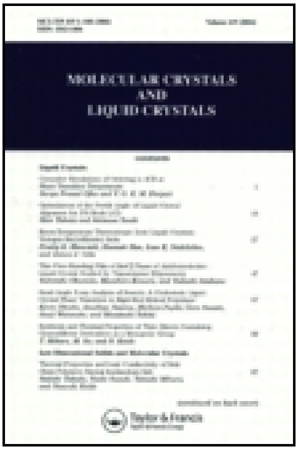

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Reversible Storage of Light-Induced Gratings in Low Molar Mass Liquid Crystals

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Version of record first published: 24 Sep 2006.

To cite this article: H. J. Eichler, R. Elschner, R. Macdonald, G. Heppke & H. Schmid (1994): Reversible Storage of Light-Induced Gratings in Low Molar Mass Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 250:1, 293-302

To link to this article: http://dx.doi.org/10.1080/10587259408028214

Mol. Cryst. Liq. Cryst., 1994, Vol. 250, pp. 293–302
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Printed in the United States of America

Reversible Storage of Light-Induced Gratings in Low Molar Mass Liquid Crystals

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(Received September 27, 1993; in final form December 15, 1993)

Low molar mass liquid crystals which exhibit an anisotropic glassy state are investigated for erasable recording processes. Optical gratings were written with intensities less than 1000 W/cm^2 obtained from an argon–ion laser and read out by diffraction of a weak He–Ne laser. Grating build-up times of less than 5 ms have been observed. Diffraction efficiencies of several percents were measured as a function of intensity and grating periods down to 5µm. The stored gratings are erased by homogeneous laser heating. It is shown that the observed recording phenomena is connected with optical heating and light-induced transitions from the glassy to the liquid crystalline state of the material.

Keywords: *Glassy liquid crystals, nonlinear optics, optical storage*

1. INTRODUCTION

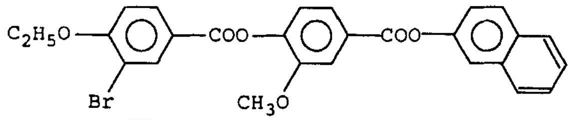
The investigation and searching for suitable media with optical properties which can be varied locally by light permanently or in a reversible way is currently an area of intense research activities.[1] Light-induced changes in the absorption, the reflectance, the refractive index, the birefringence or a combination of these properties are important, e.g., for applications in optical data processing techniques. Among other new interesting materials, liquid crystals exhibit large optical nonlinearities and have been the subject in a number of investigations during the last years.[2,3] Recently we demonstrated a novel liquid crystalline material to be applicable for reversible optical information storage.[4]

In contrast to photostimulated conformational changes in liquid crystalline polymers, which have been extensively studied for the realization of reversible optical information storage during the last years,[5,6] it is shown that the presently investigated storage process is connected with laser induced transitions between the glassy and the liquid crystalline state of particular low molar mass liquid crystals. Low molar mass liquid crystals presently have the advantage that they are easier to synthesize and that well-known preparation techniques together with other established "state-of-the-art" liquid crystal technologies allow the production of devices with high optical quality. Furthermore the viscosity of low molar mass liquid crystals is usually several orders of magnitude smaller than the viscosity of liquid crystalline polymers, leading to faster switching and response times. Therefore, glassy low molar mass liquid crystals may be good candidates for the realization of faster reversible optical information storage media as will be discussed in the following.

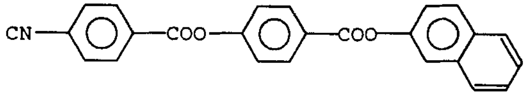
In the present paper it is shown that a reversible variation of the optical properties of the investigated material can be induced with light obtained from a low power *cw*-laser. The interference of two coherent light waves creates an intensity pattern which modulates the optical properties of the material. The resulting optical grating can be frozen-in in the liquid crystalline glassy state. The grating remains until the liquid crystal is heated up again above the glass transition temperature. The reversibility of the grating formation process, i.e., realization of multiple writing, reading and erasing cycles has been proved. The dynamics of the grating formation process depending on temperature and intensity, and the diffraction efficiency as a function of intensity and grating period is investigated. A first qualitative description of the underlying mechanism for the observed gratings is presented.

