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Polarization Holograms in a "Liquid Crystal-Porous Glass" System

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Recording of polarization gratings is realized in porous glass with pore diameter of 40 Å filled with nematic liquid crystal (LC) 4-methoxy-4'-butyl-azobenzene. Such recording is possible due to the strong decrease of the rotational diffusion of LC molecules and their photo-products in pores compared with the bulk. Reversible and irreversible components in the grating formation were observed. These could be associated with different photochemical reactions of LC molecules.

Keywords: polarization holography; liquid crystal; porous glass

INTRODUCTION

Liquid crystals are very effective non-linear media. The cubic nonlinearity of LCs, $\varepsilon_2 \approx \Delta n/I$ (Δn is nonlinear change of refractive index n, and I is light intensity) could be as high as (1-10) cm^3/erg. This makes LCs very promising

for application in information storage systems, holography, information displays. However, such applications are restricted by relaxation characteristics of the induced nonlinear changes. Typical relaxation time for the refractive index variation is 0.1-10 s, which does not satisfy demands for vast majority of applications. From this point of view, an investigation of new states of LC with other relaxation characteristics is of great interest. As we have earlier shown [1-2], the relaxation time of Δn can be dramatically increased by intrusion of LC into porous glasses (PG). In our experiments a mesogenic azobenzene compound was used. The optical non-linearity of this material is essentially due to the photo-induced conformational change of azobenzene fragments [3]. Thin holographic gratings were recorded in LC layers as well as in the plates of micro-porous glass filled with LC using polarized beams as shown in Fig.1. In contrast to the reversible recording in LC layers, holographic gratings recorded in a LC-PG system were detectable even after a long time (more than half a year). A decrease of the LC translation diffusion and an increase of the stability of LC photo-isomers in the porous medium were assumed as the factors for non-reversible recording.

In this paper we consider new aspects of non-linearity of LC in porous matrix. It is reasonable to suppose that rotational diffusion of LC in micro-pores significantly decreases compared with the bulk. Hence, irradiation of the samples with polarized light could transform initial isotropic orientational distribution of LC molecules into an anisotropic one due to the mechanism of photo-selection [4]. So, one can expect that the LC-PG system is polarization sensitive, making it useful for the recording of polarization holograms. Such a recording is realized in our study. Characteristics of the polarization

holograms are studied as well as a possible recording mechanism is discussed.

Experimental details

Samples

As porous matrices we used mesoporous glass prepared in Institute of Technical Chemistry of the Martin-Luther-University (Halle, Germany). These samples were produced by spinodal decomposition of an alkali borosilicate glass followed by combined acid and alkaline leaching [5]. Glasses of the Vicor type [6] were obtained as the result of this treatment. Pore size distribution of the used glasses was very narrow with the maximum at 40 Å. A total pore surface in the volume unit of the glass was about 200 m^2/cm^3.

Porous glasses were filled with the LC 4-methoxy-4'-butyl-azobenzene (ZhK434) by NIOPIK (Russia) having nematic mesophase in the range 21-73° C. As is well-known [7], a common reaction for azobenzene derivatives is *trans-cis* isomerization. This causes a change of molecular polarizability and local order parameter of LC, which are considered to be the reasons for the high optical non-linearity.

Polished plates of the porous glasses with a size of 10x10x0.5 mm were used for the filling of LC. Such plates were cleaned by washing in acetone and baking them at 400°C for 3h. After cooling the glasses up to 100°C, LC was filled into pores.

Filling process was realized as follows. LC was heated above the melting point to 90°C. Plates of the porous glass were dipped into the melt

and kept for 6h. Surface of the plates was thoroughly cleaned with cotton after they were removed from LC.

Method and experimental set-up.

