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PHOTOTRANSPORT IN LADDER TYPE POLYMERS

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Abstract Photoconductivity measurements are a powerful tool to investigate the charge carrier transport and recombination mechanisms in solids. We report measurements of photoconductivity in films of the ladder-type polymer BBL (benzimidazobenzophenanthroline-polymer). Both cw and transient experiments on different time scales have been carried out. The results suggest the existence of a fast photoconductive response, similar to that found in other conjugated polymers such as trans-polyacetylene. In addition the dependencies of the photocurrent upon the applied electric field, temperature and intensity of the incident light have been investigated.

Keywords: Ladder-type polymers, BBL (benzimidazobenzo phenanthroline), transient photoconductivity

INTRODUCTION

Recently ladder-type polymers have received considerable attention as a new class of materials with interesting electrical, optical and mechanical properties.[1,2] They are well known for their excellent thermal and chemical stability, high modulus and tensile strength as well as for their rather large optical nonlinearities.[3-6]

Rigid ladder-type polymers such as BBL, which is soluble and film-forming, are partially conjugated (see Fig. 1) and characterized by an

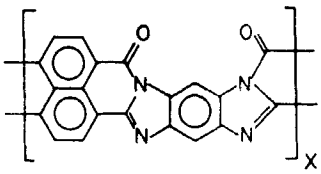

FIGURE 1 Chemical structure of BBL.

extensively delocalized π-electron system. In its pristine form BBL is an insulator with a band gap of approximately 1.8 to 2.0 eV [7] but it

can be doped chemically and electrochemically[8] to both n-type and p-type materials with conductivities up to 2 S/cm.

In this respect BBL is very similar to other conjugated systems like polyacetylene, PPV, etc.[9], which have been extensively investigated. Especially from photoconductivity measurements a lot was learned about transport and recombination mechanisms. Therefore, similar experiments may yield valuable information about photoinduced charge-carriers in ladder-type polymers like BBL as well.

EXPERIMENTAL

BBL was synthesized according to the literature procedure.[3,10] For film-formation 1 g of the resultant black powder was dissolved in 40 ml of methansulfonic acid. Evaporation of the acid on a glass slide at 150 °C forms the polymer film with a thickness in the range of 1 μm to 10 μm. The golden-yellow, flexible films were extracted from the glass with water and put on a substrate for the photoconductivity measurements. Drying it in a vacuum oven at 150 °C for 24 hours removes the remaining acid and adheres the film onto the substrate.

The photoconductivity was measured using the Auston-switch-technique.[11] A 100-500 μm gap between the 50 Ω microstrip lines served as the active area of the photoconductor.

The dark current measurements using this configuration showed almost ohmic behaviour. Dependent upon the sample size and thickness, the current was found to be in the pA range. The signal was detected using a lock-in amplifier for cw measurements or a transient digitizer (Tektronics AD 7912, 700 MHz) to measure the fast electrical response of a short pulse photoexcitation. To vary the temperature, the substrates were mounted in a nitrogen cryostat.

Measurements were made with a Rh6G dye laser which was synchronously pumped by a modelocked Nd-Yag laser. The laser output had a wavelength of 570 nm, a pulse length of about 4 ps at a repetition rate of 76 MHz with an average power of 200 mW. This was used as a cw light source for steady state photocurrent measurements with the power attenuated by a factor of 100.

For transient measurements short pulses of high energy were obtained using a regenerative amplifier in combination with a pulse

tunable amplifier to increase the energy per pulse of the dye laser output. Thus, pulses of 10 ps length with energies of 1-100 μJ at 590 nm wavelength were used for the short photoexcitation initiating the transient electrical response. The repetition rate was reduced to 30 Hz.

RESULTS AND DISCUSSION

Fig. 2 shows the transient photoconductive response of a BBL-film at room temperature due to a 70 μJ pulse of 2.1 eV (590 nm). An intense

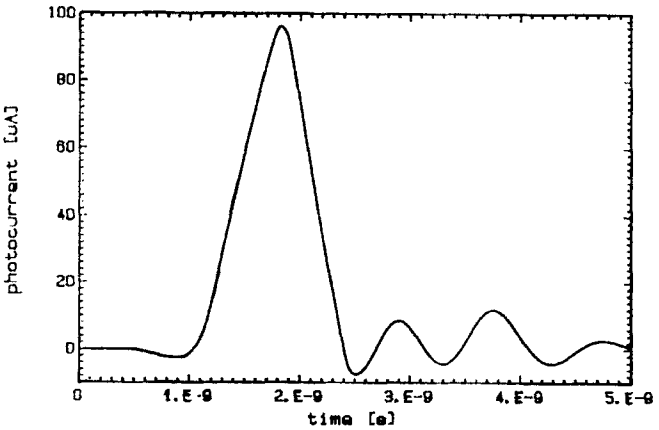

FIGURE 2 Transient photocurrent of BBL (E = 8000 V/cm).