2. EXPERIMENTS AND RESULTS

The investigations have been performed with an eutectic nematic mixture (denoted as Mi5b in the following) which consists of the two compounds



$x_A = 0.8$



$x_B = 0.2$

Both substances have a glassy nematic state. Phase sequences and transition temperatures of the mixture are given in a previous paper.[4]

The mixture was chiralized by the addition of 9.6% CB15 (BDH) in order to obtain a better orientation of the sample. The resulting pitch is 1.58 μm at 30°C. To enhance the absorption at the laser wavelength, a small amount (0.1%) of an dichroic anthraquinone dye (D37, BDH) has been added. The phase transitions of the resulting mixture are: cholesteric 119.8°C isotropic; $T_g^{on} = 19.6$°C.

The investigations have been performed with liquid crystal films of 10 μm thickness with uniaxial rubbed planar alignment. A homogeneous texture was achieved by annealing the sample at elevated temperatures, a few degrees below the clearing point.

The experimental set-up is shown in Figure 1. Two coherent recording beams obtained from an argon–ion laser ($\lambda = 514$ nm) with a symmetrically Mach–Zehnder-like beam splitter are focussed onto the sample including an intersection angle 2Θ. Due to the interference of the two beams a sinusoidal transversal intensity pattern is formed in the sample which is absorbed by the dye molecules leading to a temperature grating

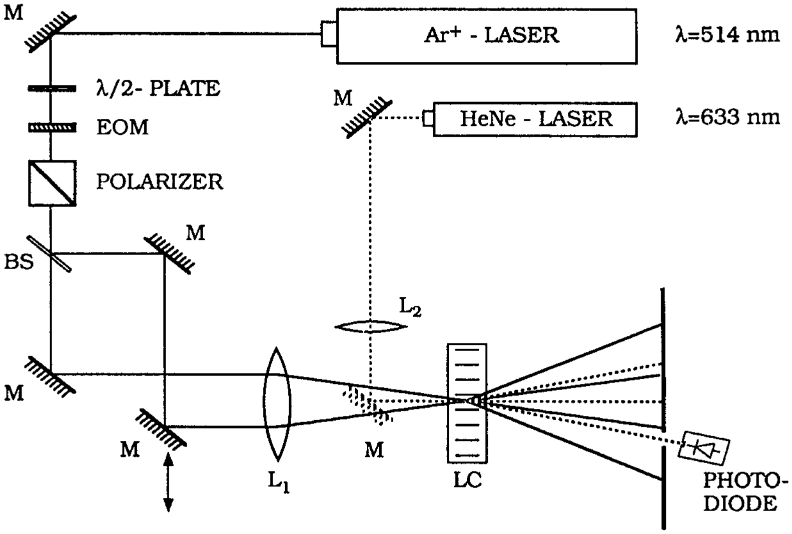


FIGURE 1 Experimental arrangement for light-induced grating investigations. The electro-optically modulated argon laser beam is splitted into two beams with a beam splitter *BS* which are recombined with mirrors *M* and a lens L_1 with an intersection angle 2Θ in the sample. The induced grating is read out by diffraction of a He–Ne laser.

which modulates the optical properties of the material. The induced optical grating is monitored by diffraction of a weak He–Ne laser beam ($\lambda = 633\,\text{nm}$). The first order diffracted light intensity is measured with a calibrated photodiode. The diffraction efficiency η of the induced grating is determined by the ratio between the input and the diffracted intensity. The dynamics of the grating formation are investigated by electro-optically chopping the argon–ion laser beam with the help of a ferroelectric liquid crystal modulator[8] and time resolved recording of the diffracted intensity. The samples are temperature controlled within ± 0.1°C at temperatures between 10°C and 100°C. The grating period has been changed between $\Lambda = 5\,\mu\text{m}$ and $\Lambda = 20\,\mu\text{m}$ by varying[9] the beam intersection angle Θ. The following experimental results have been usually obtained with samples which are initially cooled down below the glass transition temperature.

