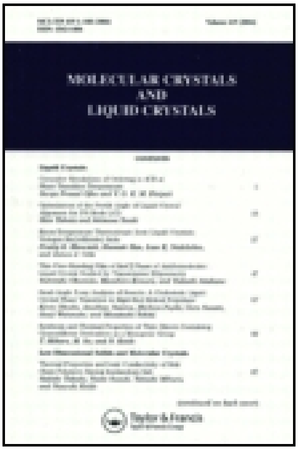

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Dual-Frequency Addressable Gratings Based on Polymer-Dispersed Liquid Crystals

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Dual-Frequency Addressable Gratings Based on Polymer-Dispersed Liquid Crystals

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Switchable diffraction gratings consisting of a dual-frequency-addressable nematic liquid crystal embedded in a polymer matrix were prepared using a holographic technique. The photopolymerization of a polymer-precursor, initiated by an optical intensity grating leads to the grating formation within a few seconds. The diffraction efficiency of the resulting grating structure can be modulated by an external electric field due to a variation of the frequency at constant voltage. The corresponding response time is a few ms, i. e. much faster than the relaxation time of the liquid crystal at zero field. The dispersion of white light and the surface modulation of a PDLC sample with one free surface are demonstrated as possible applications for PDLC gratings.

Keywords: Dual-frequency addressable liquid crystal; holographic storage; diffractive optical elements.

INTRODUCTION

The application of liquid crystals for optical information storage has been extensively studied during the last decade [1-6]. 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 [1] and by Coles and Simon [2,3]. Very efficient optical storage effects have been obtained due to a light-induced cis-trans-isomerization [4-6], i. e. a conformational change of the mesogenic units. Not only polymers, but also some low molar mass liquid crystals are suitable as storage materials due to the occurence of a glass like state [7]. Both calamitic [8] and discotic [9] low molar mass liquid crystals are suitable for erasable optical data storage due to a thermo-optical effect.

Polymer-dispersed liquid crystals (PDLC) [10] are a very interesting new class of materials for optical data storage [11-15]. PDLC systems consist of a solid polymer matrix and small droplets of a low molar mass liquid crystal which are dispersed in the polymer. PDLC films scatter light strongly because of the refractive index variations between the polymer and the randomly oriented droplets. However, they can be switched to a transparent state by applying a voltage. In a single scattering approximation [16] the light intensity transmitted through a PDLC sample depends on the thickness d of the film and the number density N/V of the droplets, according to $I = I_0 \exp(-\sigma \cdot d \cdot N/V)$. The average scattering cross section σ of droplets which are not much larger than the wavelength of the light is given by

$$\sigma \approx 2 \cdot \sigma_o \cdot (k \cdot R)^2 \left[(n_e(\Theta)/n_p - 1)^2 \cos^2\varphi + (n_o/n_p - 1)^2 \sin^2\varphi \right] \qquad (1)$$

$$\text{with} \quad n_{e,eff}(\Theta) = (\cos^2\Theta / n_o^2 + \sin^2\Theta / n_e^2)^{-1/2},$$

where σ_0 is the geometrical cross section, Θ is the angle between the optical axis of the droplet and the direction of light propagation, and φ is the azimuthal angle between the director and the polarization plane of the light. Thus, the scattering cross section becomes zero if the ordinary refractive index n_o of the liquid crystal is equal to the refractive index n_p of the polymer and if the droplets are uniformly aligned ($\Theta = 0$) due to an external field. Photochemically induced phase separation [11-13] and photothermal diffusion processes [14,15] can lead to the formation of diffraction gratings and other holograms in PDLC systems. The exposure to high light intensities causes an increase of the amount of polymer, while the liquid crystal molecules diffuse to regions with low light intensity. In contrast to conventional holographic storage materials, the diffraction efficiency of the resulting phase grating can be modulated by applying an electric field.

