Polarization-dependent photocurrent in thin film polydiacetylene single crystals

LETTER TO THE EDITOR

Polarization-dependent photocurrent in thin film polydiacetylene single crystals

Y Yang†, J Y Lee‡, A K Jain†, J Kumar†, S K Tripathy‡, H Matsuda§, S Okada§ and H Nakanishi§

† Department of Physics, University of Massachusetts-Lowell, Lowell, Massachusetts 01854, USA
‡ Department of Chemistry, University of Massachusetts-Lowell, Lowell, Massachusetts 01854, USA
§ Research Institute for Polymers and Textiles, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

Abstract. Investigations of the anisotropic photocurrent behaviour, as a function of laser intensity and sample temperature, in thin film polydiacetylene single crystals are reported. These polydiacetylenes, PTS (poly-(2,4-hexadiyne-1,6-diol bis(p-toluenesulphonate))) and BTFP (poly-bis-(4-*n*-butyl-2,3,5,6-tetra-fluorophenyl) butadiyne), have similar one-dimensional electronic band structures. However, the polarization and temperature-dependent photocurrent have completely different behaviour for PTS and BTFP. These results indicate that photocurrent behaviour in these quasi-one-dimensional semiconductors is strongly influenced by the nature and organization of the side groups.

Diacetylene monomers, of general formula R1–C≡C–C≡C–R2, undergo solid state polymerization in a monomer single crystal that can lead to single-crystal polymers with oriented conjugated chains [1]. These polymer crystals show a large degree of anisotropy in their electrical and optical properties due to a quasi-one-dimensional (Q1D) electronic band structure. Their physical properties may be tailored by selecting appropriate side groups [2]. These characteristics make single crystals of polydiacetylenes ideally suited for investigation of Q1D electronic behaviour [3]. These conjugated polymers have been studied extensively for their unique electronic and optical properties [4–6]. Recently, photoconductivity studies on polyacetylene [7, 8] and polydiacetylene [9] have indicated evidence of interchain photocarrier generation. It was conjectured that the interchain photocarrier generation may help the charge carriers to escape strong geminate recombination by hopping into adjacent chains. Investigation of anisotropic photocurrent behaviour in two types of polydiacetylene single crystals using a steady-state photoconductivity technique at different temperatures and laser intensities is reported.

Diacetylene single crystals from 2,4-hexadiyne-1,6-diol bis(p-toluene-sulphonate) (PTS) [10] and bis-(4-*n*-butyl-2,3,5,6-tetrafluorophenyl)butadiyne (BTFP) [11] monomers were grown by a confined-solution technique [12]. The molecular structure of PTS and
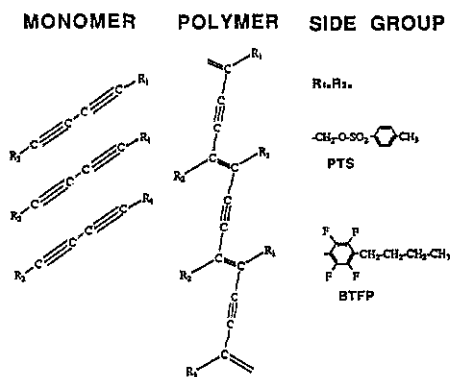
MONOMER   POLYMER   SIDE GROUP

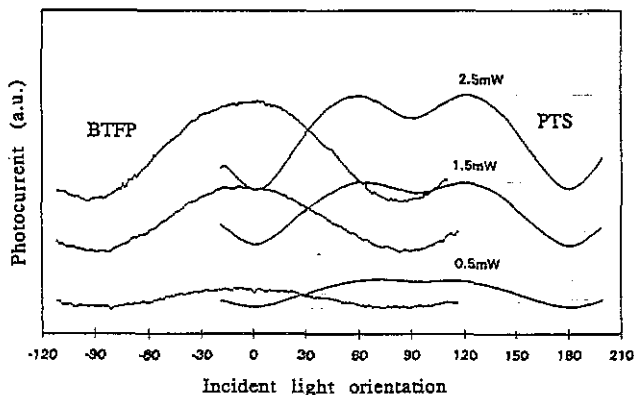Figure 1. Molecular structure of PTS and BTFP.