At the interference of two coherent beams being polarized linearly with parallel directions of polarization, the intensity of the light field is spatially

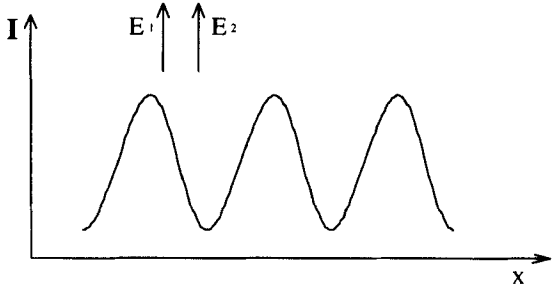

Fig.1. Spatial distribution of the light intensity I when two linearly polarized beams overlap ($\mathbf{E}_1 \| \mathbf{E}_2$). Direction of **E** is not spatially modulated.

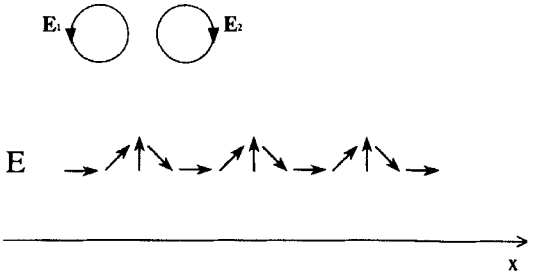

Fig.2. Spatial distribution of the light polarization **E** when two circularly polarized beams with $E_1=E_2$ overlap at a small angle. The total intensity is constant.

modulated as shown in Fig.1. Spatially modulated light can cause recording of the holographic grating in the medium, which changes own absorption or refraction under irradiation. We will call such gratings as "intensity gratings". Induced grating becomes apparent in the self-diffraction of the recording beams or diffraction of the probing beams. Many diffraction orders could be observed in case of thin holograms of this type. Intensity gratings were further recorded in the layers of ZhK 434 as well as in the "ZhK434-PG" media [1,2].

The other principal recording mechanism is realized in case of the circular polarization of the recording beams with mutually opposite rotation directions of vector **E** (Fig.2). In this case intensity of the light is not modulated, but the azimuth of the resultant linear polarization is rotated. In turn, the spatial modulation of vector **E** can induce a spatial modulation of the axis of anisotropy. This leads to a self-diffraction of the recording beams or diffraction of the probing beams. Such kind of gratings will henceforth be called as "polarization gratings". More detail information about this kind of gratings could be found, for example, in [8].

A scheme of the polarization holographic set-up is presented in Fig.3. The two recording beams (488 nm) are left and right circularly polarized by means of quarter-wave plates. The intensity ratio of the beams was approximately 1:1. The induced grating was probed with a beam of He-Ne laser (633 nm) having s-polarization. Light diffracted in the +1 order was measured by a photodetector. A shutter was used for the kinetic measurements.

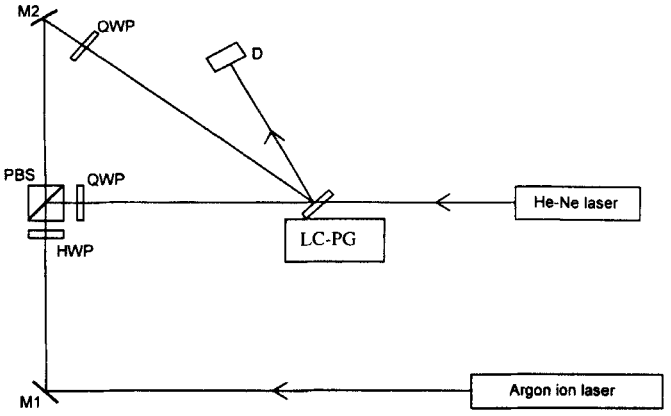

Fig.3. Polarization holographic set-up. In the figure, HWP and QWP are half-wave plate and quarter-wave plate, respectively, PBS is polarization beam splitter, M1 and M2 are mirrors, D is detector. The LC-PG layer is kept at the intersection of the argon laser beams and the He-Ne laser beam.

