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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Version of record first published: 24 Sep 2006.

To cite this article: R. Elschner & R. Macdonald (1996): Light-Induced Dynamic Grating Investigations of Glassy Liquid Crystals for Optical Storage Applications, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 282:1, 107-118

To link to this article: http://dx.doi.org/10.1080/10587259608037571

Mol. Cryst. Liq. Cryst., 1996, Vol. 282, pp. 107–118
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Light-Induced Dynamic Grating Investigations of Glassy Liquid Crystals for Optical Storage Applications

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Abstract. The dynamics of light-induced gratings in weakly absorbing glasses possessing liquid crystalline orientational order have been investigated using a gated cw-laser. It is shown that structural relaxation processes are substantially important for the formation of reversible holographic storage effects. The resulting complex dynamics of grating formation have been analyzed by applying a time-domain master-plot construction for the first time. Intensity and temperature dependence of the obtained relaxation time exhibits a Vogel-Fulcher behavior and the relaxation process can be described by a stretched exponential law of the Kohlrausch-Williams-Watt type.

Keywords: Glassy liquid crystals, nonlinear optics, optical storages

1. INTRODUCTION

Holographic optical data storages[1] offer the most promising technique for the realization of high capacity optical data storages with fast data transfer rates. Advantages stem from the fact that page-oriented volumetric storages can be realized utilizing so-called holographic multiplexing techniques[2]. Reversible holographic storage effects have been realized in various $\chi^{(3)}$-like optical nonlinear materials in which light-induced refractive or absorption changes exhibit an almost infinite slow relaxation of typically seconds up to several years, thus providing memory. Erasure and reversibility is then achieved by speeding up the relaxation process e.g. with the help of additional light waves, incoherent illumination or increasing temperature. The most prominent materials which have been investigated for this purpose during the last twenty-five years are photorefractive crystals[1,3] like $BaTiO_3$ or $LiNbO_3$ in which photoexcited charge carriers modulate the optical properties via electro-optic effects. Other materials of increasing interest are organic media like polymers[4] or polymeric liquid crystals[5,6] in which

photostimulated conformational changes can be frozen in the glassy state in a reversible way. Nevertheless, the search for new materials, which meet the demands of present and future optical information- and data-processing techniques is still one of the most important tasks under investigation for the realization of reliable all-optical storages. High photosensitivity, high storage density, fast writing and access times are as desirable as reversibility and non-destructive retrieval.

New low molar mass room temperature glasses possessing liquid crystalline orientational order have been demonstrated to be interesting candidates for reversible optical storage applications[7,8,9]. In the present contribution, recent results obtained in holographic grating experiments with glassy liquid crystals will be reviewed briefly and are compared with other optical storage materials.

Furthermore, general aspects of the dynamics of laser-induced glass transitions, which are substantial for the understanding of the studied recording and storage processes, are investigated using the transient grating technique[10]. It is shown that structural relaxation phenomena are important for the storage effects. The resulting complex dynamics of grating formation using a gated cw laser are analyzed applying a time-domain master-plot construction for the first time. The obtained 'relaxation time' has been investigated for different temperatures and light intensities.

2. PHOTO-THERMAL RECORDING AND ERASURE

Recently, a novel low-molar-mass liquid crystalline material has been demonstrated to be applicable for reversible optical data storages using holographic grating techniques[7,8,9]. The new material consists of an eutectic mixture of two ß-naphtylester which exhibit the phase transitions: crystalline 136°C nematic 140°C isotropic. At usual cooling rates of several K/min crystallization is, however, avoided and the supercooled fluid undergoes a glass transition at T_g = 35°C. Consequently, a nematic-like non-equilibrium state is frozen in below the glass transition temperature which reveals many properties of conventional glasses in combination with the orientational order of liquid crystals. It should be noted further, that an additional transition from an uniaxial into a biaxial nematic phase has been observed at T = 95°C in conoscopic investigations[11].