Figure 2. The polarization-dependent photocurrent in PTS and BTFP at three different laser intensities.

BTFP are shown in figure 1. Polymerization was carried out using techniques reported elsewhere [13]. Two gold electrodes were vacuum deposited on micron-thick PTS and BTFP single crystals, with typical dimensions of 2×5 mm and of 0.1×10 mm, respectively. The two electrodes are separated by a 240 μm wide gap and arranged such that an electric field can be applied parallel to the polymer backbone. A CW Ar^+ laser beam with 488 nm wavelength was used as the light source for the photoconductivity measurements. The photoinduced current was measured by standard phase-sensitive detection technique using a mechanical light chopper and a lock-in amplifier. The polarization of the laser beam can be rotated by adjusting a half-wave plate and the intensity of the laser beam can be adjusted by a neutral-density filter. All the measurements were carried out with the samples mounted on top of the cold finger in a closed-cycle helium gas cryogenic Dewar which can be cooled down to 10 K. The pressure in the Dewar was kept at about 10^{-5} torr. In the temperature-dependent photoconductivity measurements, the temperature of the sample was monitored by a Si diode thermometer placed adjacent to the polydiacetylene single crystals on the same substrate.

The dependence of photocurrent on the polarization direction of the incident light is shown in figure 2 for PTS and BTFP at three different laser intensities. The data are corrected to take into account the anisotropic reflection from the samples. PTS data were taken at 180 K, where maximum photocurrent is observed [14]. In PTS, at low laser
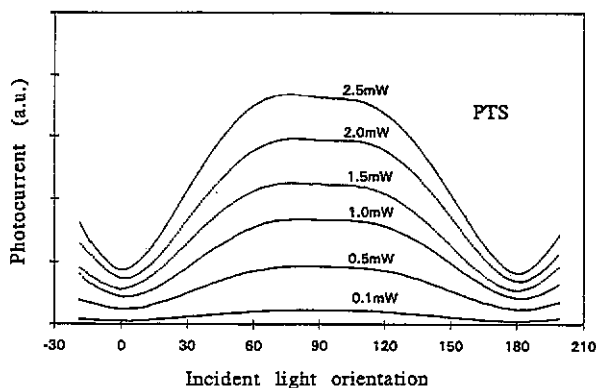
Figure 3. The polarization-dependent photocurrent in PTS at six different laser intensities; data were taken at room temperature.

intensity, the photocurrent is a maximum for polarization directions oriented at 90° to the backbone. Minimum photocurrent occurs when the polarization is parallel to the chain. However, at higher laser intensities, a dip is observed in the photocurrent when the polarization is exactly perpendicular to the backbone direction. The behaviour of the photocurrent along the chain as a function of polarization of the incident light is quite different for BTFP compared to that of PTS. The minimum photocurrent in BTFP occurs when the polarization is perpendicular to the backbone direction and the maximum occurs when the incident light polarization is parallel to the backbone direction. The photocurrent behaviours at different laser intensities are similar. Earlier reports [9] on PTS have shown that the photocurrent for incident light polarized perpendicular to the backbone is larger than the photocurrent for light polarized parallel to the backbone. The detailed behaviour of the photocurrent with the incident light polarization and intensity, however, have not been reported.

