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Preliminary communication

Optical storage effect in a discotic columnar liquid crystal

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Exposing a uniformly aligned discotic columnar liquid crystal to an argon ion laser beam results in a reorientation, thereby changing the optical properties of the liquid crystal. We have studied this new optical storage effect for a polymer dispersed metallomesogenic compound which exhibits a columnar phase at room temperature. The writing energy is $\approx 3{\cdot}5\,\mathrm{J\,cm^{-2}}$. The stored information can be erased by heating and subsequent shearing of the sample.

Mesophases are very suitable for photo-induced changes of the optical properties since their turbidity and birefringence depend strongly on alignment and order parameter. Thus, optical storage effects using liquid crystals have been extensively studied during the last 25 years. Among the first reported memory effects in liquid crystals was a laser-addressed smectic display where a thermo-optical effect leads to the transition from a uniform homeotropic, transparent state to a disordered, scattering state [1, 2]. In order to achieve long-term stability of the stored information, materials with a glass-like state have found special interest, e.g. polymers [3–8] and some low molar mass liquid crystals which form a glass-like condition [9–12]. Among the latter materials are metallomesogenic compounds [12]. Low molar mass liquid crystals with fine dispersed particles [13] and polymer dispersed liquid crystals [14, 15] are also suitable for photo-addressed storage. In these different systems, the respective photo-induced change of the optical properties may originate from a variety of effects, e.g. photothermal non-linearities [1–5, 9–11], photochemically induced reorientation [6–8], photopolymerization [14] or phase separation [15].

The present paper describes the results of investigations on a non-chiral, hexagonal columnar phase $\mathrm{Col_h}$; this phase consists of disk-like molecules. In addition to a preferred parallel alignment, the molecules are stacked into columns which in turn are arranged in a two-dimensional hexagonal lattice (figure 1). The electro-optical properties of columnar liquid crystals have found recent interest because tilted chiral columnar phases show ferroelectric behaviour [16]. Recently, an optical storage effect due to realignment of the optical axis was found in a polymer dispersed liquid crystal (PDLC) containing this chiral tilted columnar phase [17]. However, neither the chirality nor the tilt of the director with respect to the column axis seemed to be a precondition for the storage effect. Thus, we have studied the same effect for a non-chiral, non-tilted columnar liquid crystal. The material investigated is particularly useful because it shows the columnar phase at room temperature; also it absorbs green light, thereby making optical addressing by an argon laser beam possible.

The investigated liquid crystal material is the dibenzotetraaza [14] annulene nickel complex consisting of the disc-like molecules represented in figure 1. On heating, the phase sequence Cr -12°C $\mathrm{Col_h}$ 260·1°C I is shown. The synthesis and the mesomorphic properties of this compound have been described earlier [18–20]. We have studied the pure liquid crystal and a mixture consisting of 33 wt % of the liquid crystal and 67 wt % of poly(vinylbutyral) (from Aldrich). For the latter purpose, both compounds were dissolved in chloroform to obtain a homogeneous solution. The solution was cast on an ITO coated glass substrate and the solvent allowed to evaporate before covering the sample with a second ITO coated glass slide and heating under gentle pressure. The sample thickness was controlled by glass spacers to give a uniform thickness of 11 μm. A uniform planar alignment of the liquid crystal was achieved by shearing the two cover slides with respect to each other at a temperature of 114°C.