The present work shows that dual-frequency addressable (DFA) liquid crystals [17] are useful in order to decrease the electrooptic switching times of diffraction gratings formed in a PDLC-system. The sign of the dielectric anisotropy depends on the frequency for these nematic liquid crystals. At low frequencies both the reorientation of the molecules and changes of the electron density contribute to the dielectric constant and thus the parallel orientation of the director with respect to the field results in a higher dielectric constant than perpendicular orientation, i. e. $\epsilon_a := \epsilon_{||} - \epsilon_{\perp} > 0$. However, the rotation of the molecules around their short axis does not contribute to the dielectric constant for frequencies above a critical value f_c, so that ϵ_a becomes negative for $f > f_c$. Thus, it is possible to align or to dissalign the director with respect to an electric field for $f < f_c$ and $f > f_c$, respectively. In both cases, the switching time is faster than the relaxation time for the switching-off process. In order to make use of this advantage, the nematic liquid crystal used in previous studies [14] was replaced by a dual-frequency addressable mixture. Moreover, the grating formation due to photopolymerization is found to be much faster than the thermo-optically induced diffusion process studied previously [14].

EXPERIMENT

The investigated PDLC samples were prepared using the nematic mixture ZLI-2461 from E. Merck (Darmstadt, Germany) and the photocurable polymer precursor NOA-65 (Norland, North Brunswick, NJ, USA). The liquid crystal ZLI-2461 shows the transition temperatures K < - 20°C N 130°C I. The dielectric anisotropy of ZLI-2461 is positive at low frequencies, ϵ_a (100 Hz) $\approx + 2.4$, and negative at high frequencies, ϵ_a (30 kHz) $\approx - 1.84$ [18]. The critical frequency f_c with $\epsilon_a(f_c) = 0$ is about 3.3 kHz. The polymer precursor NOA-65 is a thiol-ene mixture consisting of trimethylolpropane diallyl ether, trimethylolpropane tris thiol, isophorone diisocyanate ester, and a benzophenone photoinitiator [19]. The mixture can be cured using UV radiation. The solubility of ZLI-2461 in NOA-65 is limited to less than 30 wt.-%. The ordinary refractive index of ZLI-2461 at room temperature is $n_o \approx 1.5$ (Fig. 1). This value does not precisely coincide with the refractive index of the polymer, $n_p = 1.52$, but nevertheless a resonable switching contrast and a transmittance of ≈ 70 % at high voltages could be obtained in the PDLC system. In order to study the electrooptic properties of the PDLC, a glass cell with transparent ITO electrodes was filled with the homogeneous mixture of ZLI-2461 and NOA-65 and exposed to UV radiation (type A) from a metal halogen lamp. Exposure with I = 10 mW / cm^2 for five minutes resulted in a heterogeneous, translucent PDLC film.

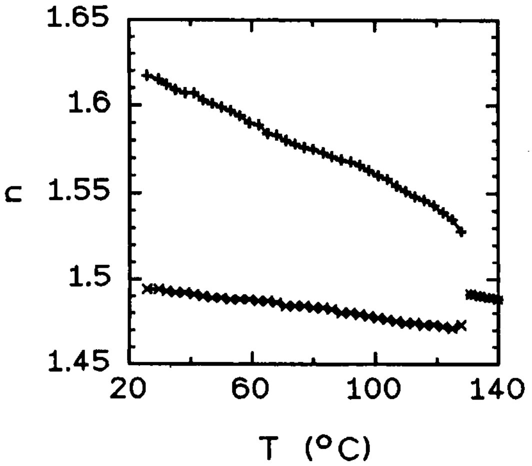

FIGURE 1 Temperature dependence of the refractive indices of the nematic mixture ZLI-2461 (Merck).

Grating structures were generated by exposing the non-cured homogeneous mixture to the interference pattern of two coherent beams from an Ar-ion laser with λ = 514 nm [14]. The two beams can be considered as plane waves. Their propagation direction differs by a small angle $\Theta = 3.3°$. Thus, the interference pattern is an intensity grating with the lattice constant $\Lambda = \lambda / \{2 \sin(\Theta/2)\} \approx 9\ \mu m$ [20]. The lateral intensity profile of each beam is a Gaussian (TEM$_{00}$ mode). The values for the laser power given below correspond to a FWHM value of D = 220 μm of this intensity profile. The reported power values correspond to power per beam. The power was modulated bewteen $P = 0$ and $P = 300$ mW/beam by means of a Pockels cell. Thus, the maximum intensity used in the following experiments was $I \approx 2 P / (\pi D^2) \approx 400$ W / cm^2. In order to initiate the radical photopolymerization in the thiol-ene photo-polymer by visible light, the dye rose bengal (≈ 1 %) and the co-initiator N-phenylglycine (≈ 0.5 %) were added to the mixture of ZLI-2461 and NOA-65 prior to exposure. The same dye and initiator were successfully used in earlier studies for the photopolymerization of a penta-acrylate [12,13].