In order to further understand this double-hump photocurrent behaviour in PTS, the polarization-dependent photocurrent at room temperature is plotted in figure 3 at different laser intensities. The data in figure 2 are also normalized to a minimum photocurrent value for both systems and replotted in figure 4. The data in figures 2, 3 and 4 suggest that the double-hump feature of PTS becomes more pronounced at higher laser intensities. This feature is also enhanced at a temperature around 180 K, where the highest photocurrent is observed. It is postulated that interchain photocarrier generation helps the charge carriers to escape strong geminate recombination by hopping into adjacent chains. This reaches its maximum efficiency when the incident light polarization is oriented at 90° to the backbone [9]. However, as charge-carrier concentration increases, there is an increase in bimolecular recombination as well. Above a certain carrier density threshold, the number of charge carriers participating in conduction is reduced by this bimolecular recombination even though more carriers are generated by increasing the laser intensity. Hence, at higher laser intensities, the photocurrent in PTS begins to saturate for the incident light polarization perpendicular to the polymer backbone. At an incident polarization angle offset from 90°, carriers still escape geminate recombination by hopping to neighbouring chains. However, at these intermediate angles there is stronger absorption than that at 90° incident polarization. This results in larger carrier densities in a thinner top slice of the single crystal. Even accounting for
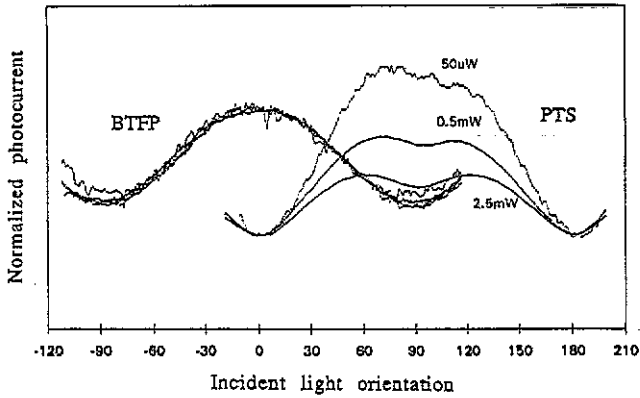
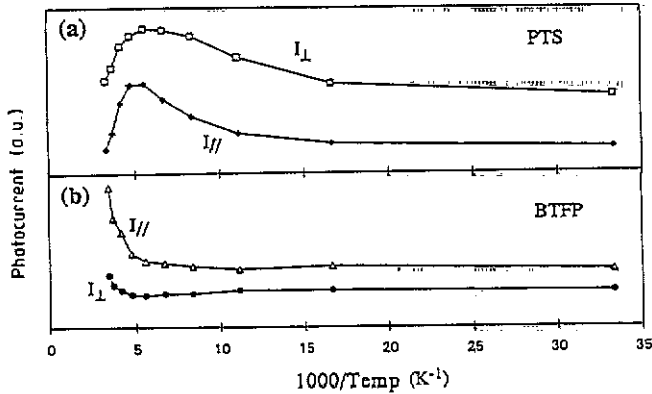**Figure 4.** The normalized polarization-dependent photocurrent in PTS and BTFP.

Figure 5. The temperature-dependent photocurrent for (a) PTS and (b) BTFP. $I_{\parallel}$ and $I_{\perp}$ are photocurrents with incident light polarization parallel and perpendicular to the polymer chain, respectively.

bimolecular recombination, more photocarriers reach the electrodes at these offset angles to produce a maximum in the photocurrent. Photocurrent maxima are seen offset from 90° with a dip at 90° as the laser intensity is increased. The polarization angle for maximum photocurrent continues to shift away from 90° as incident intensities are increased. The normalized photocurrent of BTFP is also shown in figure 4. The overlapped normalized photocurrent of BTFP indicates that bimolecular recombination does not occur in BTFP at the intensities at which the experiments were done.

The temperature-dependent photocurrents of PTS and BTFP are plotted in figure 5 for both parallel and perpendicular polarizations. For PTS, the photocurrent showed a maximum at about 180 K as the temperature was varied from 295 K to 30 K—this result is in agreement with previously reported data [14]. A modified Onsager geminate recombination model [15], which incorporated both diffusion and ballistic electron motions in Q1D materials, was used to explain the temperature-dependent photocurrent behaviour of PTS. As PTS cools down from 300 K to 180 K, the photocurrent is dominated by the carrier mean free path, s. The increasing mean free path, s, gives PTS an increasing

photocurrent during this temperature excursion. As the temperature falls below 180 K, the carrier's mean free path in PTS starts to saturate. The Coulomb capture radius (which controls the geminate recombination process) becomes the dominating factor in determining the photocurrent behaviour at temperatures below 180 K. A decreasing photocurrent is therefore seen due to the enhanced geminate recombination process.