Optical studies were performed on the samples at room temperature. The thin films were exposed to the

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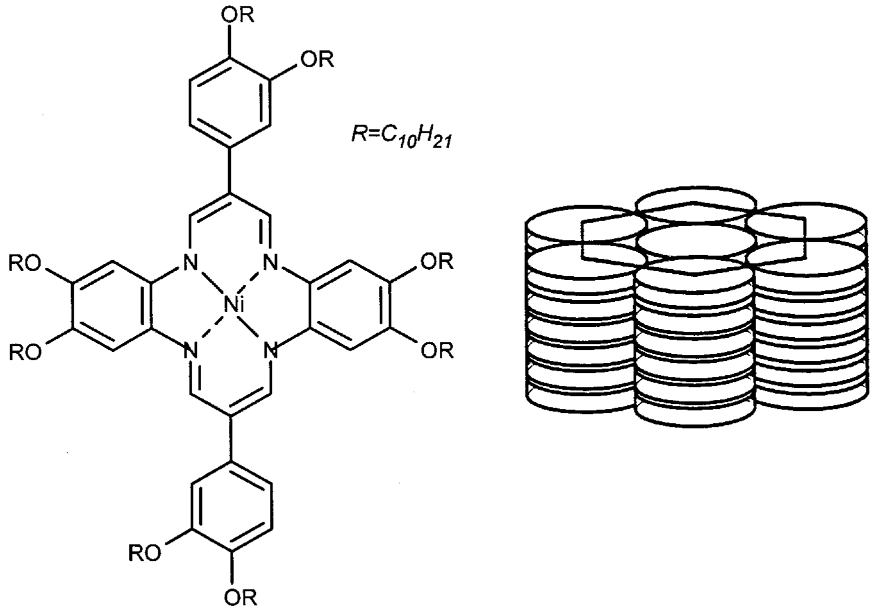


Figure 1. Chemical structure of the investigated liquid crystal and a schematic presentation of its molecular arrangement in the columnar phase.

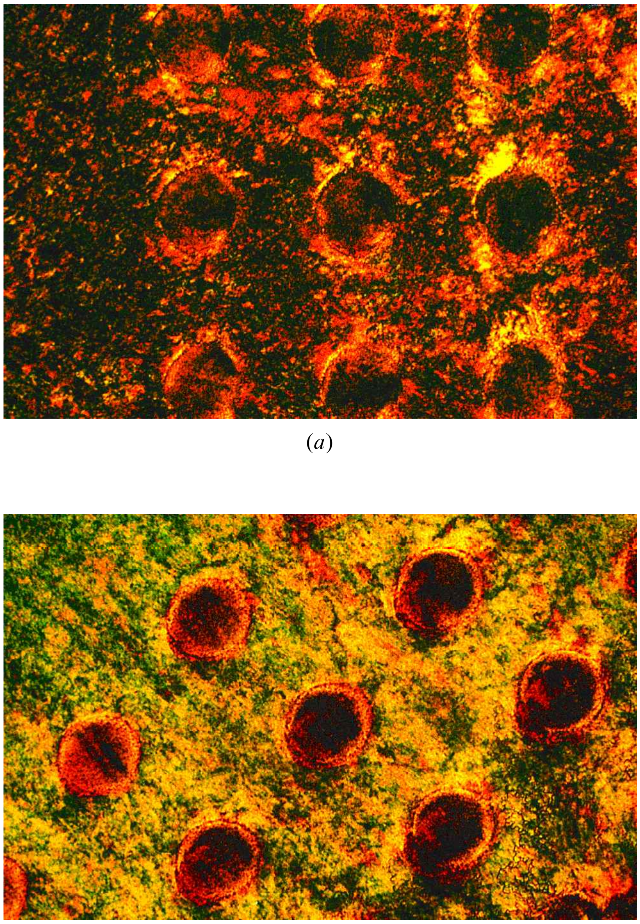
monochromatic beam ($\lambda=514\,\mathrm{nm}$) of an Ar ion laser (Innova, Coherent) which was modulated by a Pockels cell. The laser operates in the TEM$_{00}$ mode, i.e. the transverse intensity distribution of the laser beam is Gaussian. By focusing the laser beam, its full width at half maximum intensity at the position of the sample was varied between $d=50$ μm and $d=100$ μm. All quantitative data given below correspond to a beam diameter $d=91$ μm. The maximum laser power used in the experiments was 200 mW.

