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Photocurrent generation and transport in a partially polymerized polydiacetylene

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Abstract. Steady-state and transient photoconductivities have been investigated as a function of electric field, light intensity and temperature in single crystals of partially polymerized polydiacetylene, 1,4-bis(3-quinol)-1,3-butadiyne, with conjugating side groups. The polarization dependence of the steady-state photocurrent was also investigated. The one-dimensional Onsager theory of geminate recombination qualitatively accounts for the experimental results. Deviation from the theory is observed in the temperature dependence of the transient peak photocurrent at temperatures below 100 K.

1. Introduction

Polydiacetylenes are conjugated polymers that can be obtained in the form of single-crystal quasi-one-dimensional solids. A large number of polydiacetylenes have been obtained by solid state polymerization in the monomer crystal ($R_1-C\equiv C-C\equiv C-R_2$) (Cantow (1984) and references therein). In polydiacetylene, the strong overlap of the p_z orbitals of the backbone carbon atoms leads to a delocalized electronic structure along the chain direction. In the other orthogonal directions non-bonded weak interaction between the chains (van der Waals forces) are operative. Semiconducting behaviour is expected along the chain direction in these materials whereas in the orthogonal directions the behaviour is that of molecular crystals. Its electronic and optical properties are primarily determined by the π -electrons of the backbone. Experiments on these polymeric single crystals are important to understand the behaviour of quasi-one-dimensional materials and in particular the applicability of the Onsager (1938) theory of geminate recombination.

Steady-state and transient photoconductivity measurements have been reported by a number of researchers (Donovan and Wilson 1981a, b, Blum and Bassler 1988, Moses *et al* 1987) on single crystals of poly-(2,4-hexadiyne-1,6-diol bis(*p*-toluenesulphonate)) (PDA-TS), the prototypical polydiacetylene system. In DA-TS monomer single crystals, complete polymerization can be obtained. The one-dimensional version of the Onsager theory of pair dissociation in a single-crystal PDA-TS sample was reported by Seiferheld *et al* (1983) and Donovan and Wilson (1981b). The superlinear behaviour of photocurrent observed at high fields ($E > 10^4$ V cm⁻¹) was explained by taking into account the field dependence of the primary ionization process (Seiferheld *et al* 1983). Fast transient photoconductivity measurements (picosecond) by Moses *et al* (1987) revealed a temperature-dependent initial fast component (picosecond) and a strongly temperature-dependent longer-time component

(nanosecond). The temperature independence of the initial photocurrent was interpreted as due to hot carriers. From their experiment, Moses *et al* (1987) concluded that the Onsager geminate recombination theory which is widely applied to molecular crystals and low-mobility disordered semiconductors is not applicable to PDA-TS in the picosecond regime. Recently, Yang *et al* (1992) observed that the nature and organization of the side groups (R_1 and R_2) strongly influence the photocurrent behaviour.

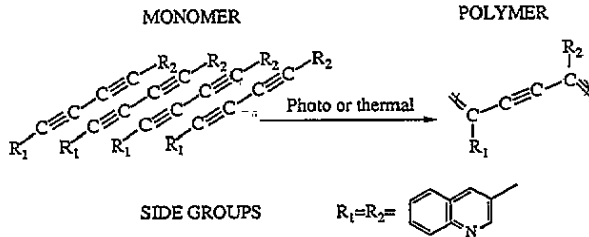


Figure 1. Chemical structure of the polymer PDA-DQ.

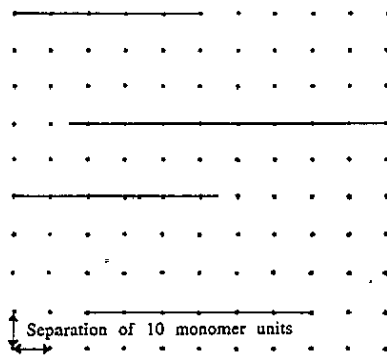


Figure 2. Schematic view of polymer chains in the monomer crystal. A degree of polymerization of about 60 has been assumed.

Recently single crystals of partially polymerized 1,4-bis(3-quinol)-1,3-butadiyne (PDS-DQ) were obtained by γ -ray irradiation in monomer single crystals (Talwar *et al* 1990). Monomer-to-polymer conversion in PDA-DQ was only 25% (Kamath *et al* 1993). Figure 1 shows the chemical structure of the polymer. The 3-quinolyl side group ($R_1 = R_2$) is symmetrically attached to the backbone through π -conjugation. At this level of polymerization the polymer chains form a solution in the monomer and are isolated from each other (figure 2). We expect to observe the effect of trap-dominated transport in PDA-DQ crystals because of its partially polymerized nature.