Dual-frequency addressing was realized by mixing the output of two function generators operating at 100 Hz and 30 kHz, respectively. The two signals were superimposed by means of a differential amplifier. Thus, it is possible either to modulate the low frequency voltage V_{LF} with the high frequency voltage V_{HF}, or to switch between the two frequencies at constant rms-value. For the latter purpose, the two signals were gated by an external trigger source.

RESULTS

Mixtures consisting of 28.6 % (by weight) ZLI-2461 and 71.4 % NOA-65 were cured with UV radiation ($I = 350$ mW in the spectral range 320-400 nm) in order to investigate the electrooptic properties of the system without any light-induced structure. Curing of cells with a thickness of $d = 10$ μm resulted in highly scattering, translucent samples. These samples can be switched to a transparent state by applying a voltage V_{LF} with a frequency $f = 100$ Hz, lower than the critical frequency f_c (Fig. 2). This effect corresponds to the alignment of the director along the field direction since the dielectric anisotropy ϵ_a of the liquid crystal is positive for this frequency. For this uniform alignment, the effective refractive index becomes equal to n_o, independent of the plane of polarization of the transmitted light. Like in normal mode PDLC devices [10], the changes of the refractive index and thus the scattering cross section are minimized since $n_o \approx n_p$. However, when a voltage with a frequency of 30 kHz = f > f_c is applied, the transmittance of the sample becomes even lower than the transmittance in the field-off state. The latter behavior corresponds to the alignment of the director perpendicular to the field since $\epsilon_a < 0$. The increase of the scattering cross section in this case indicates that the difference $n_{e,eff} - n_p$ between the effective extraordinary refractive index and the refractive index of the polymer becomes larger. The electrooptic characterics (Fig. 2) can be significantly modified by modulating the low frequency voltage V_{LF} (f = 100 Hz) with a high frequency signal V_{HF} (f = 30 kHz). The voltage V_{LF} drives the switching to the transparent state while the voltage V_{HF} stabilizes the scattering state. As a result of this competition, both the threshold voltage and the steepness of the curve at the transition increase with increasing amplitude of the high frequency voltage V_{HF}. A similar effect is known to occur in twisted nematic cells containing a dual frequeny addressable liquid crystal, and was extensively studied in the latter systems in order to enhance the multiplexing rate [21].

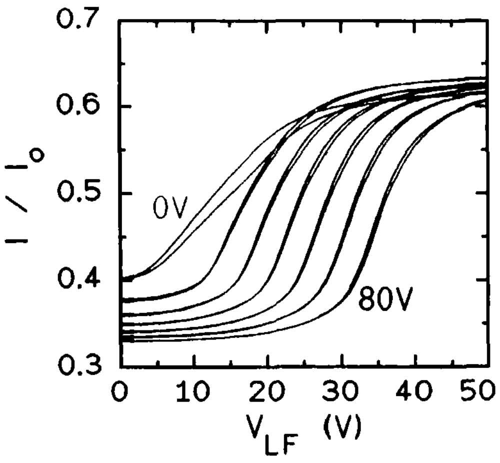

FIGURE 2 Transmittance versus low frequency voltage (rms) for the dual-frequency addressed PDLC without grating structure (sample thickness 10 μm). The applied voltage is modulated by a high frequency signal V_{HF} with constant rms-value of 0 V, 30 V, 40 V, 50 V, 60 V, 70 V, and 80 V, respectively.

