

[25] S. D. Phillips and A. J. Heeger, Phys. Rev. B **38**, 6211 (1988).

[26] A. D. Walser, R. Dorsinville, R. Tubino, and R. R. Alfano, J. Appl. Phys. Lett. (to be published).

[27] T. Ito, H. Shirakawa, and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. **12**, 11 (1974).

[28] G. Lugli, U. Pedretti, and G. Perego, J. Polym. Sci. Polym. Lett. Ed. **23**, 129 (1985).

[29] P. Piaggio, G. Delepiane, R. Tubino, L. Piseri, and G. Lugli, Solid State Commun. **49**, 895 (1984).

[30] A. D. Walser and R. R. Alfano, Appl. Phys. Lett. **52**, 592 (1988).

[31] J. Orenstein, Z. Vardeny, G. L. Baker, G. Eagle, and S. Etemad, Phys. Rev. B **30**, 786 (1984).

[32] L. Lauchlan, S. Etemad, T. C. Chung. A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B **24**, 3701 (1981).

[33] S. Jayaraman and C.H. Lee, Appl. Phys. Lett. **20**, 292 (1972).

[34] E. M. Conwell and S. Jeyadev (private communication).

[35] G. Leising, Synth. Met. **28**, D215 (1989).

[36] P. D. Townsend and R. H. Friend, Phys. Rev. B **40**, 3112 (1989).

[37] H. Bleir, S. Roth, Y. Q. Shen, D. Schafer-Siebert, and G. Leising, Phys. Rev. B **38**, 6031 (1988).