The photocurrent behaviour as a function of electric field, light intensity and temperature is reported in this paper on a partially polymerized PDA-DQ single crystal. The system studied is a mixture of polymer and monomer. Owing to the single-crystal nature of the samples the polymers form as extended chains and are aligned in the direction of the applied electric field. In spite of the partially polymerized nature of this material, the one-dimensional Onsager theory of geminate recombination was found to account qualitatively for the experimental results at temperatures above 160 K.

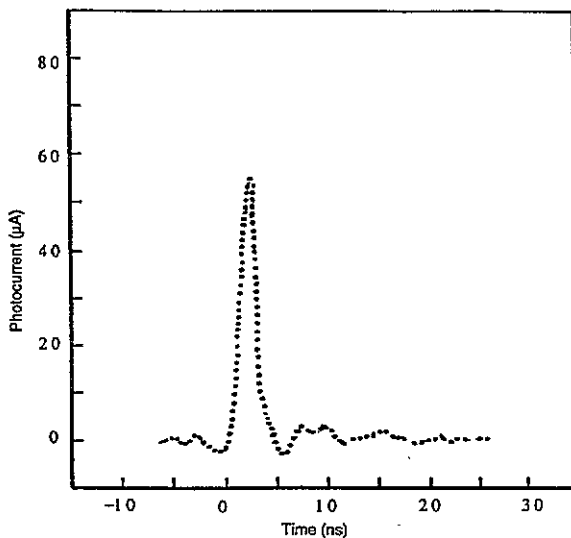


Figure 3. Transient photocurrent in PDA-DQ excited by 3 ns laser pulses (electric field, 10^4 V cm $^{-1}$; $I = 0.051$ μ J/pulse).

2. Experimental details

Transient photoconductivity measurements were performed in an Auston (1984) switch transmission line configuration. A crystal of thickness about 40 μ m was mounted on a microscope cover glass substrate and gold electrodes were fabricated by vacuum deposition. The sample was mounted onto a cold finger of a cryostat that can be cooled to 10 K. The sample (typical area, 110 μ m \times 90 μ m) was uniformly illuminated by N₂ laser pulses of 3 ns duration (FWHM) with a repetition rate of 20 Hz. Electrical signals were amplified with a 300 MHz amplifier and were recorded on a sampling oscilloscope of rise time 375 ps. Steady-state photoconductivity measurements were performed on the same sample geometry. CW light of wavelength 488 nm from an Ar⁺ laser was chopped at 20 Hz and was used as a light source. The signal across a 1 M Ω resistor which is in series with the sample was detected with a lock-in detector. The direction of polarization of the incident beam was perpendicular to the polymer chain direction. The polarization dependence of the steady-state photocurrent was measured using a half-wave plate which was driven by a motor. In all the measurements, the electric field was along the polymer backbone. All the measurements were done under vacuum conditions of 10^{-4} Torr or lower.

3. Results

Figure 3 shows the transient photocurrent response of the partially polymerized PDA-DQ single crystal excited by N₂ laser pulses of 3 ns duration. The signal rise time of 3 ns is determined by the overall time constant of the electronic circuits. The decay time constant extracted from the pulse is 1.5 ns. Figure 4 shows the electric field E dependence of the steady-state photocurrent i at different light intensities. At low fields (less than 4000 V cm $^{-1}$), the photocurrent varies as E^n with $1 < n < 2$. At high fields, the photocurrent varies as E^2 . Figure 5 shows the behaviour of the photocurrent as a function of

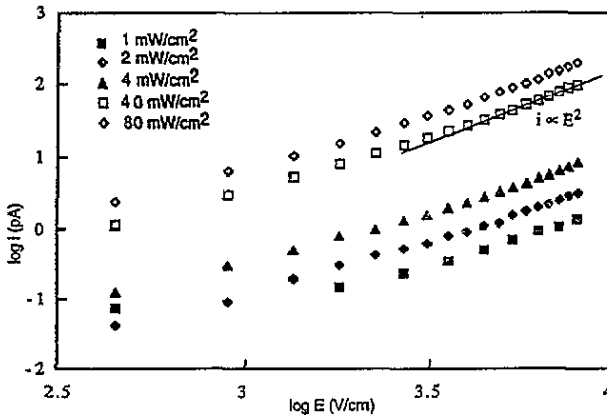


Figure 4. Electric field dependence of the steady-state photocurrent on a log-log plot at different light intensities (temperature, 296 K: —, $i \propto E^2$).