Both the pure liquid crystal and PDLC showed no birefringence when viewed in the polarizing microscope before the shearing process, indicating that the initial orientation was homeotropic, i.e. the director and thus the optical axis were aligned perpendicular to the substrate. However, a uniform birefringent texture could be induced by sliding the two glass substrates with respect to each other at high temperature. Due to the high viscosity, shearing of the pure liquid crystal led to separation of the liquid crystal from the glass surface and thus to a very inhomogeneous sample. However, shearing of the polymer-containing sample at 114°C resulted in a very uniform, transparent birefringent sample.

Dark spots (figure 2) could be induced in the samples by exposure to the laser beam at sufficiently high intensity. These spots appeared dark between crossed polarizers, independently of the azimuthal orientation of the sample with respect to the polarizers (figure 2). This observation indicates that the optical axis is perpendicular to the substrate; we conclude that the liquid crystal was reoriented to its initial homeotropic alignment. This effect could be observed for both the pure liquid crystal and the PDLC, however, due to their better homogeneity we report here only on the polymer-containing samples. In this case, the reorientation leads not only to the loss of birefringence, but also to a higher turbidity of the illuminated spot. Thus, the spots can also be seen without polarizers.

The photo-induced change of the samples is characterized by two thresholds. For a beam diameter of $d=91$ μm, no change of the sample was observed for laser powers up to 50 mW. Below 90 mW, only a slight change of the birefringence could be detected. Only for a laser power $P \geqslant 90\,\mathrm{mW}$ did the complete change (figure 2) appear. Finally, for $P > 180\,\mathrm{mW}$ decomposition of the sample occured. In order to study the dynamics of the photo-induced reorientation, we measured the intensity of light transmitted by the sample when the laser beam is switched on. The increase in intensity due to rising intensity of the incident light is followed by a decay which can be attributed to the reorientation [figure 3 (*a*)]. Above the threshold of 90 mW, the time constant is of the order 10 ms; below this threshold only a very slow process (with time constants above 1 s) was observed [figure 3 (*b*)]. The time constants τ given in figure 3 (*b*) are defined by the time required for the final intensity to approach 90%. The solid line given for the very slow process is a fit corresponding to $\ln(\tau) \propto P$ and may serve as a guide to the eye. For the fast process occurring at $P \geqslant 90\,\mathrm{mW}$, the solid line is a least square fit of $\ln(\tau) = a \times \ln(P) + b$ to the data, with $a = -1{\cdot}96$. Thus, the dependence of the time constant on the laser power is approximately described by the relation $1/\tau \propto P^2$.

To summarize, we have observed an optical storage effect in a polymer dispersed non-chiral columnar liquid

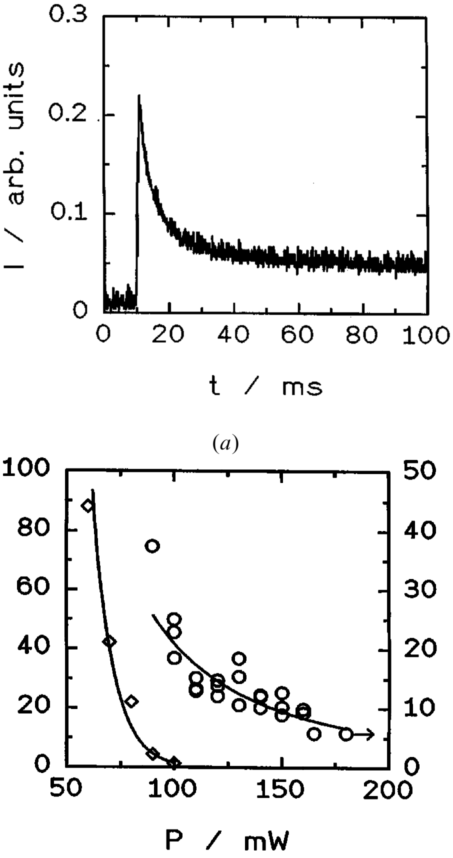


(*a*)

