Liquid Crystals

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Liquid crystalline photoconductors

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The influence of molecular order as well as of orientation of charge carrier units on photoconductivity has been investigated for the liquid crystal photoconductors H5T (**1**), thiadiazole (**2**) and oxadiazole (**3**). The discotic H5T (**1**) and both smectic systems **2** and **3** exhibit a higher photocurrent in the highly ordered mesophase than in the polycrystalline or isotropic state. For **1**, results concerning charge carrier transport mechanism and Dember effect are given indicating an electronic charge transport comparable with the one known for single crystalline anthracene.

1. Introduction

For the last 30 years polymer organic photoconductors have been used as photoconductive media in the field of xerography and laser printing. The efficiency of photocopier and laser printers is due to the mobility of charge carriers in the photoconductive layer. Polyvinylcarbazole (PVK), which is well-known, exhibits a mobility in the range of $10^{-6}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. As this is too slow for application in the field of fast laser printers or copiers, toxic selenium and tellurium compounds are still in use. The development of organic photoconductors having a suitably high charge carrier mobility remains therefore an interesting challenge.

To achieve a fast and effective transport of charges through an organic medium it is required that the charge carrier units are positioned such that sufficient mutual orbital overlap of the units is guaranteed. It is clear that only highly ordered systems will fulfil this condition. Thus, single crystalline anthracene shows a charge carrier mobility of $10^{-1}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, whereas amorphous polymers such as PVK provide charge carrier mobilities in the range of 10^{-6} to $10^{-8}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (see figure 1).

Which charge carrier mobility may be expected from LC photoconductors? So far, all attempts to answer this question have failed. Japanese researchers [1] found only ionic carrier transport in nematic photoconductive materials. Chapoy *et al.* [2(*a*)] investigated a LC matrix doped with photoconductive carbazole. However, this medium proved to be inappropriate in view of the low solubility of carbazole in the matrix as well as interactions between carbazole and the matrix. Regarding photoconductivity in lyotropic polypeptides see [2(*b*)]. In collaboration with H. Ringsdorf (Mainz), D. Haarer and P. Strohriegl (Bayreuth) we have focused on designing a LC photoconductor having enhanced charge carrier mobility.

In LC mono-domains the order and orientation of the mesogenic units is certainly less than in single crystals. To achieve a macroscopic orientation of a polymer is even more problematic. It has been argued that small amounts of impurities and the presence of disorder (domain boundaries) may give rise to enough traps which destroy the mechanism of fast electronic carrier transport.

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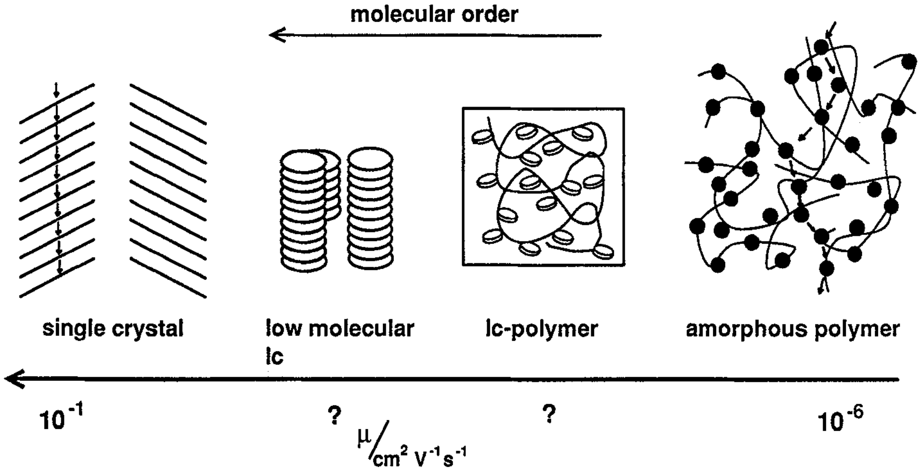
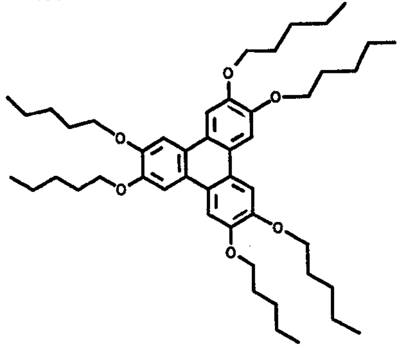


Figure 1. Correlation between molecular order and charge carrier mobility.

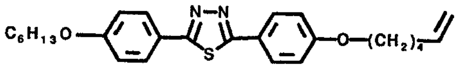
Discotic photoconductor



Hexapentyloxytriphenylene (H5T) (**1**) [5]

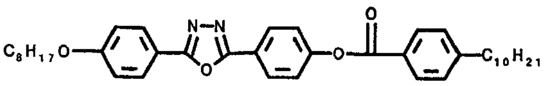
C 68°C D_{ho} 122°C I

Calamatic photoconductors



Thiadiazole (**2**) [3]

C 80°C S_A 181°C N 198°C I



Oxadiazole (**3**) [4]

C 101°C S_C 129°C N 146°C I

The most promising approach appeared to be the provision of discotic LCs having a columnar phase and a homeotropic orientation analogous to single crystals containing stacks of, for example, anthracene molecules. As a model compound we chose discotic hexapentyloxytriphenylene (H5T) (**1**) (see structure).