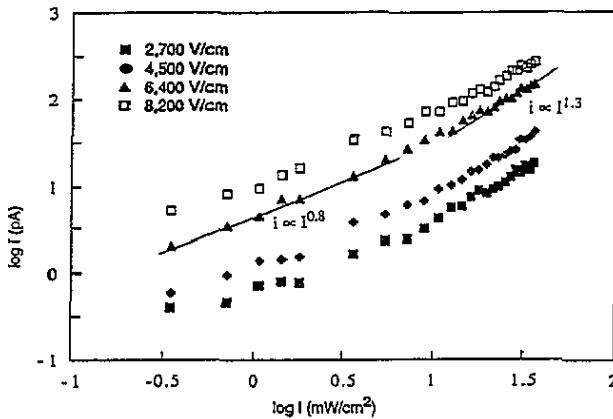


Figure 5. Intensity dependence of the steady-state photocurrent on a log-log plot at different electric fields; where $i \propto I^{0.8}$ at low intensities (less than 9 mW cm^{-2}) and $i \propto I^{1.3}$ at high intensities (temperature, 296 K: —, fit to the data).

light intensity I at different applied fields. At low light intensities (less than 9 mW cm^{-2}), the photocurrent varies as $I^{0.8}$, changing to $I^{1.3}$ behaviour at high light intensities.

Figure 6 shows the peak-photocurrent variation with electric field at various light intensities. At all measured light intensities, the peak photocurrent is proportional to $E^{1.1}$. Figure 7 shows the variation in peak photocurrent with intensity at different bias fields. The peak photocurrent varies as $I^{0.9}$. Figure 8 shows the polarization dependence of the steady-state photocurrent. The photocurrent is largest when the polarization is perpendicular to the chain direction and least when the polarization is along the chain direction. After reflectance correction, the anisotropy factor i_{\perp}/i_{\parallel} of the photocurrent reduces from 1.5 to 1.4. In the case of parallel polarization, 10% of light is reflected compared with 6% for perpendicular polarization.

Figure 9 shows the temperature T dependence of both steady-state and the transient photocurrents. The temperature dependence for both the steady-state and the transient

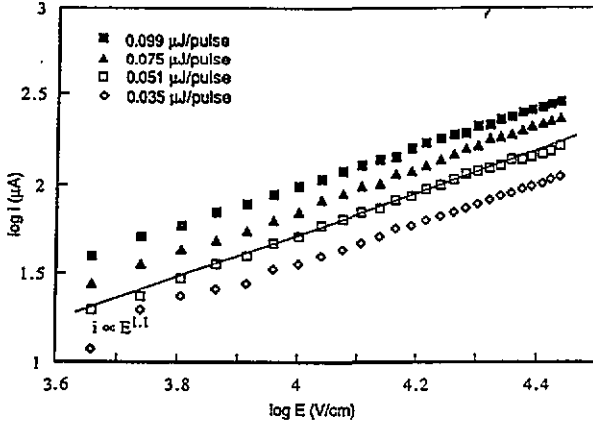


Figure 6. Peak photocurrent as a function of the electric field on a log-log plot at different intensities (temperature, 296 K: —, $i \propto E^{1.1}$).

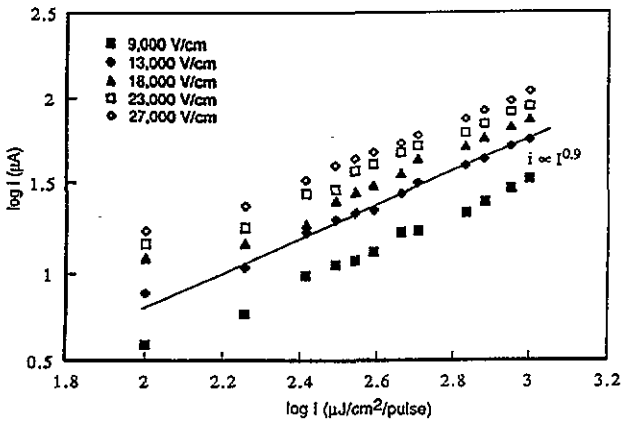


Figure 7. Peak photocurrent as a function of intensity on a log-log plot at different electric fields (temperature, 296 K: —, $i \propto I^{0.9}$).

photocurrents shows a peak at around 130 K. Both the steady-state and the transient photocurrents decrease with decreasing temperature down to 160 K. At temperatures below 100 K, the peak photocurrent is independent of temperature whereas a weak temperature dependence is observed for the steady-state photocurrent.