The aim of the present study was to use the properties of the dual-frequency liquid crystal in order to enhance the dynamic properties of the electrooptic switching. For this purpose, an ac voltage with constant amplitude was applied to the sample (Fig. 3a) and the frequency of this voltage was switched between f = 100 Hz ($\epsilon_a > 0$) and f = 30 kHz ($\epsilon_a < 0$). As expected, the frequency modulation results in a switching between the translucent and the transparent state of the sample (Fig. 3a). The time constants for both switching processes (from 100 Hz to 30 kHz and from 30 kHz to 100 Hz) decrease with increasing voltage (Fig. 3b). Both switching times can be reduced to a few ms by sufficiently high field strength. The response time for switching to 30 kHz is slightly larger than the response time for switching to 100 Hz. This behavior can be explained by the fact that the absolute value of the dielectric anisotropy ϵ_a is lower for 30 kHz than for 100 Hz, since the torque on the director is proportional to $\epsilon_a E^2$. The solid lines in Fig. 3b are least square fits to the relation $\tau^{-1} = a\ E^2 + b$. The behavior is in agreement with the relation for bipolar droplets with $\epsilon_a > 0$ [22]

$$\tau^{-1} = \gamma^{-1} \left[\epsilon_o\, \epsilon_a\, E^2 + K\,(l^2 - 1) / a^2 \right], \tag{2}$$

where γ is the rotational viscosity (typically $\gamma \approx 0.1$ Pa s), K is an elastic coefficient ($K \approx 5 \cdot 10^{-12}$ N), and l and a are the aspect ratio and the length of the semi-major axis of the elliptical droplets, respectively. In order to compare these results with the dynamics of a conventional PDLC system, the relaxation time τ_{off} was measured which is effective when an applied voltage with f = 100 Hz is switched off. This relaxation time, $\tau_{off} \approx 100$ ms, is almost independent of the applied voltage as expected from equation (2) for E = 0, $l \approx 1.05$ and $a \approx 3\ \mu$m. The relaxation time is much larger than the response time for switching from 100 Hz to 30 kHz. Thus, it is favorable to switch the frequency rather than the amplitude of the voltage in order to achieve a fast induction of the scattering state.