In the case of a calamitic system only a smectic LC having a homogeneous orientation will fulfil the required spatial condition, i.e. efficient mutual orbital overlap parallel to the applied field. Our group has investigated thiadiazole (**2**) [3] synthesized by P. Strohriegl and oxadiazole (**3**) synthesized by C. Tschierske [4] (see structures).

2. Experimental

For the measurement of the photocurrent the sample was placed between two conducting transparent glass plates with indium-tin-oxide as electrode material (see figure 2). (The orientation of the samples was achieved by slow cooling of the melted compounds.) The cell thickness was of the order of 10 μm adjusted by a 8 μm Mylar foil. The area of the electrode was about 4 mm^2. A DC voltage of 9 V was applied to the cell which corresponds to an electric field of 900 $\mathrm{kV\,m^{-1}}$. The sample was illuminated by a chopped halogen light (frequency: 10 Hz) focused onto the plane of the sample. (Rise and decay times are in the range of 5 to 10 ms; about 10 to 20 times shorter than the chopping frequency.) The detection of the photocurrent was achieved by measuring the voltage drop over a resistance of 10 000 Ω with a lock-in-amplifier (EG&G 5210). The temperature of the sample was controlled via a modified heating stage (Mettler FP 80/82); the heating rate was 2 $\mathrm{K\,min^{-1}}$.

3. Results and discussion

3.1. *Temperature dependence of the photocurrent*

3.1.1. *Discotic system H5T1*

In the polycrystalline solid state no photocurrent was detected (see figure 3). At 65°C, the C–D_{ho} transition, the photocurrent rises spontaneously and with increasing temperature runs through a minimum, rises again and finally collapses at the transition

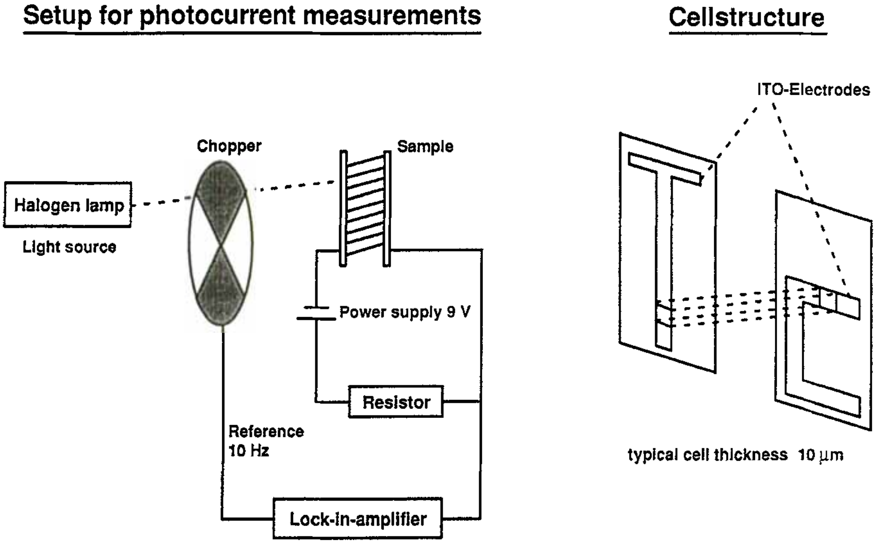


Figure 2. Essential components of the experimental set-up.

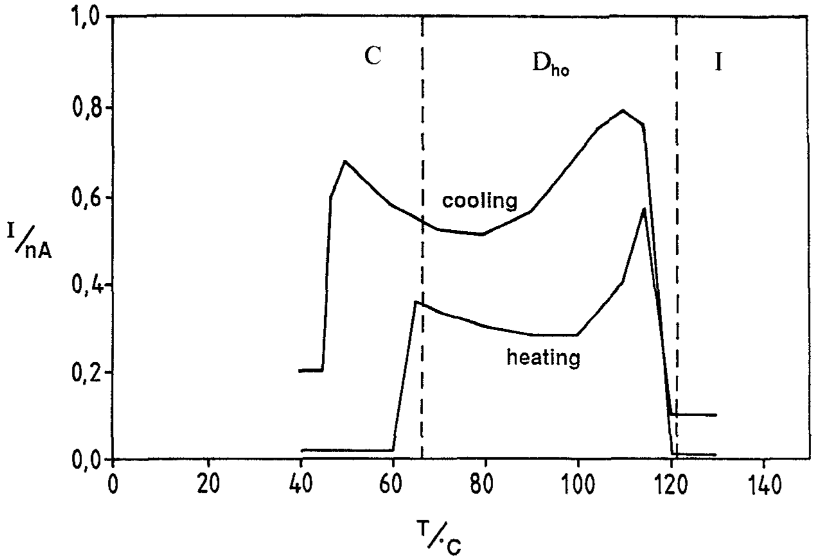


Figure 3. Photocurrent of H5T (**1**) as a function of temperature.

to the isotropic state (122°C). The photocurrent at 70°C is about 10 times higher than the dark current. During cooling, a higher photocurrent is detected due to a better orientation of the charge carrier units.