For BTFP, the photocurrent decreases as the temperature is decreased from 295 K to 150 K and remains almost constant at temperatures below 150 K down to 30 K. The initial increase in photocurrent as temperature drops below room temperature in PTS is not seen in BTFP. For BTFP, in the temperature range 300 to 30 K, the mean free path, s, appears already saturated. Alternatively, the ballistic model proposed by Blum and Bassler [15] may not be applicable for BTFP.

This totally different behaviour of polarization and temperature dependence of photocurrent is significant in light of the fact that the behaviour of polarization dependence of absorption in these two crystals is very similar [11]. The absorption in both PTS and BTFP single crystals is dominant when the incident polarization is along the chain direction. The single crystals also show very similar behaviour of the electric field dependence of the photocurrent; the photocurrents for both types of crystals increase superlinearly with electric field for electric fields higher than 8000 V cm^{-1}. The wavelength-dependent photocurrents for PTS and BTFP are also very similar in the range 514–458 nm.

The molecular structure of the side groups and their organization in the two polydiacetylenes are quite different. In BTFP there is a strong possibility of π conjugation between the side groups and the backbone [11]. However, in PTS the side groups are attached to the backbone by σ bonds. Side groups are thus shown not only to play an important role in defining the bandgap [17] but also to influence the photocurrent behaviour quite significantly. In summary, PTS and BTFP have many similar backbone electronic properties. However, they have some significant differences possibly due to differences in the side group molecular structure, organization and electronic structure. These results also emphasize the inapplicability of general models (for instance Onsager's geminate recombination model) for describing the photocurrent behaviour in these Q1D semiconductors without due consideration to the details of molecular structure.

References

[1] Cantow H J (ed) 1984 Polydiacetylene *Advances in Polymer Science* (Berlin: Springer)
[2] Clough S B, Kumar S, Sun X F, Tripathy S K, Matsuda H, Nanaishi H, Okada S and Kato M 1989 *Nonlinear Optics of Organics and Semiconductors (Springer Proceedings in Physics 36)* ed T Kobayashi (Berlin: Springer) p 149
[3] See for example 1985 *Polydiacetylenes* ed D Bloor and R R Chance (Nato ASI Series E: Applied Sciences-No 12) (Dordrecht: Martinus Nijhoff)
[4] Blanchard G J, Heritage J P, Von Lehmen A C, Kelly M K, Baker G L and Etemad S 1989 *Phys. Rev. Lett.* **63** 887
[5] Carter G M, Thakur M K, Chen Y J, Hryniewicz J V 1985 *Appl. Phys. Lett.* **47** 457
[6] Robins L, Orenstein J and Superfine R 1986 *Phys. Rev. Lett.* **56** 1850
[7] Phillips S D, Yu G and Heeger A J 1989 *Synth. Met.* **28** D669
[8] Danielsen P L 1986 *J. Phys. C: Solid State Phys.* **19** L741

 [9] Blum T and Bassler H 1989 *Phys. Status Solidi* b **153** K57
[10] Pope M and Swenberg C E 1982 *Electronic Process in Organic Crystals* (New York: Oxford University Press)
[11] Nakanishi H, Matsuda H, Okada S and Kato M 1989 *Nonlinear Optics of Organics and Semiconductors (Springer Proceedings in Physics 36)* ed T Kobayashi (Berlin: Springer) p 155
[12] Thakur M K and Meyler S 1985 *Macromolecules* **18** 2341
     Thakur M K, Tripathy S K and Sandman D J US patent no 4 793 893
[13] Lee J Y and Tripathy S K 1990 *Polymer Preprints ACS Division of Polymer Chemistry* **31** 414
[14] Lochner K, Reimer B and Bassler H 1976 *Phys. Status Solidi* b **76** 533
[15] Blum T and Bassler H 1988 *Chem. Phys.* **123** 431
[16] Donovan K J and Wilson E G 1986 *J. Phys. C: Solid State Phys.* **19** L357
[17] Orchard B J and Tripathy S K 1986 *Macromolecules* **19** 1844