Figure 2 displays an example of a single write-, read- and erase-cycle of a light-induced grating. After switching on the argon–ion laser, the temperature in the interference region increases within some *μs* so that the material is heated up above the glass transition into the liquid crystalline phase and the grating formation takes place. The induced grating remains if the argon laser is switched off. Erasure has been achieved by illuminating the recorded grating with a single argon–ion laser beam of about two times higher power than needed for the recording process. More than 20 write-, read- and erase-cycles have been realized so far on the same spot without remarkable changes in the diffraction efficiency of the stored gratings.

During the recording process we observe oscillations in the diffracted signal. The origins for these oscillations are still under investigation and not clear at the moment.

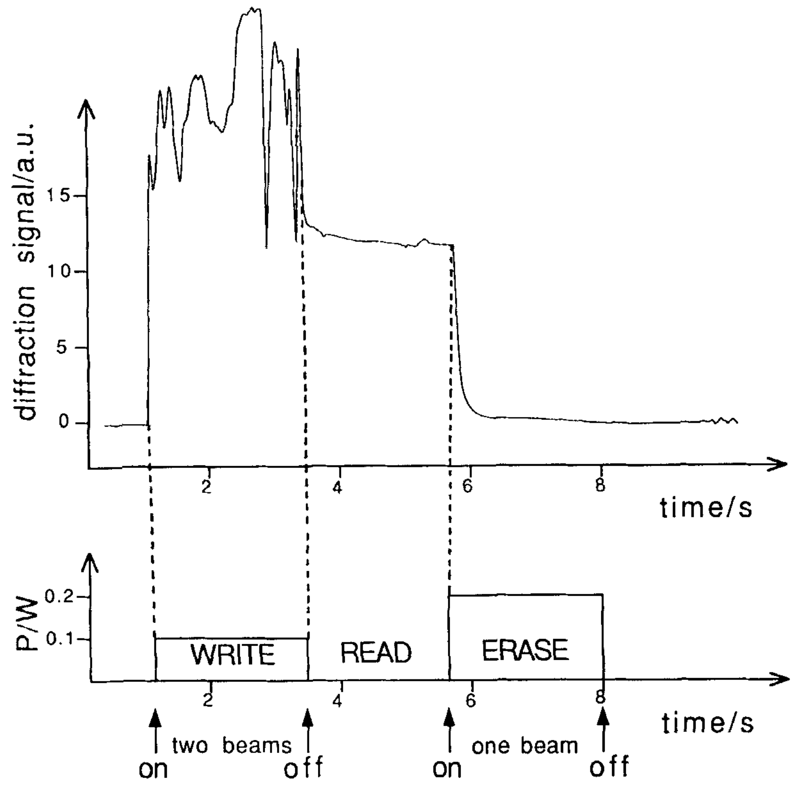


FIGURE 2 Diffracted signal for one single write-, read-, and erase-cycle of our system. *P* denotes the power of the argon–ion laser. The sample temperature was 10°C.

There is no change in the diffraction efficiency if the temperature is sufficiently below the glass transition temperature. Due to the glassy state the material is in a metastable thermodynamic state and tends to relax back to equilibrium which means to crystallization of the material in our case. In the represented material crystallization appears after approximately three days at temperatures near T_g. On the other hand it is also important to consider the kinetics of the grating relaxation which is obviously in our case a very slow process because we observed no detectable change in the stored patterns even after some weeks of storage at $T = 5°C$, which is enough for many applications in optical storage techniques. In the temperature region close to the glass transition (approximately 10 K above T_g) we observed also a week storage effect but without long-time stability of the stored gratings. Even in this temperature region the material can be used for storage applications if a periodic refresh of the data is employed. After further increase of the temperature the hologram persists no longer than some milliseconds.