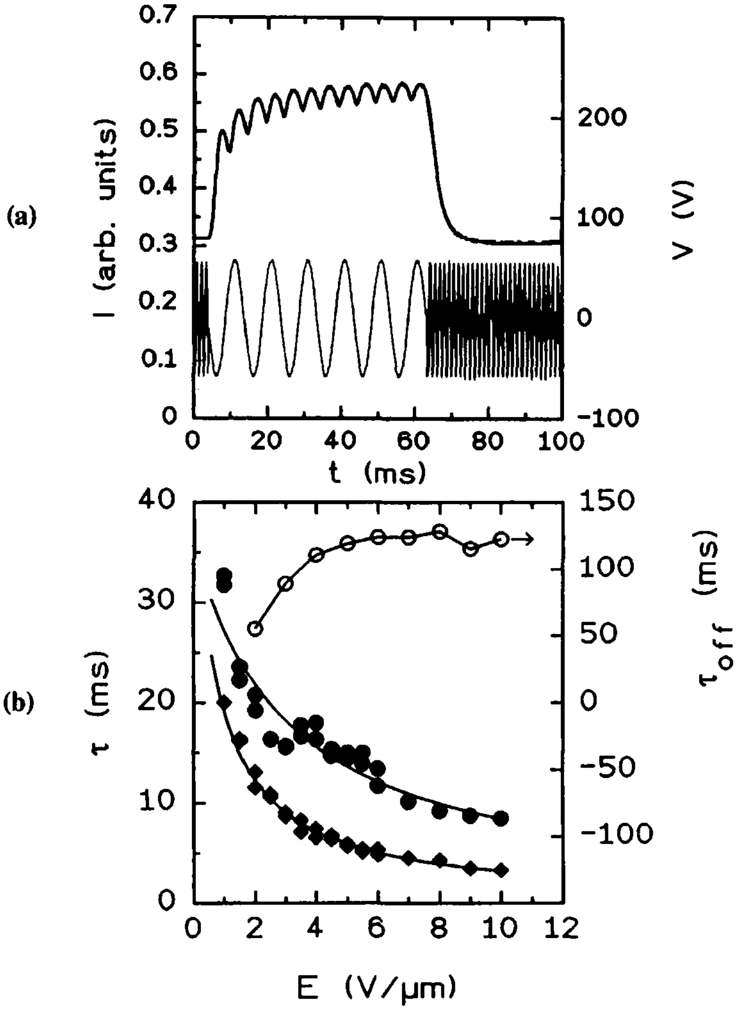

FIGURE 3 (a) Optical response of the non-structured PDLC (top: transmittance without polarizers) due to an applied voltage (below) with constant amplitude and changing frequency of 100 Hz and 30 kHz, respectively. (b) Switching times versus voltage for (●) switching from 100 Hz to 30 kHz at constant amplitude (left scale), (◆) switching from 30 kHz to 100 Hz at constant amplitude (left scale), and (o) switching-off the voltage of 100 Hz (right scale).

In order to make use of these advantages for switchable diffractive optical elements, grating structures were induced in the PDLC using the holographic technique described above. Small amounts of the dye rose bengal (1.0%) and the co-initiator N-phenylglycine (0.5%) were added to a mixture of ZLI 2461 (19.8%) and NOA-65 (78.7%) in order to make the system sensitive to the visible light (λ = 514 nm) emitted from an Ar-ion laser. Cells with a thickness of $d = 4\ \mu m$ or $d = 10\ \mu m$ were filled with the mixture and then exposed to the interference pattern of two coherent laser beams. The photopolymerization occuring at the places with high laser intensity results in the formation of a grating-like variation of the refractive index which can be detected by the diffraction of a probe beam. The dynamics of the grating formation is characterized by a two step mechanism (Fig. 4a). The time constant τ_1 of the fast step is in the ms range (7.6 ms for 50 mW / beam), while the complete curing requires an exposure time τ_2 of the order of several seconds (Fig. 4b). Presumably, the first step corresponds to an initial photochemical or photophysical reaction at positions with high light intensity, while the rate of the slower process is due to diffusion of the reactive monomer molecules to the locations with high intensity. The solid line in Fig. 4b is a least square fit to the function $\tau_2 = a - b \cdot \ln W$. The diffraction properties of the induced grating structure can be characterized by the diffraction efficiency $\eta = I_1 / I_\Sigma$ which is given by the ratio of the intensity I_1 of the first order diffraction spot and the intensity I_Σ of the incident beam. The diffraction efficiency η_1 which is reached after 50 ms due to the fast process increases linearly with the laser intensity which was used to induced the grating (Fig. 4c). However, the diffraction efficiency η_2 of the final grating structure is nearly independent of the laser intensity, $\eta_2 \approx 0.5$ % for $d = 4\ \mu m$. For thicker samples, diffraction efficiencies of several % were obtained. A spatial modulation of the refractive index by $\delta n \leq 0.01$ can be estimated from the relation $\eta = (\pi\ \delta n\ d\ /\ \lambda)^2$ [20].