4. Discussion

The general features of the photocurrent behaviour of PDA-DQ with respect to the electric field, light intensity and temperature are similar to those of PDS-TS (Siddiqui 1980, Donovan and Wilson 1986). In polydiacetylenes, the electronic transition from valence band to conduction band occurs when the photon energy exceeds the band-gap energy (Lochner *et al* 1978). The photocurrent due to defect ionization can also occur when the photon energy is less than the band-gap energy (Siddiqui 1980). Photogenerated electron-hole

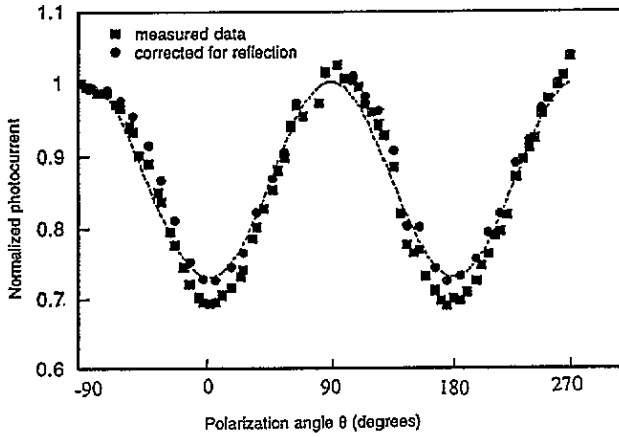


Figure 8. Anisotropy of the steady-state photocurrent with respect to the direction of polarization of the incident beam, where θ is angle between the direction of polarization and the chain direction: ---, fit to the function $A(1 + B \sin^2 \theta)$ with $A = 0.73$ and $B = 0.37$.

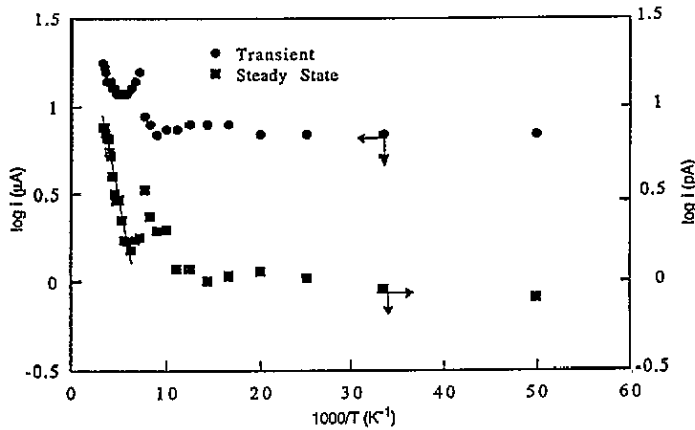


Figure 9. Temperature dependence of the steady-state and peak transient photocurrents.

pairs thermalize by phonon emission and trapping in defects. There is a distribution of thermalization lengths for the photogenerated carriers. A thermalized electron experiences a potential of its own partner (hole) and the applied potential. The carriers thermalizing beyond the potential well contribute to the temperature independent peak photocurrent. The majority of the carriers are assumed to be thermalized within the potential well (Donovan and Wilson 1986). The thermalization distance a is related to the activation energy E_a for the bound electron-hole pair to create free carriers and is given by the relation

$$a = e^2 / 4\pi\epsilon\epsilon_0 E_a \tag{1}$$

where e is the charge of the electron, ϵ is the relative dielectric constant and ϵ_0 is the permittivity of free space. Only a fraction of the pairs which escape geminate recombination by thermally activated diffusive random walk can contribute to the field- and temperature-dependent photocurrent. The probability that the carriers escape geminate recombination

from their mutual Coulomb potential well in one dimension is given by (Blossey 1974, Lochner *et al* 1976)

$$\phi(E) = (eEa^2/kTr_c) \exp(-r_c/a) \quad a < r_c \quad E < E_c = kT/er_c \quad (2)$$