Experimental results and discussion

Recording of the polarization holograms in the geometry presented in Fig.2 was realized in the studied media "ZhK434-PG". Dependence of the intensity of the diffracted beam I_d on the recording time is presented in Fig.4. Curve $I_d(t)$ is characterized by saturation. The time constant of the curve $I_d(t)$ depends on the intensity of the recording beams; increasing of the recording intensity led to a decrease of the time needed for saturation. The diffraction efficiency $\eta=I_d/I_t$ (I_t and I_d are intensities of the testing beam and its +1 diffraction order, respectively) corresponding to the saturation part of the curve $I_d(t)$ was about 0.1. Maximal value of η practically did not depend on

the recording intensity. At the same time, diffraction efficiency was not a linear function of the irradiation dose. Recording of polarization holograms was realized only for the high intensity of the recording beams ($I_1+I_2 \geq 3$ W/cm^2). At the low recording intensity ($I_1+I_2<0.5$ W/cm^2) holographic recording was not successful even for long times of irradiation.

Relaxation curves for two different recording times are presented in Fig.5. These curves have reversible and irreversible components. Intensity of the irreversible component essentially depends on the time of irradiation; it increases with increasing irradiation dose. The intensity of the reversible component also slightly grows with the increasing of irradiation time. Note that the reversible component is weaker than in case of intensity holograms [1,2]. It could be evidence of a new mechanism of non-linearity.

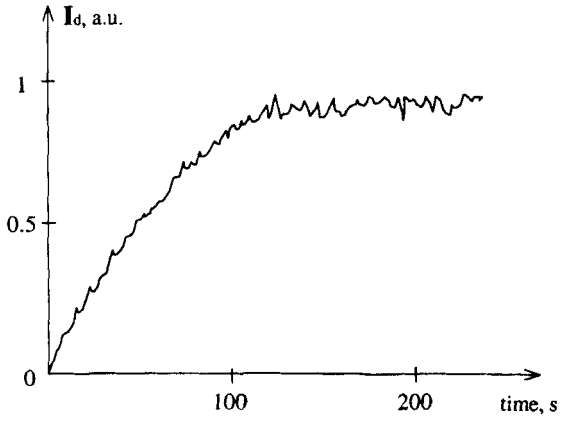

Fig.4. Dependence of the intensity I_d of the +1 diffraction order of the probing beam on the recording time. Intensity of the recording beams where $I_1=I_2$ =1.5 W/cm^2. Volume period of the grating was 9 μm.

Temperature studies of the samples with the recorded gratings were carried out. The intensity of the irreversible component gradually decreases with an increase of the temperature. However, we did not observe critical behavior of this component at the transition to isotropic phase (73°C). The polarization grating was detected even at the 150 °C.

Recording of polarization holograms should be associated with the orientational arrangement in a system under the action of polarized light. We have detected such an arrangement in the measurements of light induced birefringence. In our experiments plates of porous glass filled with ZhK434 and placed between crossed polarizers were irradiated with a polarized beam from an Ar-laser (λ=488 nm) and probed with the light of a He-Ne-laser (λ=633 nm). The argon laser beam was polarized at 45° to the crossed polarizers. A change of the intensity of the testing beam under irradiation with the exciting beam was observed. Kinetic dependencies of the intensity of the probing beam, I_t, for the recording and relaxation processes were qualitatively similar to the corresponding curves measured with the holographic technique (Fig.4 and Fig.5).

Recording of polarization holograms as well as of birefringence in only the layers of ZhK434 were not successful under various experimental conditions. The observed difference between this and the case of LC in pores could be explained by the difference in the orientational movements of LC molecules. Because the size of molecule (about 10 Å) is comparable with the pore size (40 Å), one can assume that LC molecules are frozen in the porous matrix and their thermal movements are greatly restricted. This should drastically decrease the rate of the rotational diffusion of LC molecules.

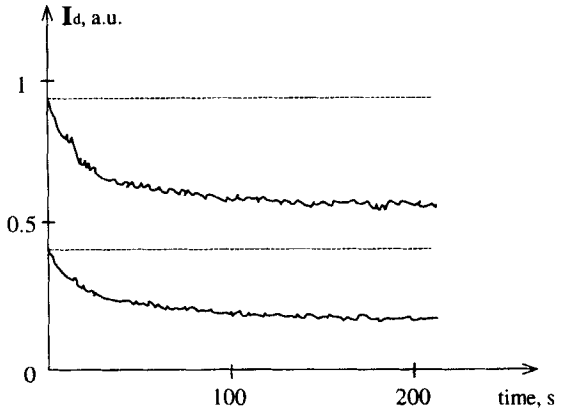

Fig.5. Relaxation curves $I_d(t)$ corresponding to the recording curve in Fig.4 for two times of the recording: 1-25 s; 2- 100 s.