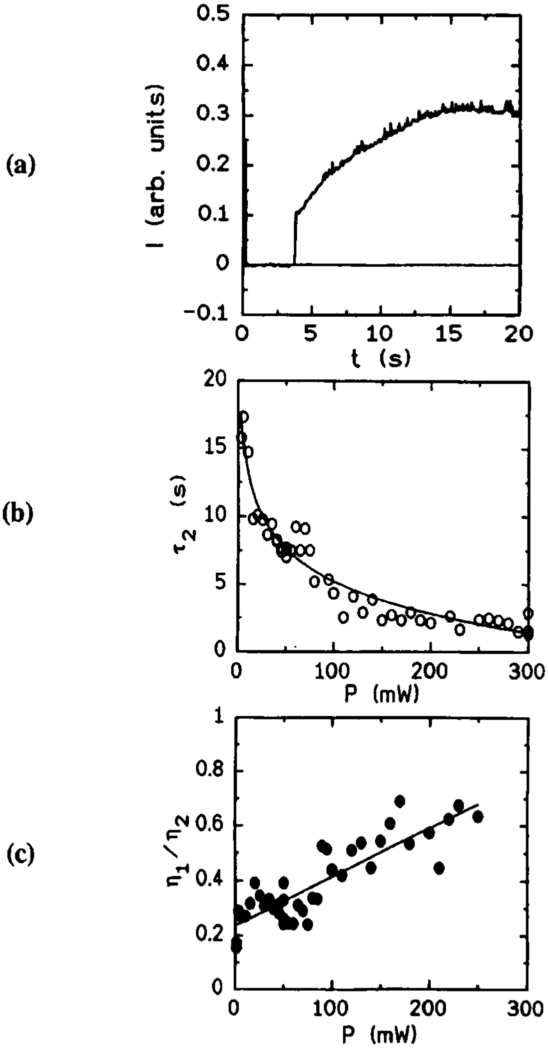

FIGURE 4 Characteristics of the grating formation due to exposure of the non-cured sample to a holographically generated optical intensity grating. (a) Intensity of the first order diffraction spot versus time (40 mW/beam). (b) Time constant τ_2 of the complete grating formation. (c) Ratio of the diffraction efficiencies η_1 (obtained after exposure for 50 ms) and η_2 (obtained after finishing the curing process) versus laser power per beam.

The diffraction efficiency of the induced grating structure can be modulated by applying an electric field. An applied voltage with f = 30 kHz stabilizes the diffracting state (since $\epsilon_a < 0$) and leads to a slight increase of the diffraction efficiency. However, a sufficiently high voltage with f = 100 Hz which corresponds to $\epsilon_a > 0$ turns the sample to a transparent state with very low variation of the refractive index and thus low diffraction efficiency. When the same addressing scheme as presented in Fig. 3a is used, the 100 Hz voltage leads to a large value of the transmitted intensity I_0 and low intensities I_1, I_2 of the diffraction spots, while the 30 kHz voltage causes a low intensity I_0 of the transmitted light and large intensities I_1, I_2 of the diffraction spots of higher order (Fig. 5). The change of the intensities due to the frequency switching increases with increasing rms value of the applied voltage (Fig. 6a). Saturation occurs at $E_{rms} \approx 50$ V / 4 μm. The electrooptic

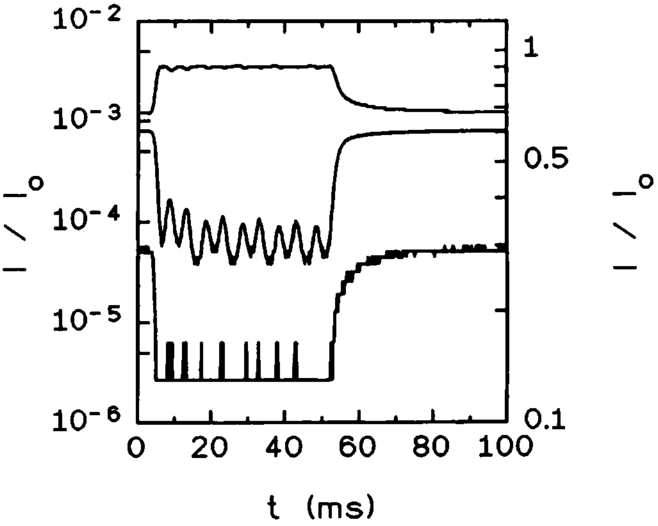

FIGURE 5 Optical response of the diffraction spots due to a frequency modulated voltage as presented in Fig. 3 (a). Top: zero order diffraction spot (right scale), center: first order diffraction spot (left scale), bottom: second order diffraction spot (left scale).