To investigate the dynamics of the grating formation, the sample has been illuminated with a pulsed intensity grating of about 40 ms duration and the temporal development of the diffraction signal was monitored with an oscilloscope. Figure 3a

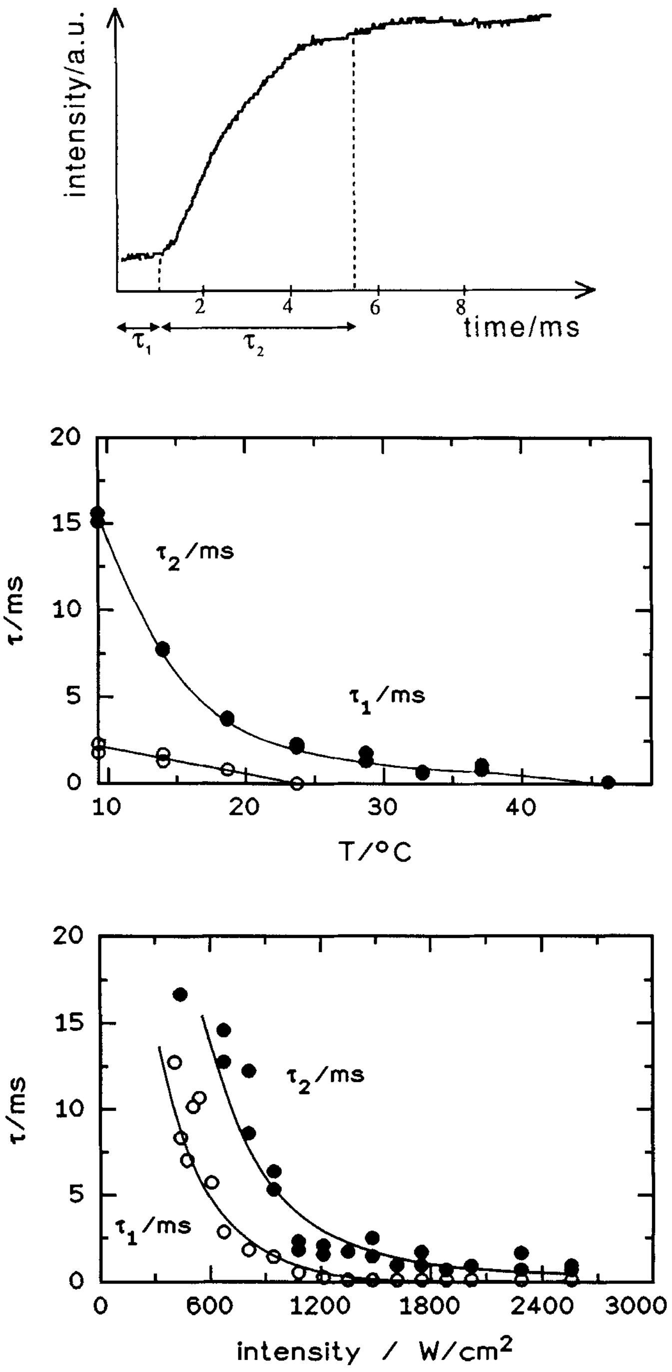


FIGURE 3a–c. a) Intensity of the first diffraction order as a function of time. Illumination with the intensity grating starts at $t = 0$. b) Temperature dependence of the time constants τ_1 and τ_2 (intensity = 540 W/cm^2). c) Intensity dependence of the time constants τ_1 and τ_2 (sample temperature = 10°C).

shows a typical time dependency of the diffracted signal. The illumination starts at $t = 0$ and the observed diffraction dynamics can be characterized phenomenologically by two time constants. After a characteristic "delay"-time τ_1 the grating formation starts, leading to an increase of the diffracted signal which can be described by a second time constant τ_2. As shown in Figure 3b both time constants decrease with increasing temperature. As will be discussed below, τ_1 corresponds to the time which is needed to heat the film from the glassy to the liquid crystalline state. It therefore decreases with smaller temperature differences between the initial sample temperature and the glass transition temperature and almost vanishes at $T = T_g$. The second time constant τ_2 is connected with the grating formation process in the liquid crystalline phase and thus correlated with structural relaxations of density and molecular orientation above T_g. The time constant τ_2 is determined by the "excess" intensity which is the difference between the input intensity and the intensity needed to heat from the initial temperature to T_g. Therefore τ_2 decreases with increasing the initial temperature or by using higher laser intensities as can be seen in Figure 3c.