A delay of the orientational movements of LC molecules in pores makes plausible the following mechanism of orientation. Let us assume that initial orientational distribution of LC molecules is isotropic. Irradiation of the porous plate filled with LC leads to the absorption of the actinic light and photo-transformation of LC molecules (*trans-cis* isomerisation, *etc.*). Because of the strong absorption dichroism of azobenzene derivatives, the most effective absorption and photo-transformation will be realized for the molecules oriented parallel to the direction of the light polarization. It should cause anisotropic orientational distribution of *trans*-isomers of LC with the axis of orientation perpendicular to **E** (Fig.6). In case of low-rate rotational diffusion and long life time of the photo-transformed molecules this distribution remains even after switching off the light. Neglecting dichroism

of photo-transformed molecules in comparison with *trans*-isomers, one can expect anisotropic absorption of the polarized light as well as birefringence in the irradiated area. Such mechanism of the anisotropy is usually called as "photoselection" or "angular hole burning" [4]. We have also observed this in azopolymer filled into porous glass [9].

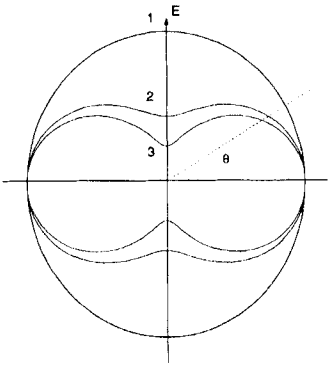

Fig.6. Demonstration of the molecular photo-selection: change of the angular distribution of the *trans*-isomers of LC under irradiation with polarized light; $t_3 > t_2 > t_1 = 0$ s.

Additionally, the presence of reversible and irreversible components in the relaxation curves should be explained (Fig.5). Note that the reversible component can not be due to the recording of thermal grating because the light intensity is not modulated in case of the polarization recording. Heating of LC with the light can hardly cause the appearance of the reversible component. We have additionally checked that a heating of the sample leads to a decrease in the efficiency of polarization gratings. We suppose that reversible and irreversible components are caused by various photochemical

reactions of ZhK343 in the pores. The reversible component is more likely to be connected with the reversible *trans-cis* isomerisation of LC molecules from the center of the pore. Its relaxation time should be dependent on the lifetime and the coefficient of the rotational diffusion for the *trans-* and *cis-*isomers. The irreversible component could be associated with other irreversible photo-transformations such as photo-degradation of LC molecules. Change of the color of LC in the irradiated area from the yellow to brown could be evidence of such a reaction. Similar changes were not observed in the LC bulk. Hence, the photoreaction causing a change in the color of LC is more probably realized in the interface layer LC-porous glass. It could be associated with the interaction of LC molecules with the reactive groups from the surface of porous glass, for instance, with hydroxyl groups, adsorbed water, *etc.* Possible photochromic processes in the interface area were considered earlier in [1]. Note that change of the color of LC in PG was detected only for the high intensities of the exciting light ($I \geq 3$ W/cm^2). This means that photochromic processes can be also connected with the destruction of LC. The studies of the photochemistry of ZhK434 in PG are in progress.

Conclusions

Recording of polarization gratings is realized in plates of mesoporous glasses filled with photosensitive nematic LC. Such recording is possible due to the strong decrease of the rotational diffusion of LC molecules and their photo-isomers in pores with the small diameter. An induction of the anisotropy in the studied system through the mechanism of photo-selection is thus made possible. In the case of polarization grating such a mechanism causes spatial

modulation of the axis of LC orientation. Reversible and irreversible components of the polarization grating could be associated with different photochemical transformations of LC molecules in pores. We suppose that the reversible component is associated with the reversible *trans-cis* isomerization, while the irreversible component is probably due to the photoreaction of LC molecules with the molecular fragments from the pore surface.

Acknowledgements
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