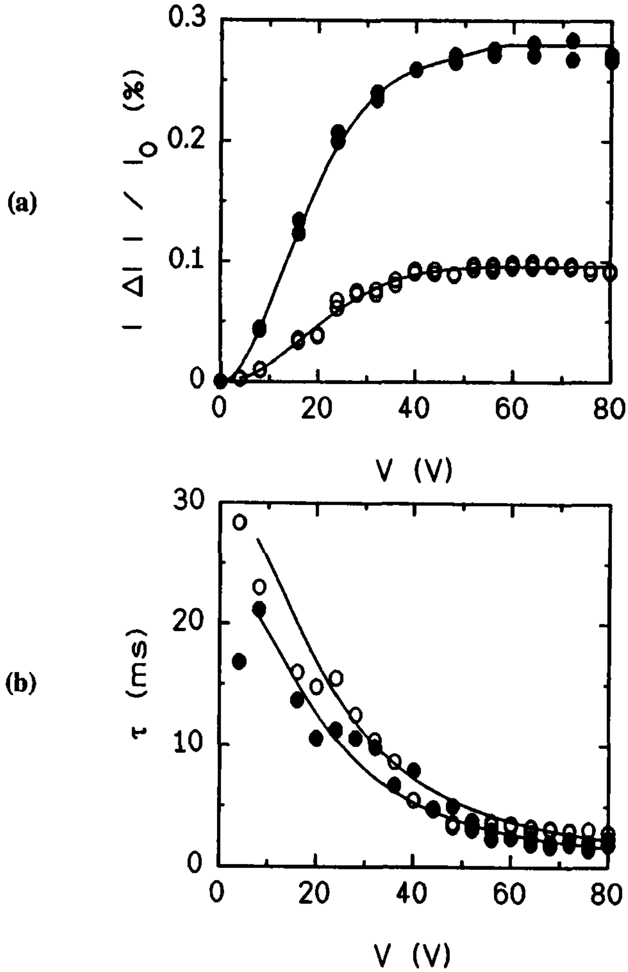

FIGURE 6 Electro-optical response of the diffraction efficiency versus rms-voltage (sample thickness d = 4 μm). (a) Normalized change of the intensity for (●) the zero order and (o) first order diffraction spot due to switching the frequency between 100 Hz and 30 kHz at constant amplitude. (b) Response time for (●) switching from 100 Hz to 30 kHz and (o) from 30 kHz to 100 Hz at constant amplitude.

switching times of the diffraction efficiency (Fig. 6b) are a few ms for both switching from 100 Hz to 30 hHz and from 30 kHz to 100 Hz, respectively. This behavior is in agreement with the switching times which were observed in the non-structured PDLC films (Fig. 3b). Again, these switching processes are much faster than the relaxation occuring when the voltage is switched off. The latter is characterized by a time constant of ≈ 100 ms. Thus, switching between two frequencies $f_1 < f_c$ and $f_2 > f_c$ provides faster electro-optic response than switching a low frequency voltage on and off.

POSSIBLE APPLICATIONS OF NEMATIC PDLC GRATINGS

The suitability of PDLC materials for diffractive beam deflectors and holographic storage materials has been pointed out in previous works [11-14]. Additional possibilities for application are demonstrated in Fig. 7. The dispersion of white light due to diffraction at a PDLC grating (Fig. 7a) can be used to develop a monochromator where the grating can be electrically addressed in order to modulate the intensity of the diffracted light. Fig. 7b shows that not only the refractive index but also the shape of the sample surface can be spatially modulated. For the latter purpose, the glass-forming nematic liquid crystal mixture Mi5b [8] was dispersed in the thermoplastic polymer poly-(vinyl-butyral), PVB. A thin film consisting of 53.5 % Mi5b, 44.5 % PVB and 2.0 % of the anthrachinone dye D-37 (BDH) was cast on a glass substrate and the free surface was exposed to the interference pattern of two coherent Ar-ion laser beams (λ = 514 nm, P = 50 mW / beam). The subsequent investigation of the surface in a Michelson interferometer (Fig. 7b) indicates a modulation of the surface by about 0.1 μm for a film thickness of 40 μm. This behavior can be attributed to a photo-thermally induced phase separation of the two components and subsequent surface modulation due to the different thermal expansion coefficients. A more detailed investigation of this effect is in progress.