To explain the observed grating formation process we will assume that it is mainly given by laser-heating and opto-thermally induced birefringence changes in the liquid crystalline phase. For simplicity we assume that for a given polarization of the laser radiation, the refractive index changes established by heating can be written as[10]

$$\delta n = \left(\frac{\partial n}{\partial T}\right)\delta T \tag{1}$$

where $(\partial n/\partial T)$ is the thermo-optic coefficient determined by changes in density and the scalar order parameter mainly. Most probably the density ρ and the scalar Maier–Saupe parameter[11] S are changed due to laser heating. We will further assume that approximately $(\partial n/\partial T)_{LC} \simeq \text{const.}$ and $(\partial n/\partial T)_{glass} \simeq \text{const.}$ but[12] $(\partial n/\partial T)_{glass} \ll (\partial n/\partial T)_{LC}$ at temperatures near the glass transition.

The steady state laser-induced rise in temperature in the case of thermal grating excitation is given by[9]

$$\delta T = \frac{\alpha I}{\rho c_p D q^2} \tag{2}$$

where α is the absorption coefficient, ρ the density, I the laser intensity, q the grating wave-number, D the heat diffusion constant and c_p the heat capacity. For thin gratings the diffraction efficiency in a plane-wave approximation is proportional to the square of the induced refractive index change[9]

$$\eta = \left(\frac{\pi d \delta n}{\lambda}\right)^2 \tag{3}$$

where λ is the probe laser wavelength and d the film thickness. Equations 1–3 describe a quadratic dependence between the diffraction efficiency of the induced grating and the laser intensity. If δT is divided into the values $\delta T_1 = T_g - T_0$ which is the temperature difference between the initial temperature T_0 and T_g and δT_2, the temperature rise above T_g, then

$$\delta T = \delta T_1 + \delta T_2$$

$$\delta T_2 = \begin{cases} \delta T - \delta T_1 & \text{for } \delta T > \delta T_1 \\ 0 & \text{for } \delta T \leqslant \delta T_1 \end{cases} \tag{4}$$

Together with Equations 1 and 4 the induced refractive index change can be written as

$$\delta n = \left(\frac{\partial n}{\partial T}\right)_{glass} \delta T_1 + \left(\frac{\partial n}{\partial T}\right)_{LC} \delta T_2 \simeq \left(\frac{\partial n}{\partial T}\right)_{LC} (\delta T - \delta T_1). \tag{5}$$

Equations 2, 3 and 5 describe a quadratic relation between η and I and implies the occurrence of a threshold intensity I_{th} corresponding to the temperature rise $\delta T - \delta T_1 = 0$. The experimentally observed diffraction efficiency as a function of the laser intensity is shown in Figure 4. Agreement between the model and experimental data is good for intensities between 380 and 2000 W/cm^2. Based on this model the calculated threshold intensity is $I_{th} = 378$ W/cm^2 which is in good agreement with the measured value 377 W/cm^2.

With increasing intensity the diffraction efficiency first increases to a maximum of several percent at about 2000 W/cm^2 but then saturates and decreases by increasing the intensity further. At intensities below 380 W/cm^2 the induced temperature rise is insufficient to heat above the glass transition and changes in density and order parameter are negligibly small. Thus no refractive index change and no grating has been observed. The deviation between the observed and the calculated diffraction efficiency for $I > 2000$ W/cm^2 can be explained by the diffusive character of the thermal nonlinearity in connection with finite beam induced gratings. The plane-wave approximation used with Equation 3 is violated with finite laser beams at high intensities, because the grating is then riding on additionally refractive index changes which have the shape of a laser-induced Gaussian lens. This is a result of the transverse intensity profile of the two interfering laser beams. As a consequence, diffraction at the laser-induced lens together with grating diffraction leads to complicated diffraction patterns,[13] in particular with higher laser intensities. In these cases Equation 3 is no longer valid.