To enhance absorption of the incident laser light, a small amount (0.1 - 1%) of a dichroic anthraquinone dye (D37 by Merck) was added which results in a somewhat lowered glass transition temperature of $T_g = 34°C$ for the mixture. The liquid crystal was sandwiched between two 1mm thick glass plates separated by 10 μm spacers. The inner surfaces of the container were coated with uniaxially rubbed polymer films to achieve homogeneous planar orientation. Sample temperature was controlled between 10 and 100°C with an accuracy of ± 0.1°C.

The experimental setup for holographic grating investigations is shown in Fig. 1. Two coherent beams obtained in a Mach-Zehnder-like beam splitter from an argon-ion laser (λ = 514 nm) intersect in the sample including an angle 2θ. The resulting sinusoidal interference pattern has a fringe spacing of $\Lambda = 2 \ldots 15$ μm which is absorbed by the dye molecules leading to a temperature grating and modulations in the optical properties of the material. The resulting optical grating was monitored either by self-diffraction of the beams or diffraction of another laser beam at λ = 633 nm. The intensity of the first diffraction order has been used to read out the grating with the help of calibrated photodiodes. Dynamics of grating formation and relaxation were investigated by electro-optically chopping the cw-laser with the help of a Pockels-cell into pulses of several ten milliseconds duration with duty-cycles of typically 1:6 and time-resolved recording of the diffracted probe beam. Additionally, the intensity could have been switched between a low (write) and a high (erase) level using an ferroelectric liquid crystal modulator and one of the interferometer arms could have been blocked with a mechanical shutter.

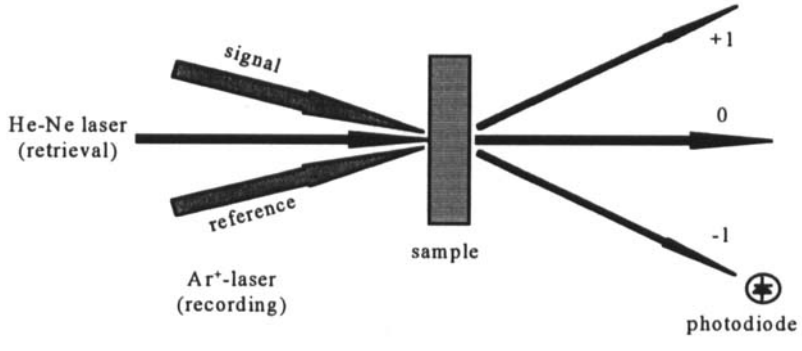

Fig.1: Simplified experimental setup for laser-induced dynamic grating investigations

Fig. 2 displays examples of all-optical recording, reading and erasure of holographic gratings. If both, the signal and reference beam are impinging onto the sample with an intensity of some tens to hundreds of Watts/cm^2, grating formation takes places leading to an increase in the diffracted signal. If the two beams are switched off, the signal drops down somewhat but a persistent grating with diffraction efficiency of several percents remains. The stored gratings can be optically erased by the more or less homogeneous illumination with a single laser beam at (about two times) higher intensity. After erasure, a new grating can be recorded, and so on. It is worthwhile to note that more than 10^3 cycles have been realized in the example given in Fig. 2 and no significant decrease in the stored grating modulation can be observed. Assuming an exponential degradation and more than 10^4 cycles can be extrapolated from these results until the persistent part of the grating drops down to half of the initial modulation depth.

Without erasure, stored gratings with life-times more than one year have been proved so far. It must be noted that beside 'local' optical erasure the holographic gratings can be also washed out 'globally' by heating up the whole sample clearly above the glass transition and subsequent cooling.

