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Storage of laser-induced holographic gratings in discotic liquid crystals

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Abstract. We demonstrate that low molar mass discotic liquid crystals can be used for holographic storage. Grating structures are optically induced and stored in the glassy state of the investigated liquid crystal. The material is suitable for multiple storage processes since the stored information can be erased by heating the sample above the glass transition temperature.

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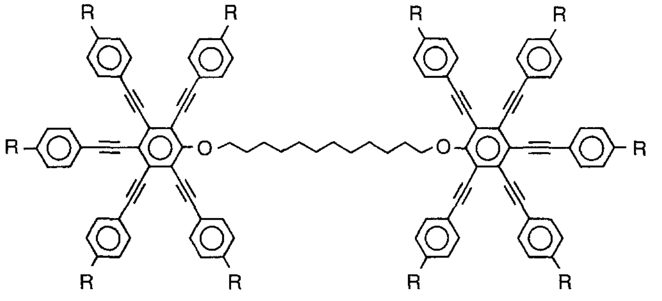
Methods and materials for optical data recording are of great scientific and commercial interest. Besides the digital storage process, holography [1] provides an efficient technique to obtain high information densities [2]. For *permanent* storage, photographic layers or photoresist materials can be applied. Light-induced changes of the refractive index in photorefractive crystals [3] or changes of the absorption occurring in inorganic photochromic materials and in dye doped polymers are suitable for *reversible* recording [2].

During the last decade, *liquid crystalline* materials for optical information storage have been extensively studied [4–6]. Liquid crystalline phases ("mesophases") consist either of rod-like organic molecules (→ "calamitic" liquid crystals) or of disk-like molecules (→ "discotic" liquid crystals). Mesophases are characterized by orientational order, i.e. preferential parallel alignment of the liquid crystal molecules. Nematic liquid crystals show only this *orientational* order, while smectic and columnar phases show additionally a layer structure or columnar arrangement of the *position* of the molecules, respectively. The high birefringence of liquid crystals can be used to induce large refractive index variations due to changes of the preferred molecular orientation (director) or the degree of orientational order. Most of the mesogenic storage materials investigated so far are liquid crystalline side chain polymers, where the rod-like mesogenic parts of the molecule are connected to a flexible backbone. The suitability of liquid crystal polymers for thermo-recording due to local heating of the sample by a laser beam has been demonstrated by Shibaev [4] and Coles and Simon [5, 6]. Very efficient optical storage effects have been obtained due to a light-induced *cis–trans*-isomerization [7, 9], i.e. a conformational change of the mesogenic units. Photochemically induced phase separation [10] and diffusion processes [11] can lead to the formation of switchable holograms for polymer-dispersed liquid crystal systems. Wedler et al. [12] have shown, that also *low molar mass calamitic liquid crystals* can be used for storage effects due to the appearance of a glass-like state. The great advantage of these materials is their low viscosity in the temperature range above the glass transition. Consequently, detailed experiments have been performed on these new liquid crystals using the holographic grating technique [13, 14], and their suitability as erasable recording materials has been demonstrated. The light-induced storage was attributed to a thermally induced nonlinearity.

In this paper, we present first results using *discotic* liquid crystals as a novel kind of storage materials. In contrast to calamitic liquid crystals, the discotic liquid crystals consist of disk-shaped molecules and thus exhibit negative birefringence, i.e. the ordinary refractive index n_o is larger than the extra-ordinary refractive index n_e. The investigated liquid crystal is a dimer of two disk-shaped molecular units. The compound shows a nematic discotic N_D phase which can be supercooled and frozen in a glass-like state. We have found that permanent grating structures can be induced in this compound by illumination with light in the visible wavelength range.

1 Experiment

The material under investigation consists of the compound (1) which exhibits the phase sequence C(rystalline) 92°C N_D 107°C I(sotropic), where N_D denotes the nematic discotic phase. On rapid cooling ($|dT/dt| > 10^3$ K/min) the discotic nematic phase can be stored in a glassy state. The glassy state is stable for several months at room temperature. On heating, the glass transition temperature is ≈ 48°C. In order to enhance the absorption of visible



(1)

light, a small amount (< 1%) of the dichroic anthraquinone dye D37 (from Merck Ltd., former British Drug House, Poole, GB) was added to the sample. The addition of this dye does not affect the transition temperatures considerably. The investigations were performed with liquid crystal films of 10 μm thickness. Homeotropic alignment was achieved by surface treatment of the glass substrates and by annealing the sample at temperatures a few degrees below the clearing point. Subsequently, the samples were rapidly cooled to room temperature, i.e. into the glassy state. During the measurement, the temperature of the surrounding of the sample was controlled within an accuracy of ± 0.1°C.