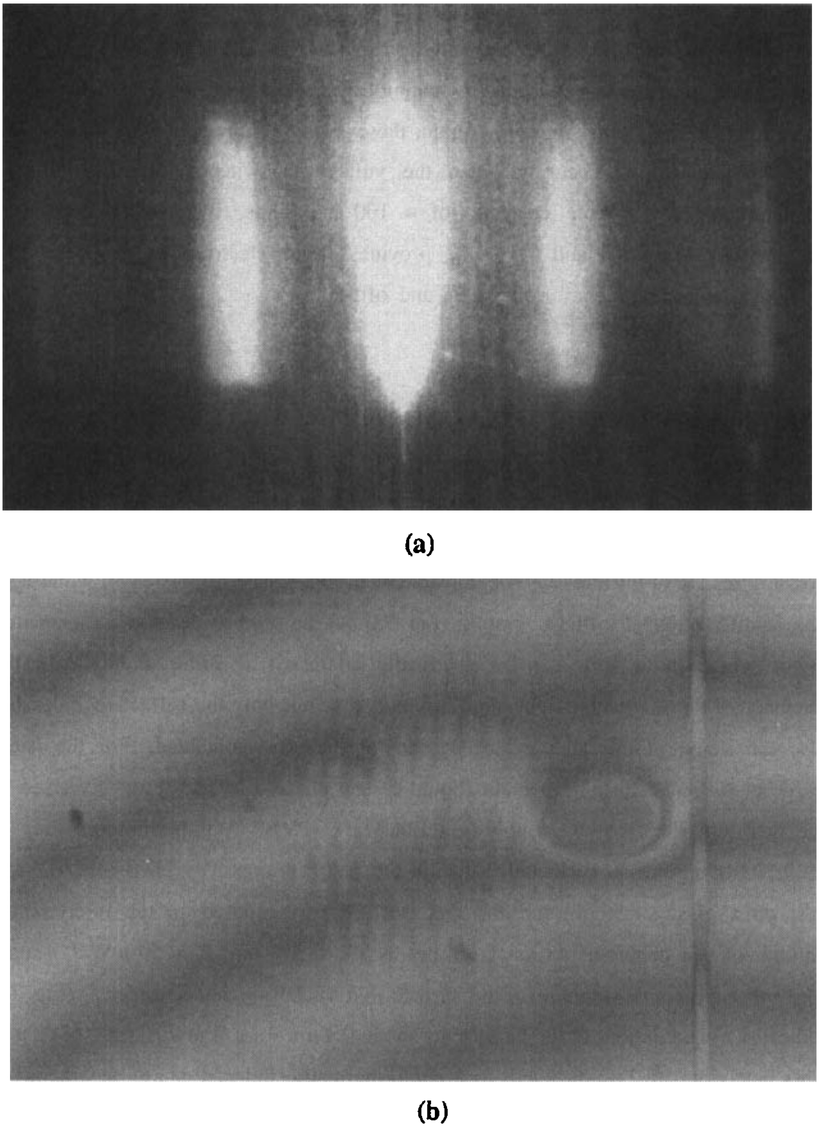

FIGURE 7 Possible applications of PDLC gratings. (a) Dispersion of white light using a nematic PDLC grating. (b) Michelson interferogram indicating the surface modulation of a PDLC grating with one free surface.
(See Color Plate I).

CONCLUSIONS

The present investigation has shown that the photopolymerization of the thiol-ene polymer precursor NOA-65 can be initiated by visible light using a suitable dye / initiator combination. The holographic grating formation due to photopolymerization is much faster (time constant of a few s) than the grating formation due to photo-thermally induced phase separation (time constant of a few minutes [14]). Dual- frequency addressing of a nematic liquid crystal makes it possible to increase and to decrease the diffraction efficiency of the resulting grating structure with time constants as low as a few ms, thereby avoiding the rather slow relaxation ($\tau_{\rm off} \approx 100$ ms) which occurs for the switching-off process. In principle, electro-optic response times even lower than 1 ms can be expected if the lattice parameter of the grating is in the sub-μm range. Moreover, the diffraction efficiencies can be enhanced by increasing the sample thickness and adjusting the refractive indices of the liquid crystal and the polymer more carefully. The optical writing energy of ≈ 100 J / cm^2 which is required to store optical information in the investigated PDLC system is much larger than the writing energy of typically 0.1 J / cm^2 which is required for optical storage in azo-polymers [5] and filled nematics [23], and larger than the writing energy of ≈ 10 J / cm^2 reported for glass-forming low-molar mass liquid crystals [8]. Nevertheless, the unique opportunity to modulate the generated optical pattern due to electric addressing makes the application of PDLC systems for holographic storage, beam deflectors, switchable dispersive gratings or other diffractive optical elements very interesting.

Acknowledgements

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