3.1.2. *Calamitic system*

Like H5T(**1**), both thiadiazole (**2**) (see figure 4) and oxadiazole (**3**) (see the table) show a strong correlation between the photocurrent and the degree of order (in the case of oxadiazole, sensitizers rhodamine B (2 per cent) and Astrazonorange (0·2 per cent) were added since **2** absorbs in the shortwave range): (i) the photocurrent in the mesophase is higher than in the polycrystalline or isotropic state, and (ii) the more ordered smectic mesophase shows a higher photocurrent than the nematic phase.

3.2. *Electronic charge transport in H5T*(**1**)

Even using a simple measuring set-up (a more detailed investigation of the charge carrier transport is under way by D. Haarer using the time of flight method (TOF)), we have obtained interesting photoeffects from which the mechanism of the charge carrier transport may be explained.

The following results relate to H5T(**1**) showing similar properties compared to crystalline semiconductor anthracene. In all experiments the sandwich cell was heated to 70°C (D$_{ho}$ phase).

(i) A greater photocurrent is observed with the illuminated electrode positive.
(ii) Without applying an external field, the illuminated electrode is charged negatively. A photoinduced open-circuit-voltage (V_{oc}) of about 4 mV was detected using chopped light.

Both effects can be explained by different mobilities of two charge carrier types: electrons and holes. Thus, the photovoltage (experiment (i)) corresponds to the well-known Dember effect [6]. The negative charge of the illuminated electrode is caused by the accumulation of slower electrons. At the same time the appearance of a Dember

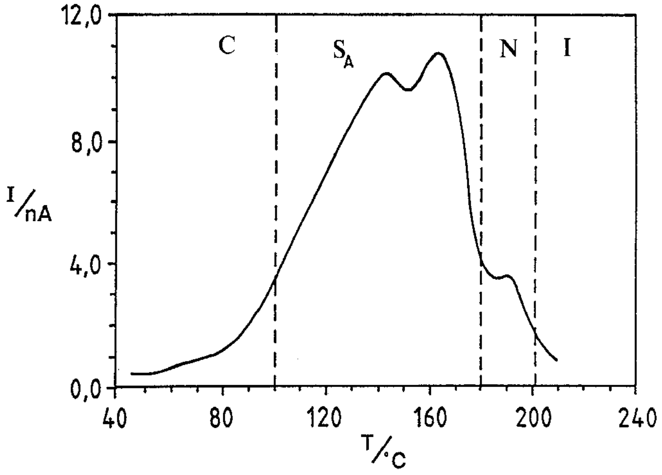


Figure 4. Photocurrent of thiadiazole (2) as a function of temperature.

Photocurrent of oxadiazole (3) as a function of temperature; phase behaviour of the mixture 3/2 per cent rhodamine B/0·2 per cent Astrazonorange: C 98°C S_B 102°C S_C 121°C N 145°C I.

Phase	Temperature/°C	Photocurrent/nA
C	80	0·5
S_C	110	64·4
	120	38·5
N	130	17·6
	140	3·8
I	150	1·6

effect provides evidence for anisotropic mobility. In particular, this effect shows that H5T(**1**) in the D_{ho} phase is an anisotropic semiconductor indicating that an electronic charge transport takes place.

3.2.1. *Spectral dependence of the photocurrent*

Unlike in (i) and (ii) this experiment was carried out with a sandwich cell illuminated with xenon light (Xe, XBO 150 W). With increasing absorption coefficient more electron hole pairs are generated resulting in an increasing photocurrent. Near the absorption edge of 360 nm the photocurrent reaches its maximum followed by a rapid decrease due to a growing number of recombinations of electron hole pairs. This behaviour typical for semiconductors can be explained by the fact that with increasing absorption coefficient the excitation will occur in increasingly thinner layers, until finally a pure surface excitation prevails. Thus, if the surface recombination rate is high, compared with that in the volume of the photoconductor, the equilibrium concentration of charge carriers will be less when these are generated close to the surface (high absorption region) than when they are distributed through the body of the material (lower absorption) [7].

4. Conclusion

The temperature dependence of the photoconductivity of several LC materials has been measured. Both discotic and smectic systems do show a higher photocurrent in the LC phase than in the polycrystalline or isotropic state. Obviously both the order in these mesophases and the orientation of the charge carrier units in a homeotropic D_{ho} phase or in a homogenous smectic phase are appropriate to guarantee efficient charge transport. For H5T(**1**) all photoeffects shown provide evidence for the existence of an electronic charge transport in the LC phase.

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