where the Coulomb capture radius $r_c = e^2/4\pi\epsilon\epsilon_0kT$, and k is the Boltzmann constant. Assuming that $\epsilon = 4$ for PDA-DQ crystals, the critical field E_c obtained is $1.8 \times 10^4 \text{ V cm}^{-1}$ at $T = 296 \text{ K}$. The Onsager theory of geminate recombination in one dimension predicts that the probability that a carrier escapes geminate recombination increases linearly with increasing applied electric field and decreases exponentially with decreasing temperature. The photocurrent i is related to the number N of absorbed photons by the relation

$$i = eN(\eta\phi)s/d \quad (3)$$

where η is the quantum efficiency for electron-hole pair creation, d is the electrode spacing and $s = v\tau$ is the distance that a carrier travelled during its lifetime τ . According to the model of solitary wave acoustic polarons (SWAPs), a saturation of drift velocity v was predicted in one dimension (Wilson 1983). This was experimentally verified by Donovan and Wilson (1981a) in PDA-TS for times less than 50 ns. For longer times (greater than 100 ns), trap-limited transport of SWAPs was reported. The trap-limited velocity increases approximately linearly with increasing electric field and appears to saturate at acoustic velocities (Donovan *et al* 1989). In the trap-limited transport proposed by Blum and Bassler (1988), the average velocity of the charge carriers follows the relation $\langle v \rangle \propto E^{0.15}$ at low fields (less than $5 \times 10^3 \text{ V cm}^{-1}$) and a linear relation for $E > 2 \times 10^4 \text{ V cm}^{-1}$. Movaghar *et al* (1984) have theoretically described such dispersive trap-limited transport in one dimension. We expect trap-limited transport in partially polymerized PDA-DQ single crystals because of the high density of chain and other defects. Since η is field independent, the peak-photocurrent variation is mainly due to the probability that a carrier escapes from the potential well. Hence in one dimension the peak transient photocurrent varies linearly with electric field. In the case of the steady-state photocurrent, all the photogenerated carriers are collected at the electrodes ($s = d$). The photocurrent is solely determined by the carrier generation rate in the absence of bimolecular recombination. This condition is satisfied in high-quality molecular crystals (Chance and Braun 1976) and in crystalline PDA-TS (Donovan and Wilson 1981a). Carrier trapping and recombination are expected to occur in a partially polymerized PDA-DQ crystal. Assuming a dielectric constant of 4 for PDA-DQ which is same as that of PDA-TS (Rehberg 1979) yields $a = 61 \text{ \AA}$. The Coulomb capture radius r_c at 296 K is 142 \AA . Hence the carriers are thermalized within the Coulomb capture radius. The ϕ -dependence on E is determined by the relative magnitude of the electron mean free path l and r_c . For $l > r_c$, ϕ is independent of E whereas, for $l < r_c$, ϕ is field dependent. In the case of non-conductive molecular crystals such as anthracene (Pope and Swenberg 1982) and polydiacetylenes (e.g. PDS-TS) (Siddiqui 1980) the condition $l < r_c$ is satisfied. On the assumption that all the incident light is absorbed within the penetration depth of $1 \mu\text{m}$ (Seiferheld *et al* 1983), figure 5 gives a steady-state photocurrent density of $9 \times 10^{-7} \text{ A cm}^{-2}$ at $E = 2700 \text{ V cm}^{-1}$ and $I = 3.2 \text{ mW cm}^{-2}$. Further assuming that, on average, most of the photogenerated carriers reach the electrodes gives a quantum yield $\eta\phi$ of 7×10^{-4} .

The steady-state photocurrent variation with electric field is slightly superlinear ($i \propto E^{1.3}$) at low fields (less than 3000 V cm^{-1}). This is due to space-charge perturbation on the electric-field-dependent free-carrier generation rate (Lochner *et al* 1976). The E^2 -dependence of the photocurrent at high fields (greater than 4000 V cm^{-1}) is an indication of