Grating structures were generated by the interference of two coherent beams of an argon ion laser (Fig. 1). The two beams (with $\lambda = 514$ nm) intersect in the sample at an angle of $2\theta = 3.32°$, thereby causing an intensity modulation with the spatial periodicity $\Lambda = \lambda/(2\sin\Theta) \approx 9$ μm. The transverse intensity distribution of the single laser beams is a Gaussian with a diameter $d \approx 250$ μm (full width at half of the maximum intensity). The power of the laser was varied up to $P = 160$ mW/beam, corresponding to a maximum intensity $I = 2 \cdot P/(\pi \cdot d^2) \approx 160$ W/cm^2. The resultant optical grating was studied non-destructively by investigating the diffraction pattern of the 2 mW HeNe laser beam ($\lambda = 633$ nm, $d_{\text{FWHM}} \approx 80$ μm). The diffraction efficiency η: $= I_1/I_\Sigma$ is defined as the ratio between the intensity of the first diffraction spot I_1 and the input intensity of the reading beam I_Σ [15]. In order to study the dynamics of the grating formation, the intensity of the first diffraction spot was recorded as a function of time.

So far, we have only studied the optical response due to a grating-like variation of the *intensity* of the Ar laser beams, which is generated by the interference of two beams with the same plane of polarization. We obtained the same results whether the planes of polarization of the two beams were both vertical or both horizontal. This indicates, that the absorbing (rod-like) dye molecules exhibit random orientation in the discotic liquid crystal. In principles, it is also possible, to generate a grating-like variation of the *ellipticity* of the light at constant intensity by the superposition of one beam with horizontal and one with vertical plane of polarization. The investigation of this case, in which we expect a much lower response, is beyond the scope of this paper and may be subject to future studies.

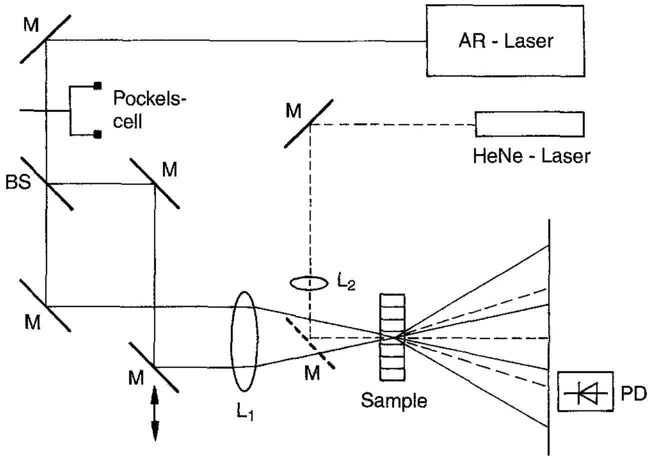


Fig. 1. Experimental setup used for the grating formation by interference of two laser beams. M – mirrors, BS – beam splitter, L – lenses, PD – photo diode

2 Results and discussion

Our experiments indicate that grating structures can be induced in the investigated liquid crystal, provided that the liquid crystal is initially in its glassy nematic state and the temperature of the surrounding of the sample is below the glass transition temperature. Figure 2 shows the time dependence of the first-order diffraction spot from the reading HeNe beam when the sample is exposed to the intensity grating of the writing Ar laser beams at room temperature. If the illumination is started, the diffracted signal increases with a time constant τ_1 of some 10 ms and the diffraction efficiency reaches a first plateau of $\eta_1 \approx 0.5\%$. If the illumination of the sample is continued, a second rise of the diffraction efficiency can be observed. The rise time τ_2 of this second process is in the range of several seconds, i.e. about two orders of magnitude larger than τ_1. Due to the second process, the diffraction efficiency reaches a maximum value $\eta_{\max}$ of several per cent. In order to describe the dynamics of the two-step mechanism of the grating formation phenomenologically, we define τ_1 and τ_2 as the exposure times which are necessary to induce 90% of the first- and the second-saturation value of η, respectively. For high Ar laser intensities, exposure times much larger than τ_2 lead to a decay of the induced grating structure.