(*b*)

(*c*)

Figure 2. Photographs of a sheared sample observed by polarizing microscopy. The dark spots with a diameter $d \approx 90\ \mu m$ are generated by the Ar ion laser beam. (*a*) Crossed polarizers, parallel and perpendicular to the shearing direction; (*b*) polarizer and analyser oriented at 45° and 135° with respect to the shearing direction, respectively; (*c*) test image consisting of 256 × 256 pixels, generated by a laser beam with $P=130\,\mathrm{mW}$.



(*a*)

(*b*)

Figure 3. (*a*) Time dependence of the transmitted light intensity when the laser beam with $P=130\,\mathrm{mW}$ is switched on at $t=10\,\mathrm{ms}$. (*b*) Influence of the laser power on the time constant τ of the photo-induced change of the transmittance: diamonds correspond to the left vertical scale (unit: s), circles to the right vertical scale (unit: ms).

crystal. Suitable modulation of the laser intensity can be used for digital storage [figure 2 (*c*)]. The optical contrast originates from two sources, a loss of birefringence and an increase of the turbidity. The loss of birefringence can be explained by a reorientation of the liquid crystal from a planar to a homeotropic alignment with respect to the substrates. This effect should be expected only for the pure liquid crystal. However, studies by electron microscopy on a very similar system [17] have indicated an inverse morphology of the PDLC, i.e. the sample contains islands of the polymer floating in the liquid crystal rather than separated liquid crystal droplets embedded in the polymer. Thus, we expect that the alignment induced by the substrates still has a considerable influence on the director orientation in the entire sample. The second effect, the increase of the turbidity at the illuminated spots, can be attributed to refractive index matching and mismatching between liquid crystal and polymer. Columnar liquid crystals exhibit a negative birefringence, i.e. $n_o > n_e$. The ordinary refractive index n_o is typically much larger than the refractive index of poly(vinylbutyral) ($n_p \approx 1{\cdot}49$ at 25°C), which we used as a polymer matrix. To give typical values for a discotic mesogen: $n_o \approx 1{\cdot}68$ and $n_e \approx 1{\cdot}49$ were measured for the nematic discotic phase of hexakis [(4-octylphenyl)-ethynyl]benzene [21]. Since the effective refractive index for planar alignment is an average value between n_o and n_e, we expect this value to be closer to n_p than the ordinary refractive index, which is effective for homeotropic alignment. The mismatching between n_o and n_p may explain the turbidity occurring in the illuminated areas.

An intensity of $I = P/(\pi d^2) \approx 350\,\mathrm{W\,cm^{-2}}$ is necessary to achieve good optical contrast. The time constant for the photo-induced change is of the order 10 ms. Thus, the writing energy per area is about $3{\cdot}5\,\mathrm{J\ cm^{-2}}$. For glassy low molar mass liquid crystals [10], a writing intensity of several hundreds of $\mathrm{W\,cm^{-2}}$ and a writing energy of $1\,\mathrm{J\,cm^{-2}}$ have been reported [10], which is quite similar to our results. In comparison, the photo-isomerization of azo polymers [7] requires much lower intensity, $\approx 10\,\mathrm{mW\,cm^{-2}}$, but the writing time for the latter materials may be from some seconds to some tens of seconds. However, for filled nematics [13], response times below 1 μs and a writing energy of $0{\cdot}1\,\mathrm{J\,cm^{-2}}$ have been reported [13]. Nevertheless, columnar liquid crystals can be considered as promising candidates for optical storage materials. Their properties may be enhanced by more careful adjustment between the wavelength of maximum absorbance and the laser wavelength, by choosing materials with a lower clearing point, etc. More detailed investigations on the mechanism of the photo-induced change, the influence of the temperature on pixel formation, the grey scale capability and the morphology of the samples are in progress.

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