injected carriers leading to space-charge-limited currents (Siddiqui 1984). However, at the same field strength the square-law dependence of the photocurrent on the electric field is not observed in the transient photoconductivity measurements. In the intensity dependence of the steady-state photocurrent, both sublinear and superlinear behaviour is observed. The sublinear behaviour ($i \propto I^{0.8}$) is due to some contribution from bimolecular recombination. The superlinear dependence ($i \propto I^{1.3}$) at high illumination may be due to the onset of the exciton-exciton collision annihilation process which produces free carriers. The exciton-exciton collision annihilation mechanism yields a photocurrent variation as I^2 (Silver *et al* 1963). The field-independent drift velocity predicted by trap-limited transport (Blum and Bassler 1988) explains the almost linear ($i \propto E^{1.1}$) peak-photocurrent variation with electric field. The peak-photocurrent variation is mainly due to the linear variation in the escape probability with electric field. The impurities present in the material may be responsible for this slight non-linearity (Tubino *et al* 1988). The peak-photocurrent variation with intensity is almost linear ($i \propto I^{1.09}$). The decay constant of the transient pulse in PDA-DQ is 1.5 ns. Moses *et al* (1987) observed a decay constant of 40 ns in PDA-TS. This difference is attributed to the rapid trapping of carriers in defects present in PDA-DQ because of its partial polymerization. The photocurrent variation with polarization angle θ is fitted to the function $A(1 + B \sin^2 \theta)$ (Phillips and Heeger 1988) with $A = 0.73$ and $B = 0.37$. Anisotropy of the photocurrent with respect to the direction of polarization can be explained by either bimolecular recombination or the lifetime of carriers generated on different chains. It is known that, when the direction of polarization is parallel to the chain direction, the penetration depth is much lower than when it is perpendicular to the chain direction (Uitz *et al* 1987). Hence the carrier density is larger when the polarization is parallel to the chain direction. This favours bimolecular recombination which causes a reduction in photocurrent. Another explanation is that the probability of interchain excitation is more when the direction of polarization is perpendicular to the chain direction. Hence, the perpendicularly polarized light favours the carriers escaping geminate recombination to adjacent chains (Bleier *et al* 1987). It should be noted that the polymer chains are widely separated from each other owing to the partially polymerized nature of the crystals. However, the conjugating side groups transverse to the main chain may play an important role in charge generation as well as transport.

The temperature dependence of the steady-state photocurrent indicates an activated process above 160 K with an activation energy of 59 meV which is comparable with that of PDA-TS (56 ± 2 meV) obtained by Reimer and Bassler (1978a, b). The activated process observed in the temperature dependence of the photocurrent shows the presence of free-carrier production from a bound electron-hole pair. The steady-state photocurrent decreases weakly with decreasing temperature below 100 K. In the temperature dependence of the steady-state and transient photocurrents a peak in the photocurrent is observed at around 130 K. At higher temperatures (above 160 K), the peak-photocurrent variation with temperature is an activated process while at lower temperatures (below 100 K) the peak photocurrent is independent of temperature. The temperature independence of the peak photocurrent reveals that the Onsager theory of geminate recombination is not applicable to PDA-DQ samples in the nanosecond time scale below 100 K. The behaviour can be qualitatively explained by assuming a distribution of thermalization lengths for the photogenerated carriers (Donovan and Wilson 1986). A thermalized electron experiences the Coulomb potential of its own partner (hole) and the applied potential. The resultant of these two potentials gives rise to a new potential well. The majority of the photogenerated carriers are assumed to be thermalized within this potential well. At higher temperatures (above 160 K), the contribution to the photocurrent from carriers escaping the potential well

by a thermally activated diffusive random walk is dominant. This gives rise to activated behaviour for the temperature dependence of the photocurrent. As the temperature is lowered, the contribution to the photocurrent from carriers escaping geminate recombination decreases. On the other hand the contribution from carriers thermalizing beyond the potential well becomes dominant. Carriers thermalizing beyond the potential well give rise to a temperature-independent peak photocurrent. The Onsager theory of geminate recombination in one dimension accounts for the almost linear dependence of the peak photocurrent on electric field ($i \propto E^{1.1}$) and the activated behaviour observed in the temperature dependence of the peak photocurrent at temperatures above 160 K. A temperature-independent peak-photocurrent behaviour is observed in PDA-TS in the picosecond regime throughout the temperature range 10–300 K (Moses *et al* 1987). This was explained as due to hot carriers. Donovan and Wilson (1986), in their transient photoconductivity studies on PDA-TS on the nanosecond time scale, also claim that the Onsager theory is inadequate to explain the temperature-dependent photocurrent behaviour below 100 K.

5. Concluding remarks

Steady-state and transient photoconductivity measurements have been carried out on a partially polymerized PDA-DQ single crystal as a function of electric field, light intensity and temperature. The molecular organization is defined as a solution of conjugated macromolecules oriented in the same direction in a monomer single crystal. The polarization dependence of the steady-state photocurrent in this sample is also investigated. The experimental results are discussed on the basis of the one-dimensional Onsager theory of geminate recombination. The temperature dependence of the transient peak photocurrent deviates from the theory at temperatures below 100 K.

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