The optically induced formation of grating-like structures within the sample can be attributed to a thermo-optical effect. Absorption of light at the positions with maximum light intensity leads to a rise of the temperature and thus to a grating-like spatial variation of the temperature. If the maximum temperature exceeds the glass transition temperature T_g, the sample transforms locally from the glass-like state into the N_D phase where the molecular orientation and the density are modulated corresponding to the respective temperature. Presumably, the faster process with the time constant τ_1 is determined by the energy absorption and heating of the sample. As soon as the local temperature starts to exceed T_g, the density change can cause a very fast change of the refractive index.

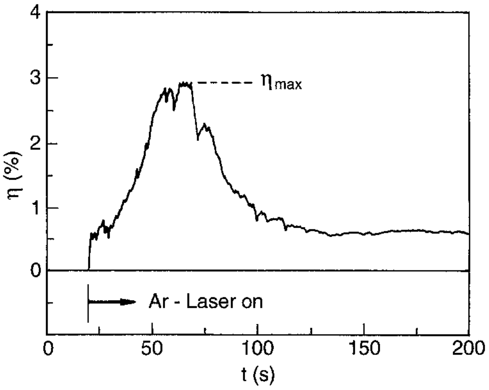


Fig. 2. Time dependence of the first-order diffraction intensity of the HeNe-laser due to exposure of the sample to the interfering Ar laser beams ($I = 120$ W/cm^2, $T = 30$ °C)

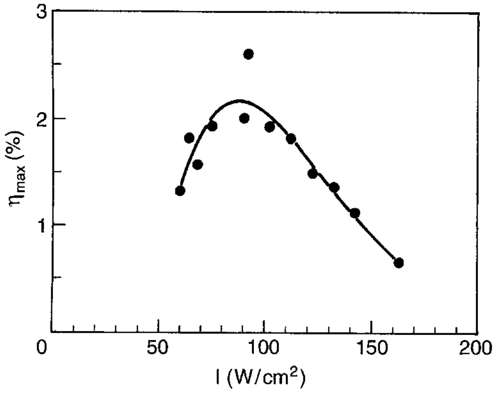


Fig. 3. Diffraction efficiency $\eta_{\max}$ vs intensity of the Ar laser beams at room temperature (exposure time ≈ 8 s)

However, the slow process (with time constant τ_2) may be due to a reorientation of the director which is slow due to the high rotational viscosity of the investigated compound. Measurements of the *electrooptic* switching time τ_{EO} in a Frederiks cell reveal values of $\tau_{\mathrm{EO}} \geq 20$ s (at $V_{\mathrm{rms}} = 9$ V), and a divergence of τ_{EO} in the temperature range close to T_g. Even close to the clearing temperature, the rotational viscosity obtained from the electro-optic response time is $\gamma = 3.54$ Pa s (at 109°C)–5.98 Pa s (at 96°C), i.e. more than one order of magnitude higher than the respective value for typical calamitic nematic liquid crystals ($\gamma \approx 0.1$ Pa s).

The decay of the grating structure for long exposure times can be explained by heat diffusion in the respective direction opposite to the temperature gradient. For high-temperatures and high laser intensities it cannot be excluded that also decomposition of the liquid crystal contributes to the decay of the grating.

The dependence of the diffraction efficiency on the intensity I of the Ar laser beams shows a threshold between 50 and 60 W/cm^2 (Fig. 3). The first saturation value of the diffraction efficiency η_1 is independent on I, while the maximum diffraction efficiency $\eta_{\max}$ shows a maximum at about 100 W/cm^2 and decreases with increasing intensity I for $I > \approx 100$ W/cm^2 (Fig. 3). The time constants τ_1 and τ_2 of the grating formation decrease with increasing intensity I (Fig. 4). Both the static and dynamic behaviour are in agreement with a thermally induced optical nonlinearity, i.e. the intensity grating of the Ar laser induces a thermal grating which in turn affects the optical properties of the liquid crystal. In this case, increasing intensity is expected to speed up the grating formation due to faster increase of the temperature above T_g. The higher-temperature gradient leads to a larger heat diffusion and thus faster decay of the temperature grating which can reduce the maximum achievable grating efficiency. A decrease of τ_1, τ_2 and $\eta_{\max}$ is also observed when the average temperature of the sample is raised by means of the temperature control.

The light-induced grating structures can be permanently stored if the exposure of the sample to the Ar laser beams is interrupted. The diffraction efficiency η decreases when the illumination of the sample is finished (Fig. 5).