short pulse with a pulse width of approximately 750 ps can be seen, followed by small oscillatory peaks, which may be due to some electrical reflections on the microstrip line. The time resolution in this case is limited by the instrumentation and therefore the observed pulsewidth can only be taken as an upper limit for the actual decay time of the initial photocurrent.

The most interesting feature of this response is its lack of dependence on temperature. This can be seen in Fig 3, where the behaviour of the transient peak-photocurrent is compared to the steady state photocurrent in the temperature range from 100 K to 300 K. (Note the scaling factor of 10000 for the fast response.) In the steady

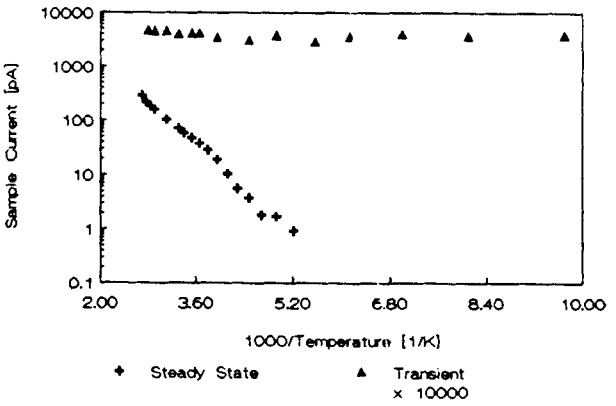

FIGURE 3 Temperature dependence of the photocurrent. Transient and steady state behaviour can clearly be distinguished.

state case we find a strong temperature dependence indicating a thermally activated process with an activation energy of approximately 200 meV.

Fig. 4 shows the dependence of the photoconductivity as a function of the incident light intensity in an applied electric field of 20000 V/cm. Within an intensity range of up to three orders of magnitude a linear and sublinear behaviour is observed for the fast and steady state photocurrent, respectively. The measurements were taken

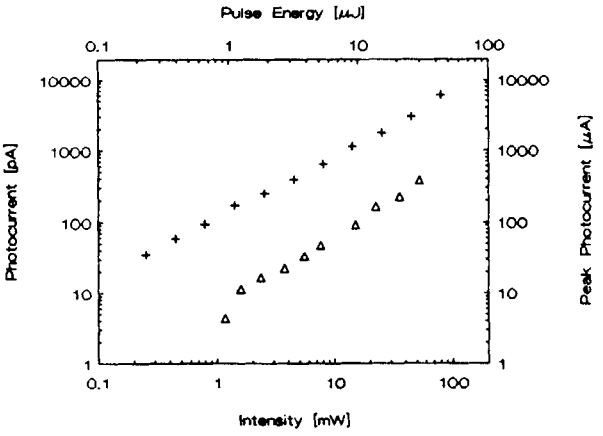

FIGURE 4 Intensity dependence of the transient (Δ, right scale) and steady (+, left scale) state photocurrent.

at room temperature, but no significant change was observed upon cooling.

Electric field measurements on the other hand are temperature dependent as displayed in Fig. 5. A change in the power law from a linear to a superlinear dependence was observed with decreasing temperature.

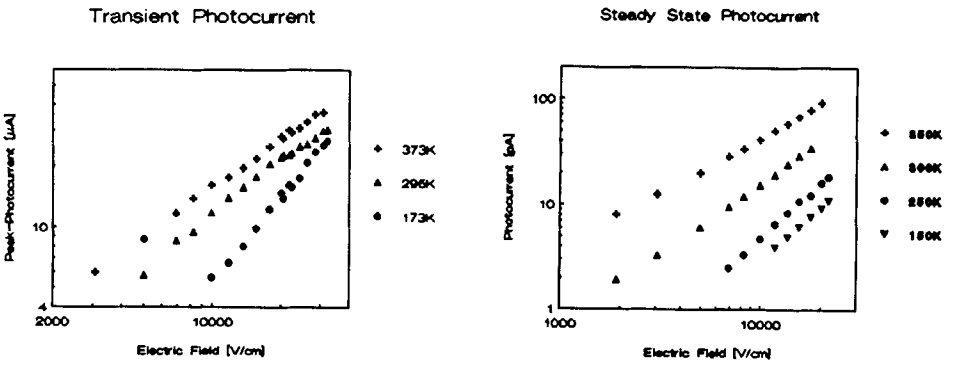

FIGURE 5 Electric field dependence of the transient and steady state photocurrent.