The diffraction efficiency drops (within some ms) to about half of its maximum value after the writing intensity is switched off. This behaviour is independently of the used laser intensity as indicated in Figure 4.

The spatial resolution of the material has been investigated by varying the grating period by changing the intersection angle Θ. Figure 5 shows the diffraction efficiency as a function of grating period.

Due to the diffusive character of the thermal nonlinearity, the grating modulation is weaker for larger grating wave numbers q (i.e., smaller spatial period Λ) and thus grating diffraction efficiency decreases with increasing q (decreasing Λ). A clearly detectable diffraction signal has been obtained for spatial periods as small as $\Lambda = 5$ μm so far.

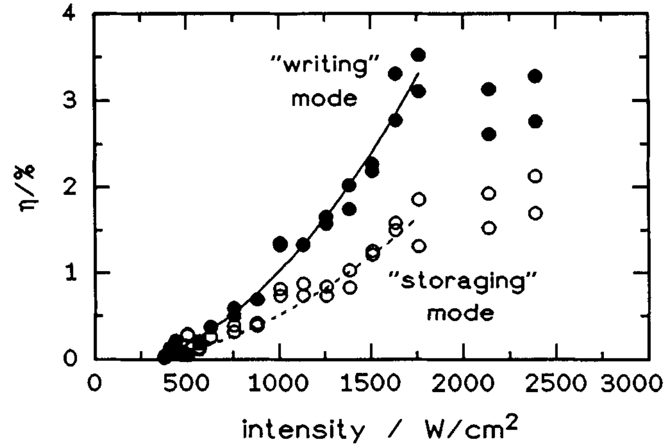


FIGURE 4 Diffraction efficiency depending on writing intensity. Solid curve: theoretical plot; Dotted curve: theoretical plot with half of the intensity used in the solid curve. "Writing mode" means write laser is on; "Storaging mode" means the write laser is off. Sample temperature = 10°C.

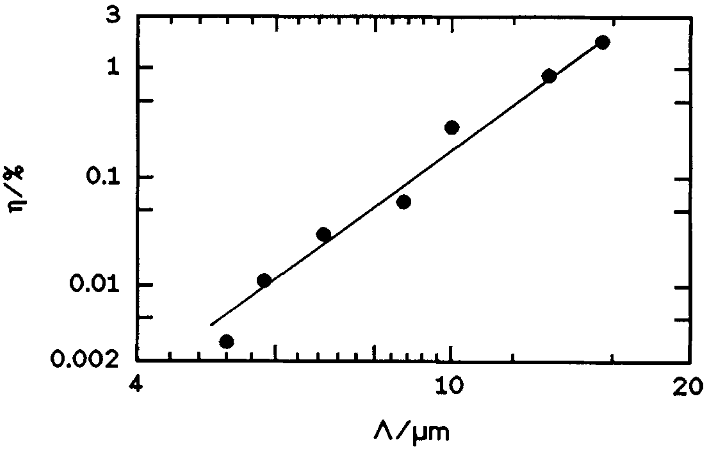


FIGURE 5 Dependence of the first diffraction order on the grating period (intensity = 786 W/cm^2; sample temperature = 10°C).

Assuming that the induced refractive index change is proportional to the induced temperature rise, then η is proportional to Λ^4 (cf. Equations 1, 2 and 3) which is in good agreement with experimental data.

3. DISCUSSION OF THE STORAGE PROCESS

As shown above, the grating formation and the investigated refractive index modulation can be explained by opto-thermally heating and laser-induced transitions between the glassy and the liquid crystalline state. According to the model, the observed storage process is connected with the freezing of structural relaxations (i.e., molecular displacement and orientation) in the vicinity of the glassy liquid crystalline phase transition.