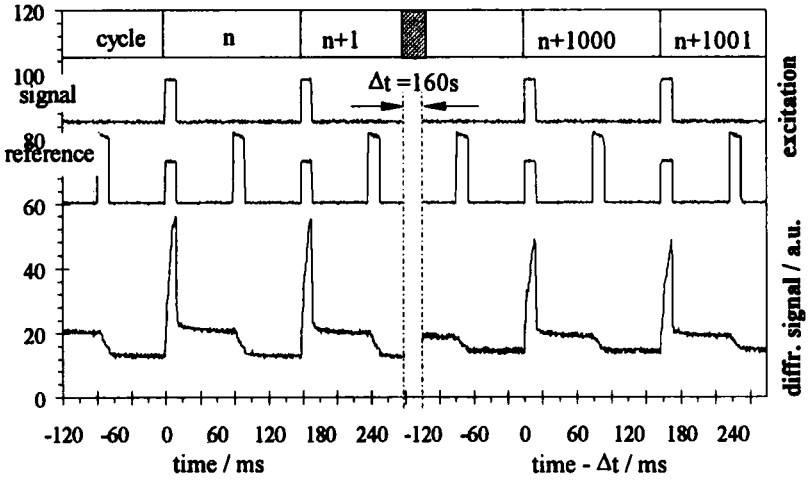

Fig. 2: All-optical recording, retrieval and erasure of holograms. Intensity (signal plus reference) was 350 W/cm^2 and temperature T = 20°C.

The investigated storage process can be explained in a very first attempt taking into account the properties of the glassy material at or below the glass transition temperature. Since crystallization is avoided, the supercooled liquid is always in a non-equilibrium state. As a consequence parameters like density or the scalar order parameter which determine the optical properties of the medium have values depending on the thermal history of the material, e.g. the heating or cooling rate. During photo-thermal excitation and subsequent relaxation of thermal gratings heating and cooling takes place very rapid with rates of 10^{-5} K/s and more, resulting in strong modulations of birefringence[8,9] which can not follow the fast thermal grating relaxation and therefore are stored in the glassy state. More precisely, the storage process is connected with the complex dynamic behavior near the glass transition which will be discussed in the following section.

3. DYNAMICS AND MASTER-PLOT CONSTRUCTION

To understand the mechanisms during laser heating and the following storage process, the dynamics of grating formation and storing have been studied for different sample temperature and light intensities. This way it was possible to investigate optically the dynamics of glass transition phenomena in the time domain.

If a liquid is cooled into a supercooled state, a dramatic increase of transport coefficients like viscosity can be observed[12]. These transport coefficients reflect the underlying molecular dynamics of the system. The time scale of these dynamics bridges the gap between microscopic and macroscopic times. The strong temperature dependence of the time scale for slow processes is referred to as structural relaxation processes. These relaxation processes can be identified as loss peaks in frequency domain spectroscopic investigations, e.g. dielectric relaxation. They are connected with the primary relaxation (α-relaxation) and the secondary relaxation (β-relaxation). In the present experiments features of the α-process are observed in the *time domain* and the relaxation function can be studied with the material response to a small laser-induced perturbation. Generally, time and frequency domain of a certain relaxation process are connected by Fourier-transformation to each other.

The investigated transient grating signals reflect the time dependence of the nonlinear material response for a rectangular excitation (Fig. 3). On the relevant time scale (> ms) the excitation of a thermal grating can be considered as a perturbation with steep flanks.

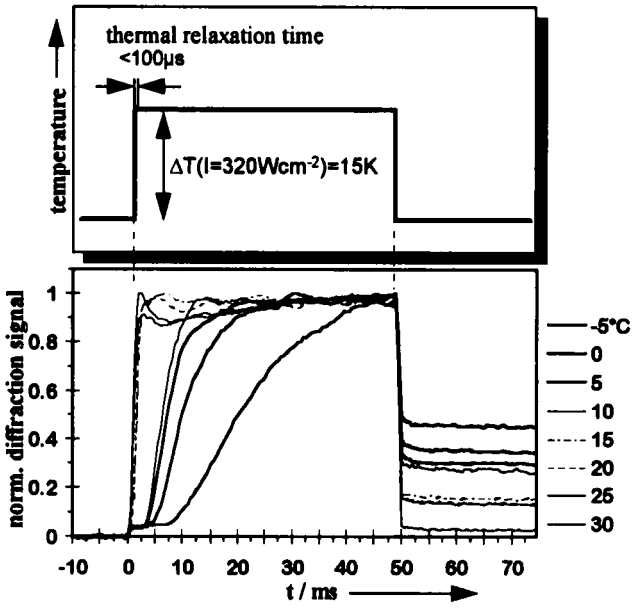

Fig. 3: Photo-thermal excitation and relaxation of optical gratings for different sample temperatures.

