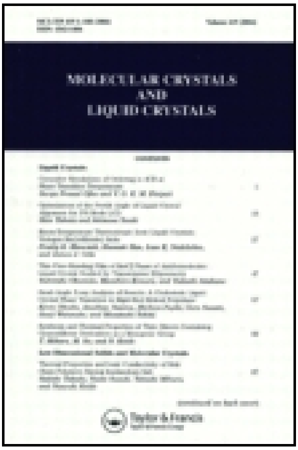

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Stephan J. Zilker, Uwe Hofmann, André Leopold, Michael Grasruck, Christoph Hohle & Peter Strohriegl (2001): Influence of the Charge Transport Characteristics on the Holographic Response of Organic Photorefractive Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 358:1, 15-22

To link to this article: http://dx.doi.org/10.1080/10587250108028267

Mol. Cryst. and Liq. Cryst., 2001, Vol. 358, pp. 15-22
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Influence of the Charge Transport Characteristics on the Holographic Response of Organic Photorefractive Materials

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Organic photorefractive materials have attracted a lot of interest recently. Their optical response times of a few milliseconds, however, are not yet adequate for the desired commercial applications. We present an investigation on the correlation between the optical response time and photoelectric quantities, such as the hole mobility and the dispersivity of charge carrier transport.

Keywords: organic photorefractive materials; charge transport; holography; hole mobility

INTRODUCTION

The photorefractive effect, known in inorganic crystals for more than 30 years, has experienced a revival following the first report of photorefractivity in organic materials in 1991 [1]. Organic materials excel by compositional flexibility, the ease of material synthesis and preparation, and by their high optical quality. The photorefractive effect is a combination of several physical processes and thus requires a rather wide experimental and theoretical approach. Two interfering laser beams create a modulated charge distribution in the material. In an applied external field, the mobile charge carriers – in most cases the holes – will drift into the dark regions of the intensity pattern where they are trapped. Thus, one obtains a modulated space charge field which leads to a variation of the refractive index upon via nonlinear optical chromophores which are incorporated into the material.

Consequently, charge transport and trapping play a crucial role in the dynamics of the hologram formation. In contrast to crystals, charge generation and transport depend strongly on the electric field, furthermore the trapping dynamics is much more complicated due to the broad energetical distribution of traps which do mostly not arise from impurities but from the inherent structural and energetical disorder of the amorphous host. Therefore, models for photorefractivity in inorganic crystals [2] are not capable to successfully describe organic materials, even if the field dependence of characteristic quantities is incorporated.

In the classical photorefractive model, the response time τ scales inversely with the photoconductivity σ_{ph} of the material,

$$\tau \sim 1/\sigma_{\mathrm{ph}} = 1/(e\,n\,\mu)\,, \tag{1}$$

where e is the unit charge and n the free carrier density. Thus, τ would be inversely proportional to the mobility μ. However, whereas Eq. 1 takes into account charge generation (via n) and charge transport (via μ) it neglects the specifics of carrier trapping. Still, this result is often assumed to be valid for organic materials as well, and has thus been a guideline for material optimization. Consequently, many groups try to use high-performance photoconductors such as low-molecular weight glasses [3] or conjugated polymers [4], reaching response times of less than 1 ms [4], well inside the range required for video applications. However, also rather low-mobility systems, such as polyvinylcarbazole, were shown to yield comparable optical response times [5, 6].

In order to provide more insight into the relation between mobility and optical response, we perform a detailed analysis of optical and photoelectrical data of several organic materials, spanning a response and mobility region of several orders of magnitude. We show that the relation given by Eq. 1 is valid only insofar as materials with higher mobility tend to have faster response. However, there are clear deviations from a strict proportionality which are discussed in the frame of the relevant charge transport mechanism.

EXPERIMENTAL

The materials where characterized in a degenerate four-wave mixing setup which has been described previously [7]. The response time τ was evaluated as the first time constant of a bi-exponential fit to the grating erasure, being performed by illuminating the sample uniformly with one writing beam. All quantities stated were obtained at an applied electric field of 70 V/μm with a writing beam intensity of 1 W/cm^2 at a wavelength of 670 nm.

