

Transient Photoconductivity in a Discotic Liquid Crystal

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Using a time-of-flight technique, different transport mechanisms, deep trapping, multiple shallow trapping, and ideal intrinsic transport, can be observed in the different temperature and phase regions of the liquid-crystalline photoconductor hexapentyloxytriphenylene. The temperature and field dependences of carrier mobilities up to $1 \times 10^{-3} \text{ cm}^2/\text{Vs}$ have been determined; this value exceeds considerably the mobilities of the most commonly used organic photoconductors. The experiments reflect a variety of transport phenomena which are novel in the field of liquid-crystalline systems.

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Organic photoconductors such as, for instance, the polymer poly(*N*-vinylcarbazole) (PVK) belong to the few examples where organic materials have penetrated sophisticated technologies like, for instance, xerography, laser-printing techniques, etc. One main disadvantage of conventional polymeric materials, however, is their low mobility, which is on the order of $10^{-6} \text{ cm}^2/\text{Vs}$ (see, for instance, Ref. [1]), even though there are a few recent publications presenting materials with mobilities of up to $10^{-3} \text{ cm}^2/\text{Vs}$ [2,3]. In general, the low mobilities of organic photoconductors are due to a trap-dominated hopping transport between the pendant, photoconductive groups, giving rise to a certain localization of charge carriers. One way to circumvent this low-mobility aspect of organic materials is to use conjugated polymers like, for instance, poly(2-phenyl-1,4-phenylenevinylene) (PPV) [4] or quasiconjugated polymers like poly(methylphenylsilane) (PMPS) [5,6]. Another approach which has been put forward in the literature is the use of liquid-crystalline (LC) systems [7]. Here the transport can, in principle, occur between the mesogenic groups [7]. To our knowledge, there has so far been no report in the literature where the effect of higher order within the mesogenic groups has led to a drastic increase of the respective mobilities of at least 1 or 2 orders of magnitude. There are some scattered data on anomalous transient photocurrents [8] and on transient currents induced by discontinuous voltage steps in LC systems [9,10], yet these phenomena cannot be interpreted as straightforwardly as the transient data which will be presented. We started our approach with a simple discotic system [11, 12], namely, hexapentyloxytriphenylene (HPT). The columnar structure of discotic liquid crystals is similar to that of many aromatic columnar single crystals which have been extensively studied and show high carrier mobilities [13]. Thus such discotic systems and especially those exhibiting the highly ordered columnar phases (D_{ho}) seem to be well suited for an electronic transport parallel to the columnar axis.

First we investigated the influence of the mesophase on charge carriers in the HPT compound, which is well suited as a model system. We recorded the transient photocurrent generated by a strongly absorbed short laser pulse in an electrically biased quartz-glass cell with semitransparent electrodes containing the HPT, using a typical time-of-flight (TOF) setup.

It turned out that this model system was a very good choice, since we could, for the first time, detect various different charge transport mechanisms in one single system, depending on the temperature and polarity: from transport dominated by complete trapping in the "frozen" polycrystalline state to completely nondispersive transport in the mesophase.

The HPT molecules under investigation reveal a discotic hexagonal columnar ordered mesophase. The transition from the crystalline to the mesophase takes place at 69°C and from the mesophase to the isotropic phase at 122°C [11]. HPT can be easily oriented homeotropically to yield relatively large uniform domains by slow cooling from the isotropic phase into the mesophase. Hereby, the discotic molecules orient as stacked arrays with the stack axis perpendicular to the electrode surface. The structure and columnar packing of HPT are shown in Fig. 1.

HPT was synthesized according to the literature [11]; it was subsequently highly purified by flashchromatography and several recrystallizations. It was filled between two quartz plates which were coated with semitransparent aluminum electrodes. The thickness of the cells was in the $10\text{-}\mu\text{m}$ range. It could be measured with an accuracy of about 4% by recording the interference patterns in an uv-visible spectrometer. The samples were temperature controlled by using a PID controller (proportional signal with integrating and differentiating features). The photoexcitation of the sample was performed with a strongly absorbed nitrogen laser (penetration depth $< 1 \mu\text{m}$). The pulsed laser had a wavelength of 337 nm , a pulse energy of 5 mJ , and a pulse width of 10 ns . The samples showed no measurable change upon

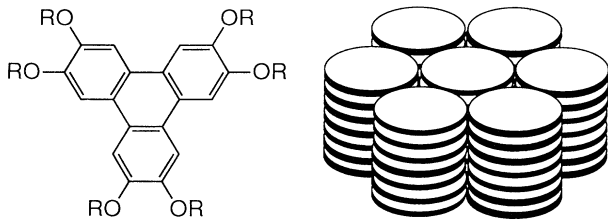


FIG. 1. Hexapentyloxytriphenylene and a schematic view of its columnar mesophase ($R = C_5H_{11}$).

irradiation and long-time field application (days).