The steepness of the flanks is given by the thermal relaxation time of the grating which is in the range < 100 µs and short in comparison with the investigated response. Obviously, the relaxation from low to high temperature looks different compared with the relaxation from high to low temperatures which will be discussed below.

It was shown in Ref. 8 that the observed diffraction signal is mainly connected with light-induced modulations of the scalar order parameter S as well as density ρ. It should be mentioned, however, that for higher intensities a further relaxation process appears, which can be attributed to flow-alignment and molecular reorientation effects as will be discussed with more detail elsewhere.

To analyze the temperature and intensity dependence of the measured diffraction signal the well-known master plot concept[12] developed in frequency domain investigations has been applied to the time domain measurements. The master plot construction is based on the so-called α-relaxation scaling law[12]. In the time-domain the

relaxation function $\phi(t,T)$ describing the response to a small perturbation can be written in many cases like

$$\phi(t,T) = \tilde{\phi}(t/\tau) \tag{1}$$

where $\tilde{\phi}$ is (explicitly) independent of temperature. The whole parameter dependence enters via the temperature dependent time scale $\tau=\tau(T)$. If ϕ is plotted as a function of the rescaled time $\tilde{t} = t/\tau$, all data display the same master curve $\tilde{\phi}$. On a logarithmic time scale the plots referring to two different temperatures T_1 and T_2 are identical except for a shift $\ln(\tau_1/\tau_2)$ parallel to the abscissa. This law holds for a lot of glass forming materials and is also referred to as the time-temperature superposition principle[12]. It represents the interesting feature that the main effect of temperature approaching the glass transition is a stretching of the relevant time scale for the molecular dynamics and all connected physical processes. The second important feature is that the temperature dependence of time scales belonging to different physical processes is similar. The so called α-relaxation scale universality[12] determines that the characteristic time scales $\tau_i(T)$, e.g. for the shear viscosity, the dielectric relaxation, the heat conductivity or neutron scattering experiments, show similar anomalous behavior. For any pair $\tau_i(T)$, $\tau_k(T)$ of the mentioned scales one finds

$$\tau_i(T)/\tau_k(T) = C_{ik} \tag{2}$$

where C_{ik} is a temperature independent constant.

The master curve construction applies also if more complex relaxation dynamics have to be analyzed. The two laws can be merged if a combination of different relaxation processes (e.g. density and order parameter) is observed

$$\tilde{\phi}(t) = \sum_i \tilde{\phi}_i(t/\tau_i(T)) = \sum_i \tilde{\phi}_i(t/C_{ik}\tau_k(T)) \tag{3}$$

In that case the plots referring to different temperatures are identical except for a shift parallel to the abscissa on a logarithmic time scale as well. Consequently, a characteristic time scale $\tau_k(T)$ can be extracted from that shift (Fig. 4).

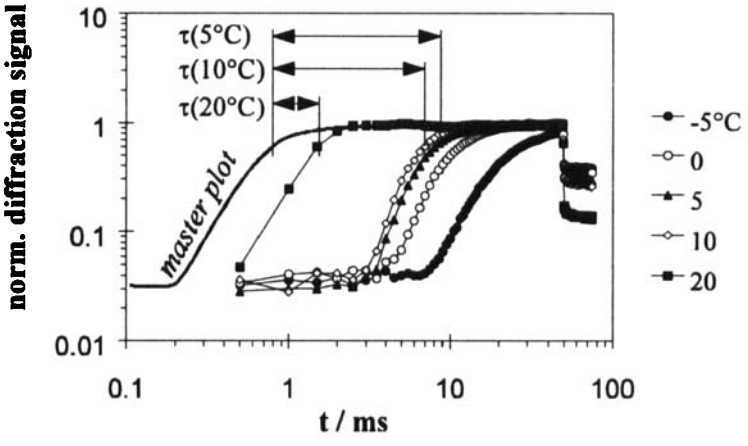

Fig. 4: Transient grating dynamics for different temperatures on a logarithmic scale. The characteristic time scale τ(T) is obtained as a shift with respect to the arbritary master plot.