The most important result is the fact that the transient response and its temperature dependence, as shown in Figures 2 and 3, are very similar to that found in conjugated polymers. For example this has been thoroughly studied in polyacetylene.[12] The general observation is a strong temperature-independent fast component followed by a slow decay lasting for nanoseconds or more which is temperature-dependent. However, in our case the limited time resolution only shows the existence of a fast initial response. The steady state measurements on the other hand allow the investigation of the photocurrent under equilibrium conditions. The observed temperature dependencies indicate different transport mechanisms.

In the case of conjugated systems it was proposed that the fast component may be due to "hot-electrons", thermalizing rapidly on a pico- or even subpicosecond time scale.[13] In this time regime the mobility and recombination processes are independent of temperature. After thermalization the carriers get trapped at defects and localized

states in the gap and from then on the transport is dominated by thermal activation.

This would be consistent with the observed temperature dependence for the steady state current, since in this case we look at a time scale long after thermalization.

Furthermore in contrast to the transient photocurrent, we observe a sublinear behaviour for the intensity dependence in the steady state case ($I_{ph} \sim Int^{0.8}$). This is another indication of the influence of the traps of the steady state photocurrent. If the transient response is due to hot electrons, traps should not affect the recombination and one would expect a linear dependence on the intensity. As thermalization occurs the traps come into play changing the dependence on the intensity of the incident light.

Finally the peculiar dependencies of the electric field measurements on the temperature should be pointed out. In the steady state case we find a change in the exponent of the power law from 1 to 1.7 with decreasing temperature. The behaviour of the transient current is similar but less pronounced with the power-law changing from 0.8 to 1.3. The reason for this is yet not clear.

In conclusion the photoconductive response of the ladder type polymer BBL shows common features in comparison to other conjugated polymers. However, in order to get more detailed information about transport and recombination kinetics an improved time resolution would be desirable.

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REFERENCES

1. L.R. Dalton, J. Thomson and H.S. Nalwa, Polymer, 28, 543 (1987)
2. L.R. Dalton, in Nonlinear Optical and Electroactive Polymers, edited by P.N. Prasad and D.R. Ulrich (Plenum, New York and London, 1988), pp. 243-271
3. R.L. van Deusen, O.K. Goins and A.T. Sicnee, J. of Polym. Sci A, 1, 1777 (1968)
   R.L. van Deusen, J. of Polym. Sci B, 4, 211 (1966)

4. S.R. Allen, R.J. Farris and E.L. Thomas, J. of Mat. Sci., 20, 2727 and 4583 (1985)
5. J.R. Lindle, F.J. Bartoli, C.A. Hoffman, O.-K. Kim, Y.S. Lee, J.S. Shirk and Z.H. Kafafi, Appl. Phys. Lett., 56, 712 (1990)
6. L.P. Yu and L.R. Dalton, Synth. Met., 29, E463 (1989)
7. F. Coter, I. Belaish, D. Davidov, L.R. Dalton, E. Ehrenfreund, M.R. McLean and H.S. Nalwa, Synth. Met., 29, E471 (1989)
8. O.-K. Kim, Mol. Cryst. Liq. Cryst., 105, 161 (1984)
9. Handbook of Conducting Polymers, edited by T.A. Skotheim (Marcel Dekker, New York and Basel, 1986), Vols. I and II
10. D. Davidov, I. Belaish, C. Rettori, M.R. McLean and L.R. Dalton, Preprint
11. D.H. Auston, in Picosecond Optoelectronic Devices, edited by C.H. Lee (Academic Press, New York, 1984), Chap. 4, pp. 73-117
12. H. Bleier, S. Roth, Y.Q. Shen, D. Schäfer-Siebert and G. Leising, Phys. Rev. B, 38, 6031 (1988)
M. Sinclair, D. Moses and A.J. Heeger, Sol. State Commun., 59, 343 (1986)
13. S.D. Phillips and A.J. Heeger, Phys. Rev. B, 38, 6211 (1988)