Laser irradiation into the main absorption band of the HPT leads to the creation of electron-hole pairs with a certain quantum yield (to be discussed in a later publication). Depending upon the polarity of the external field, electrons or holes will drift across the sample cell, causing a displacement current which can be recorded in an external circuit (see, for instance, Ref. [1]). The current can be detected over 9 orders of magnitude in time from 10 ns to 10 s and over a dynamic range of 7 orders of magnitude with a maximum sensitivity of 10^{-10} A. More details of the TOF setup have been reported elsewhere [14].

In Fig. 2 the transient photocurrents are shown in a double logarithmic plot. HPT shows a number of transient current shapes, depending on the temperature and the polarity of the external field. It is, to our knowledge, one of the few, if not the only known photoconductive system, displaying the whole "spectrum" of photoconductive transient features. In curve *a* a typical transient for the deep trapping case is shown which was measured in the crystalline phase. No transit time can be detected even in the double logarithmic plot. We believe that due to the microcrystalline structure, deep traps are formed by the domain walls which result in a completely dispersive transport mechanism in which the charge carriers are totally trapped in the sample volume. For this case of trap dominated transport a slope of -1 is expected—and measured—in the double logarithmic plot [15]. Both positive and negative carriers exhibit this phenomenon in the crystalline phase. In the mesophase, the negative carriers reveal a current decay typical of a system characterized by multiple shallow trapping as shown in curve *b*. Moreover, a transition from dispersive to nondispersive transport takes place at times shorter than the transit time (see also Ref. [14]). In contrast, the positive carriers display in the mesophase a transient current as depicted in curve *c*—which is typical for an ideal "intrinsic" transport as is observed in many inorganic semiconductors. Even in a linear plot, as shown in the inset for two values of the sample thickness (curves *d* and *e*), the current is almost constant until it drops to zero rather abruptly at the transit time t_T . This behavior resembles with minor variations data published for thin films of amorphous selenium [16]. Within our present accuracy,

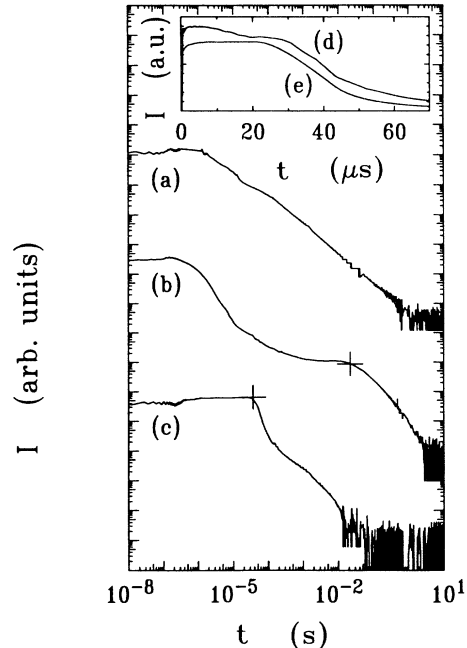


FIG. 2. Double logarithmic plot of typical transient currents I as a function of time t at an electric field of 0.4×10^5 V/cm and at various temperatures T and polarities: curve *a*, $T = 26^\circ\text{C}$, crystalline phase, holes; curve *b*, $T = 77^\circ\text{C}$, mesophase, electrons; curve *c*, $T = 77^\circ\text{C}$, mesophase, holes. The crosses mark the respective transit times at which the bulk of the charge carriers arrives at the back electrode. Inset: Time dependence for hole currents in the mesophase on a linear scale depicted for two values of the sample thickness l : curve *d*, $l = 20 \mu\text{m}$; curve *e*, $l = 12 \mu\text{m}$ ($E = 0.4 \times 10^5$ V/cm; $T = 77^\circ\text{C}$).

the transit times scale linearly with sample thickness, as a simple, nondispersive model would predict. Obviously the ordered columnar arrangement of the discotic molecules in stacked arrays provides very good overlap of the π -electron systems of the triphenylene molecules along the director axis, which—for positive carriers in the mesophase—results in a bandlike transport mechanism in one dimension. For the negative carriers a rather narrow conduction band seems to interact with a set of shallow traps, whose origin is not yet clear (see Ref. [14]).