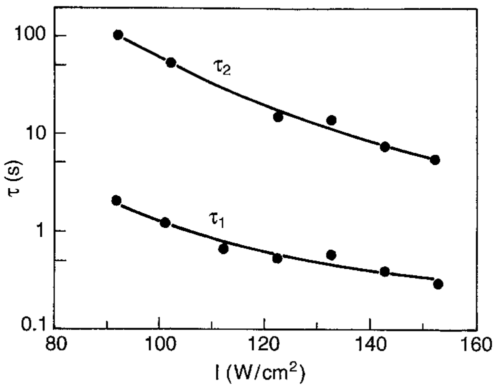


Fig. 4. Time constant of the grating formation versus intensity (same parameters as in Fig. 3)

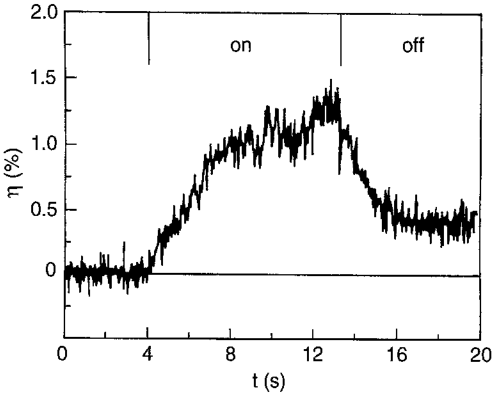


Fig. 5. Time dependence of the intensity of the first-order diffraction spot when the sample is exposed for 8 s with $I = 120$ W/cm^2 ($T = 30$°C)

However, η does not vanish but reaches a constant value of about 0.5% within a few seconds. The distortion of the liquid crystalline phase is conserved by the fast cooling into the glassy state. The stored grating shows a long-time stability. We have stored a sample after the exposure for three months at room temperature (i.e. below the glass transition temperature T_g). After these three months, the non-destructive test of the grating using a HeNe beam shows that the diffraction efficiency remained completely unchanged. However, the induced variations of the optical properties can completely be erased by heating the sample to the temperature range above T_g. The temperature rise above T_g leads to a decrease of the viscosity. Thus, the undisturbed alignment of the surrounding sample can cause a relaxation of the order parameter to its initial state. As a consequence, multiple storage processes can be realized.

3 Conclusion

In conclusion, we have demonstrated that grating structures can be stored and erased in a low molar mass discotic liquid crystal. The light intensity required to induce the grating structure is about 60 W/cm^2. The grating formation occurs within a few seconds. The process is characterized by a two-step mechanism which is now subject to more detailed investigations. When the samples are stored below the glass transition temperature T_g after exposure, the grating structure is permanently stored for at least several months. Erasing of the grating structures is possible by heating the sample to the temperature range above T_g. In our preliminary experiments, we achieved a resolution of ≈ 100 lines/mm. We expect that this resolution can be enhanced by one order of magnitude.

The opto-optical properties of our new storage material are comparable with those of low molar mass *calamitic* liquid crystals which have been recently studied [13, 14]. For both types of liquid crystals, the occurrence of a glass-like state is essential. The grating formation can be attributed to local heating above the glass transition temperature due to the intensity grating of the Ar laser beams. However, the grating formation in the discotic material is much slower (with time constants in the range of seconds) than in calamitic compounds (time constants of a few ms). This observation is in agreement with the high rotational viscosity of the discotic liquid crystal which was determined from measurements of the electrooptic switching time. The writing times for our low molar mass discotic liquid crystal are comparable to those observed in liquid crystalline polymers [7–9], although a different mechanism – the conformational change due to *cis–trans-isomerization* of the molecules – is responsible for the storage effects observed in polymers.

All liquid crystalline storage materials investigated so far exhibit much larger response times than photorefractive crystals. The electro-optic effect in these inorganic materials provides writing times as fast as $\approx 1\ \mu$s. However, a major advantage of the liquid crystalline materials is the possibility of non-destructive reading. In addition, low molar mass liquid crystals are easy to handle, e.g. a uniform alignment of the optical axis can easily be obtained. We have shown that another type of liquid crystals, namely the group of low molar mass discotic liquid crystals, is suitable as a storage material. We are confident that their properties for this purpose can be improved. For example, the diffraction efficiency can possibly be enhanced by applying an external electric field, due to a thermo-electro-optical effect.

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