Fig. 5 shows the temperature dependence of the extracted characteristic relaxation times for three intensities. The experimental data τ vs. T^{-1} was fit using a Vogel-Fulcher type[13] expression for the relaxation time

$$\tau(T) = \tau_0 \exp\left(\frac{F_N}{T - T_\infty}\right) \tag{5}$$

which is often used to describe the temperature dependence of viscosity in glasses which exhibits deviations from the Arrhenius behavior near the glass transition. The Vogel-Temperature T_∞ is a material parameter which describes where the molecular dynamics are freezed like in solids and the relaxation time diverges. T_∞ is typically located somewhere below the calorimetric glass transition temperature T_g. The constants τ_0 and F_N depend on the observed relaxation process.

The obtained characteristic time scales for many different intensities has been used to determine the temperature and intensity independent material parameter T_∞= (247 ± 3) K. It must be noted that the curvature of the hyperbolas given by F_N was intensity dependent in our case, which is a result of the different temperature steps during excitation in relation to the intermolecular energy barrier.The determined Vogel-Fulcher temperature is in good agreement with the results obtained[11] from dielectric relaxation measurements.

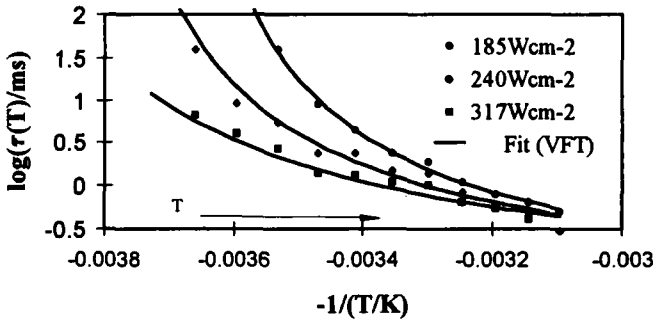

Fig. 5: Arrhenius plot of the characteristic relaxation times for different laser intensities.

Although the relaxation function ϕ can not be determined directly from the transient grating experiment reported here, it is worthwhile to stress that the observed grating dynamics and storage effects can be explained qualitatively assuming that the relaxation can be described by a stretched exponential function, the so-called[14] Kohlrausch-Williams-Watt (KWW) relaxation

$$\phi_K(t) = \exp-(t/\tau)^{\beta} \qquad 0 < \beta < 1 \tag{4}$$

This kind of relaxation is also typical for many glass forming materials. For rather small perturbations in case of linear material response the relaxation function eq. 4 can be observed directly, in principle. The perturbations are, however, not small in our experiments and things are more complicated. Instead, we simply assume that the total thermal excitation can be divided into many temperature intervals which are small enough so that eq. 4 holds approximately for each of these intervals. It must be noted, however, that the relaxation time τ is then different for each interval since it depends on temperature (see Fig. 5). The complete response is then obtained as a superposition of the different relaxation functions. A numerical calculation of the dynamic grating signal following that procedure taking into account the temperature dependence $\tau(T)$ as shown in Fig. 5 and assuming $\beta = 0.4$ is shown in Fig. 6. Compared to the experimental results given above, the calculated dynamics reveal the important features of the observed dynamics: The relaxation for increasing temperatures is different from that for decreasing temperatures and an almost persistent grating remains after switching off the excitation

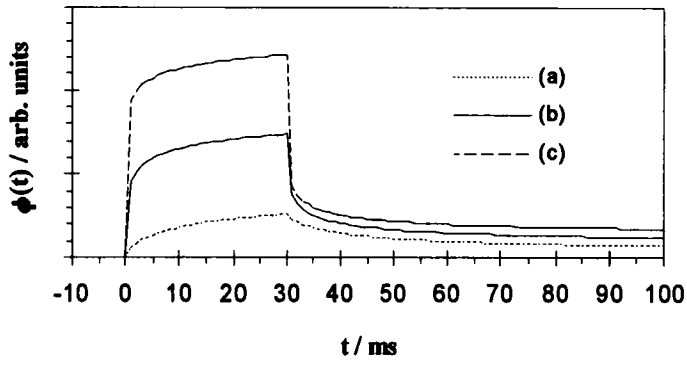

Fig. 6: Simulation of photo-thermal holographic recording for different intensities a) 100 W/cm², b) 200 W/cm², c) 400 W/cm² based on the KWW relaxation function.