The mobility μ was obtained by time-of-flight (TOF) and holographic time-of-flight (HTOF) experiments [8, 9]. HTOF was used when a high degree of dispersivity made the evaluation of standard TOF transients impossible. Hereby, the photorefractive grating is generated by a pair of nanosecond laser pulses while the diffraction from the arising refractive index modulation is continuously monitored. The HTOF values themselves do only constitute estimates but not precise values for the real mobility since they are based on the assumption that the effective drift length w of the charge carriers

$$w = \mu\tau E\,, \tag{2}$$

is large enough so that the holes can reach a position of anticoincidence with the immobile electrons. Here, μ is the mobility, τ the carrier life time and E the applied electric field. If anticoincidence is indeed reached after the geometrical drift length L_{Dr} of 2.5 μm, as determined by the experimental geometry (grating spacing and slant angle), one would obtain a maximum space charge field and correspondingly a maximum of the refractive index modulation. From the temporal position of the maximum, t_{max}, one can estimate the mobility as

$$\mu = \frac{L_{\mathrm{Dr}}}{E t_{\mathrm{max}}} \tag{3}$$

If the effective carrier drift length is smaller than L_{Dr}, then Eq. 3 overestimates the mobility. The HTOF experiment has been previously described [9].

Fig. 1 shows an overview over the materials, which range from guest host polymers such as polysiloxane (PSX) [9] and poly-(9,9'-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB) [4] to bifunctional materials such as the DCTA family [3, 10]. The DCTA materials SD, S2D, and DD, are based on the same photoconducting unit (DCTA), a triphenylamine with two carbazole substituents, to which different chromophores are covalently attached. DD contains a Disperse Red 1 chromophore, whereas S2D and SD are based on the same stilbene moiety with different spacer groups. We have studied six composites which are summarized in Table 1.

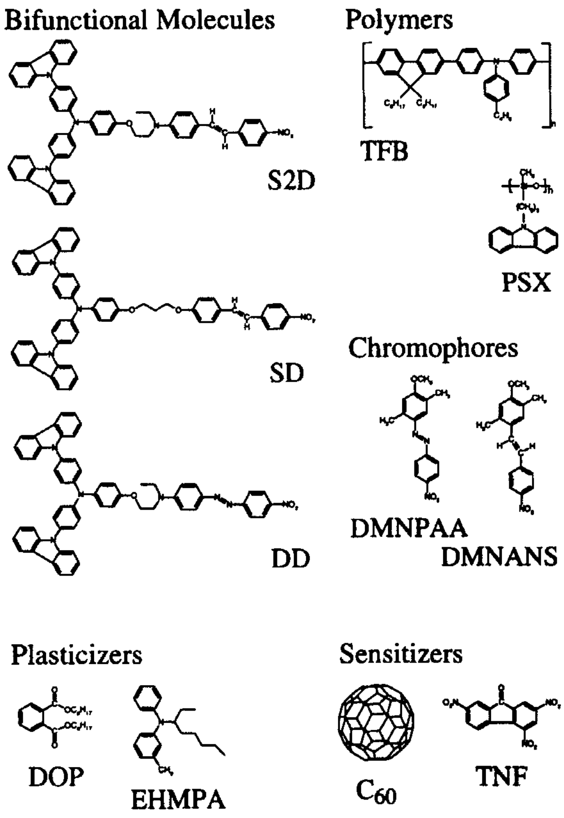

Figure 1: Investigated materials.

RESULTS AND DISCUSSION

Polysiloxane based systems were among the first materials exhibiting high optical gain and refractive index modulation [11]. However, the composite PSX which was investigated by us exhibits only very slow dynamics and very dispersive charge transport. Consequently, we could not observe a kink in the current transients obtained by time-of-flight measurements. Thus, holographic time-of-flight was used in order to determine the mobility. As reported previously [8], HTOF gives only an estimate for the mobility which cannot readily be compared with TOF results. Still, Fig. 2 shows that PSX

	PC	Chromophore	Sens.	Plasticizer	Ratio
PSX	PSX	DMNANS	TNF	–	52:47:1
SD-DOP	DCTA	S	C_{60}	DOP	71:28:1
S2D-DOP	DCTA	S2	C_{60}	DOP	71:28:1
DD-DOP	DCTA	DR	C_{60}	DOP	71:28:1
DD-EHMPA	DCTA	DR	C_{60}	EHMPA	69:30:1
TFB	TFB	DMNPAA	C_{60}	DOP	59:30:10:1

Table 1: Composition of the six investigated photorefractive systems. The composition ratio is in wt%, in the case of the DCTA-systems the first figure refers to the concentration of the bifunctional molecule (photoconductor covalently attached to the chromophore). S and S2 denote the two stilbene chromophores, DR the Disperse Red 1 molecule. PC stands for 'photoconductor'.

lies clearly in the upper left of a response time versus mobility plot.