Supposing that in a first approximation the investigated anisotropic liquid crystalline glass behaves similiar like an isotropic glass, the density and the scalar order parameter relax rather slowly with temperature changes near the glass transition. As a consequence these parameters and the glass transition temperatures T_g are not related to a thermodynamic equilibrium state,[14,15] in general. Calorimetric investigations for the nematic mixture Mi5b show for instance that T_g is shifted about 8°C if the heating rate is changed from 5 K/min to 40 K/min. In other words, the transition temperature T_g depends on the thermal history of the material. Parameters connected with translational and rotational molecular motions like density[16] and orientation control the glass transition rather than the temperature of the system. As result, the actual values of ρ and S depend on thermal history, e.g., the rate of cooling and heating in the vicinity of the glass transition temperature. If, e.g., the whole sample has been cooled down to the glassy state with a typically slow rate $T_1 = 5$ K/min the frozen-in order parameter may have a value S_1. In case of the relaxation of light-induced thermal gratings, however, the rate of cooling is much faster in the peaks and in the order of $T_2 = (\delta T \backslash \tau) \simeq 10^5$ K/min since the grating relaxation τ time is in the order of 100 μs and $\delta T \simeq 10$ K. Thus the corresponding value S_2 in the peaks is different from that in the nulls (S_1) of the grating. In this way a birefringence modulation is stored in the glassy state. This has been proved by polarization microscopic investigations of the stored gratings.

It should be noted furthermore, that structural relaxation in glass-forming materials is described within modern mode-coupling theory[17] by introduction of a so-called "memory-kernel" integral to consider processes of thermal history in the vicinity of T_g. Already the name of this integral may indicate that these processes are applicable for information storage processes and artificial memory as shown here.

Erasure of the gratings is achieved by almost homogeneous heating with the smoothly varying intensity of a single laser beam. A temperature rise high above T_g strongly decreases the viscosity of the material and the undisturbed alignment of the surrounding molecules force the order parameter to relax back to a value close to S_1. This has been also proved by polarization microscopic investigations.

4. CONCLUSIONS

The low molar mass liquid crystals under discussion represent a new class of optical storage medium. Reversible permanent light-induced gratings have been stored below the glass transition temperature. Grating formation is explained by structural relaxations (density and scalar order parameter) connected with laser heating, resulting in a modulation of the birefringence. This process is completely different compared with photochemical changes which have been used in polymers to realize reversible holographic gratings. The reversibility of the storage process and multiple write-, read- and erase-cycles have been demonstrated. The induced gratings have been written and erased within some milliseconds and the diffraction efficiency is in the order of several percents at intensities of several hundred W/cm^2. In liquid crystalline polymers containing azoaromatic groups where the optical induced birefringence changes result from photochemical reorientation of the azo moieties, the intensity required to store the light-induced grating amounted to about 10 mW/cm^2 or less, whereas the time constants for recording and erasure are in the order of some seconds to tens of seconds.[18,19] In comparison to these polymers we presently need higher intensities but shorter times to write the grating. It must be mentioned in this context that speeding up the recording times in azo polymers or similiar materials may be also possible by increasing intensity, in principle. It was discussed in several references,[7,20] however, that the kinetics of the *cis–trans* isomerization is at least the limiting factor in these materials. In practice no faster switching than seconds have been reported to our knowledge for this kind of storage effects. Consequently, even at this preliminary stage, the investigated low molar mass material with the possibility for millisecond response looks very promising for applications in optical information storage devices. Further investigations must be carried out in order to obtain a better understanding of the underlying physical processes and to optimize the conditions and the material for this kind of application.

Acknowledgements

The authors would like to thank W. Schäfer (University Halle) for providing the compounds. Financial support from the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich "Anisotrope Fluide") and the Senatsverwaltung für Wissenschaft und Technologie is gratefully acknowledged.

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