These different transport mechanisms as deduced from the shapes of the above discussed transients are also reflected in the numeric values of the respective carrier mobilities. In a straightforward TOF experiment the effective mobility μ is defined as

$$\mu = l^2 / t_T V$$

and can, thus, be obtained from the transit time t_T . l is the sample thickness and V the applied voltage across the sample. In the crystalline phase, no transit time can be detected due to the totally dispersive transport and therefore no mobility values can be obtained. For the case of

electrons in the mesophase a slightly dispersive behavior is reflected in the rather small slope at the transit time t_T . Here an effective transit time is defined at the intercept of the pre- and post-transit slopes. This procedure is commonly used in the literature [15]. The transit times t_T as defined above scale reasonably with all accessible experimental parameters, i.e., temperature T , applied voltage V , and sample thickness l .

In Fig. 3, the temperature dependence of the mobility in the mesophase is displayed in an Arrhenius plot. The negative carriers whose mobility is more than 2 orders of magnitude smaller than the hole mobility obey an Arrhenius law with an activation energy of 0.6 eV. This behavior resembles many systems which show multiple trapping features [16,17] or which can be described by a continuous-time random-walk model ([15], p. 2471). This is not unreasonable since the order parameter of the triphenylene core is believed to be constant throughout the mesophase of HPT [18]. The microscopic origin of the activated behavior of electrons is rather interesting and needs to be investigated in more detail. The hole photocurrent is quite remarkable; it shows no dispersive features whatsoever and is characterized by a rather high mobility of $1 \times 10^{-3} \text{ cm}^2/\text{Vs}$. Such mobilities have been reported for conjugated or quasi-conjugated polymers [4-6]. These high mobilities seem to characterize the large overlap between the molecular wave functions along the columnar axis of HPT. In addition, the mobility of the positive carriers does not change significantly with temperature. Since the temperature can be varied only within the 50-K range of the mesophase, this relatively constant mobility would be plausible within the framework of an intrinsic bandlike motion.

This would also explain the field-independent mobility of positive carriers in the mesophase, as shown in Fig. 4. Also the negative carriers reveal a relatively constant mobility with increasing field. This field independence of the

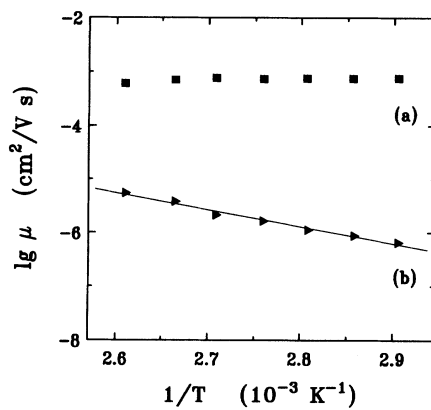


FIG. 3. Arrhenius plot of carrier mobility μ vs temperature T at an electric field of $0.4 \times 10^5 \text{ V/cm}$: (a) hole mobility; (b) electron mobility.

mobility of negative carriers is not understood at the present time. A multiple trapping transport, which would be deduced from the transient current and the Arrhenius-like temperature dependence of the mobility, would typically yield a field dependence in the form $\ln \mu \propto \sqrt{E}$ according to the Poole-Frenkel effect [16,17,19], which describes the lowering of the Coulomb barriers for charged shallow trapping sites in an external electric field.

In the above discussion, only electronic transport mechanisms were considered, i.e., electron or hole transport. Nevertheless, one has to be sure that ionic transport can be excluded. Up to now, charge carrier mobilities in liquid crystals have been investigated mainly in calamitic, especially in nematic systems, where the transport process was predominantly assumed to be ionic. For a general survey of earlier work see Ref. [20]; for mobility measurements by the TOF technique, see Refs. [21,22]. In comparison with the above quoted previous work, ionic transport in HPT is not likely for the following reasons.

(i) As a result of the high viscosity in discotic hexagonal ordered phases, an ionic mobility of $1 \times 10^{-3} \text{ cm}^2/\text{Vs}$ of the comparatively large triphenylene cation, which would have to be formed, is not reasonable. To support this notion the following rough estimate can be made: For ionic transport Walden's rule $\mu\eta = e/6\pi r$ should be valid. If we assume an ionic radius of $r \approx 10 \text{ \AA}$ (for the distance between two columns 18.9 \AA was measured by x-ray diffraction [23]) and a mobility of $1 \times 10^{-3} \text{ cm}^2/\text{Vs}$, Walden's rule yields a viscosity $\eta \approx 8 \times 10^{-5} \text{ N s/m}^2$. This value is more than 1 order of magnitude smaller than that of water at 20°C (i.e., unreasonable).