thus leading to storage effects. These storage effects can be attributed to the slowest components of the KWW relaxation at low temperatures. The assumption that structural relaxation described by a Kohlrausch-Williams-Watt function is responsible for the observed dynamics is also supported by experimental results obtained in picosecond transient grating experiments with the same material which will be discussed elsewhere.

4. DISCUSSION AND CONCLUSIONS

Compared to other reversible holographic storage materials like the above mentioned photorefractive crystals[1,3] and polymers[4,5,6] the studied low molar mass glassy liquid crystals look very promising even at this early stage of investigations. Time constants for photothermally recording and erasure are in the same order of magnitude as for photorefractive materials but are a factor of thousand faster than e.g. in azo-polymers[5,6], where optical modulations result from photochemical reorientation of the azo moieties. Beside the dynamic behavior, it is also important to compare the required recording energy density. The intensity to write holograms in azo-polymers is in the order of 10 mW/cm² or less which in combination with time constants of several seconds or even tens of seconds results in recording energy densities of about 1J/cm². In comparison, our intensities of 100 W/cm² seem to be quite high but in connection with much faster

recording times yield energy densities in the same order of magnitude. Photorefractive crystals usually require energies which are one order of magnitude smaller.

The memory time in photorefractives is in the order of some milliseconds until years but in some cases need special fixing of the holograms. The life-time of stored gratings in all kinds of glassy materials including polymers is in principle limited by relaxation of the glassy state back to equilibrium, i.e. crystallization. As shown above, that relaxation is rather slow below the glass transition temperature and persistent gratings have been stored over more than one year without detectable changes. The outstanding advantage of our material is the possibility of non-destructive retrieval, in contrast to photorefractive crystals.

The spatial resolution and thus the maximum storage density is limited in our case by heat diffusion during the recording process to 500 lines/mm so far, which is not sufficient for many holographic applications. To achieve higher resolutions of 1000 up to 5000 lines/mm as with some photorefractive materials or polymers, it seems promising to use low molar mass liquid crystalline glasses also in combination with azo-dyes which allow for light-induced conformational changes.

In conclusion, low molar mass liquid crystals which exhibit an anisotropic glassy state at room temperature have been investigated in light-induced dynamic grating experiments. It was shown that the material and the investigated photo-thermal excitation may be suitable for reversible holographic optical data-storage applications. Reversibility and reliability has been demonstrated performing more than 10^3 all-optical recording, reading and erase cycles almost without degradation of the stored gratings. Recording intensities are in the range of 100 W/cm^2 resulting in writing and erasure times of milliseconds, whereas the stored gratings persist up to more than one year so far with diffraction efficiencies of a few percents.

The complex grating dynamics have been characterized applying a time-domain master curve construction for different temperatures and light intensities. The temperature dependence of the resulting relaxation time has been explained using a Vogel-Fulcher expression. The characteristic Vogel-temperature was determined to $T_\infty = (247 \pm 3)$ K which is in good agreement with published data.

Finally, the observed dynamics and storage effects have been explained qualitatively assuming a relaxation function of the Kohlrausch type.

Both, the Kohlrausch relaxation function and the Vogel-Fulcher temperature dependence of the relaxation time are strong indications that the investigated storage effects are connected with the dynamics of the glass transition and structural relaxation phenomena.

Acknowledgments

Financial support by the Deutsche Physikalische Gesellschaft via the Sonderforschungsbereich 335 *Anisotrope Fluide* is gratefully acknowledged. The authors would like to thank Dr. H. Schmid for assistance in sample preparation.

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