The DCTA-based bifunctional materials vary in the choice of the chromophore and in the plasticizer. The latter has to be used in order to decrease the glass transition to room temperature, allowing for orientational enhancement [12] of the refractive index modulation.

Whereas a variation of the plasticizer, DOP or EHMPA, does hardly affect the mobility (compare DD-DOP with DD-EHMPA), it has a clear effect on the charge transport mechanism, making the transients in TOF experiments for DD-EHMPA more dispersive. This means that the number of deep traps is strongly increased leading to a more rapid immobilization of the charge carriers and consequently to a faster rise of the space-charge field. This is reflected by the order of magnitude difference in the response times of DD-DOP versus DD-EHMPA. The material with the slightly lower mobility, DD-EHMPA, is about 10 times faster. Thus, these two systems are the most striking exception from the proposed linear relation between mobility and response time as given by Eq. 1

A variation of the chromophore can lead to a similar result. SD-DOP and SD2-DOP vary only in the type of covalent linker which was used to attach the stilbene chromophore to the DCTA photoconductor. Once again, the material with the lower mobility (SD2-DOP) exhibits faster response.

The last system, TFB, is a polyfluorene polymer developed for organic light emitting diodes [13]. Without any dopants, it reaches hole mobilities

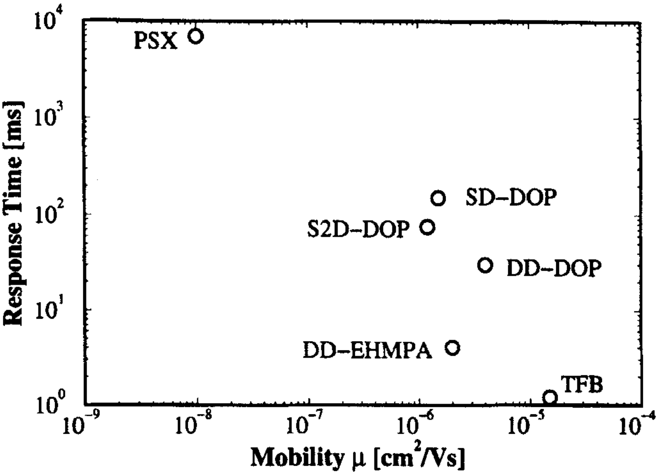

Figure 2: Holographic response time τ versus hole mobility μ for the six investigated photorefractive materials. The applied electric field was 70 V/μm.

of up to 10^{-3} cm^2/Vs, being among the highest values reported for conjugated polymers. Doped with the chromophore DMNPAA, a plasticizer and a sensitizer, the mobility is still as high as 10^{-5} cm^2/Vs, which is the highest value for an organic photorefractive system observed until now. The material shows very dispersive transport [4] and response times down to 1 ms.

Looking at the whole picture, one can clearly recognize that there is indeed a correlation between the response time and the mobility. However, the latter provides only a trend but not a functional dependence such as suggested by Eq. 1: Materials with high hole mobilities tend to be faster in a holographic experiment. However, there are clear deviations, most markedly in the case of DD-DOP and DD-EHMPA, two materials which vary only in the choice of the plasiticizing agent: Here, the material with the higher degree of dispersive charge transport does exhibit the faster optical response whereas its hole mobility is a factor of two lower. A smaller, but similar deviation is obtained for SD2-DOP and SD-DOP, where only the chromophore is varied.

Thus, the charge transport characteristics, especially the trapping dynamics, have to be considered in much more detail in order to obtain structure-property relationships for photorefractive organic materials.

CONCLUSIONS

We have presented a detailed comparison of the photoelectric and photorefractive properties of six organic materials. There is a clear correlation between fast optical response and high hole mobility. However, the dispersivity of charge transport also plays a crucial role in the dynamics of the formation of the space-charge field. For two given materials with similar hole mobility, the more dispersive one tends to show faster holographic response.

ACKNOWLEDGMENTS

The authors acknowledge stimulating discussion and continuous support by D. Haarer. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 481) and the Bayerische Forschungsstiftung. We are grateful to A. Lang and I. Otto for sample preparation and to D.D.C. Bradley and Dow Chemicals for the gift of the TFB polymer.

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