(ii) In nematic systems, the transport of the positive carriers is mostly ascribed to the molecular cation (e.g., [21] and references cited in [20]), whereas the O_2^- ion is regarded as the mobile anion in some other materials [21,24]. This fact results in higher mobilities for the neg-

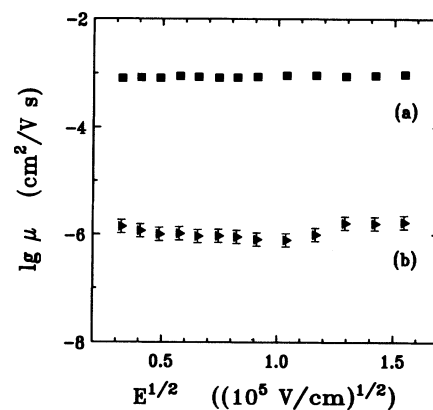


FIG. 4. Poole-Frenkel plot of carrier mobility μ vs electric field E at a temperature of 75°C : (a) hole mobility; (b) electron mobility.

ative carriers, which does not hold for HPT.

(iii) Finally, and most importantly, the temperature-independent mobilities would be in complete disagreement with ionic currents, since the viscosity of the LC system changes drastically within the investigated temperature range.

In summary, measurements of the transient photocurrent have been carried out in a discotic liquid-crystalline system. HPT is the first photoconductive system which exhibits both ideal intrinsic transport—typical for semiconductors—and deep trapping and multiple trapping transport mechanisms—typical for amorphous polymers. One of the most interesting aspects of the liquid-crystalline HPT system is the temperature dependence of the transport phenomena. The high mobility transport in the mesophase—as compared to the inefficient, i.e., trap-dominated transport in the crystalline phase—suggests that certain fluctuations of the disklike molecules within the columnar stacks may lead to a “quasi-intrinsic” transport mechanism, in which “static” trapping phenomena are suppressed by the dynamic properties of the LC system. So far this interpretation is somewhat speculative and asks for a thorough theoretical treatment that includes polaronic effects, which are known to play an important role in the field of the conductivity of conjugated polymers [25].

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- [1] D. Haarer, *Angew. Makromol. Chem.* **183**, 197 (1990).
[2] M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.* **88**, 4707 (1984).
[3] P. M. Borsenberger *et al.*, *J. Chem. Phys.* **94**, 8276

- (1991).
[4] M. Gailberger and H. Bässler, *Phys. Rev. B* **44**, 8643 (1991).
[5] R. G. Kepler *et al.*, *Phys. Rev. B* **35**, 2818 (1987).
[6] M. A. Abkowitz, M. J. Rice, and M. Stolka, *Philos. Mag. B* **61**, 25 (1990).
[7] L. L. Chapoy *et al.*, *Mol. Cryst. Liq. Cryst.* **105**, 353 (1984); L. L. Chapoy *et al.*, *Macromolecules* **16**, 181 (1983).
[8] A. Sugimura *et al.*, *Phys. Rev. Lett.* **63**, 555 (1989).
[9] H. Naito, M. Okuda, and A. Sugimura, *Phys. Rev. A* **44**, R3434 (1991).
[10] A. Sugimura *et al.*, *Phys. Rev. B* **43**, 8272 (1991).
[11] J. Billard *et al.*, *Nouv. J. Chim.* **2**, 535 (1978).
[12] W. Kreuder and H. Ringsdorf, *Makromol. Chem.* **4**, 807 (1983).
[13] D. Haarer and H. Möhwald, *Phys. Rev. Lett.* **34**, 1447 (1975).
[14] E. Müller-Horsche, D. Haarer, and H. Scher, *Phys. Rev. B* **35**, 1273 (1987).
[15] H. Scher and E. W. Montroll, *Phys. Rev. B* **12**, 2455 (1975).
[16] J. Noolandi, *Solid State Commun.* **24**, 477 (1977); *Phys. Rev. B* **16**, 4466 (1977); **16**, 4474 (1977).
[17] F. W. Schmidlin, *Solid State Commun.* **22** (1977); *Phys. Rev. B* **16**, 2362 (1977).
[18] V. Rutar *et al.*, *J. Phys. (Les Ulis, France)* **43**, 761 (1982).
[19] J. Frenkel, *Phys. Rev.* **54**, 647 (1937).
[20] G. Derfel and A. Lipinski, *Mol. Cryst. Liq. Cryst.* **55**, 89 (1979).
[21] K. Okamoto *et al.*, *Bull. Chem. Soc. Jpn.* **56**, 3545 (1983).
[22] K. Yoshino, S. Hisamitsu, and Y. Inuishi, *J. Phys. Soc. Jpn.* **32**, 867 (1972).
[23] A. M. Levelut, *J. Phys. (Paris), Lett.* **40**, L-81 (1979).
[24] T. Yanagisawa, H. Matsumoto, and K. Yahagi, *Jpn. J. Appl. Phys.* **16**, 45 (1977).
[25] R. R. Chance, J. L. Bredas, and R. Silbey, *Phys. Rev. B* **29**, 4491 (1984).