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Modification of the twist angle in chiral nematic polymer films by photoisomerization of the chiral dopant

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A method for the production of polarization sensitive recordings in liquid crystalline polymers is presented. The system is based on local modification of the twist angle of chiral nematic polymer films. The twist angle of the polymer film is varied by modifying the chemical structure of the chiral dopant. Here a photoisomerizable menthone derivative is used that has a fivefold difference in helical twisting power between the *E* and the *Z* isomer. The twist angle of the film can be varied between $-90°$ and $0°$ by introducing a nonphotosensitive chiral dopant with opposite twisting sense. Complex pictures with gray scales can be recorded in the films with black and white contrasts higher than 20. © *1999 American Institute of Physics.* [S0021-8979(99)05011-2]

I. INTRODUCTION

The control of the molecular orientation in liquid crystal phases by light has been extensively investigated. Local control of the orientation of liquid crystals offers new possibilities in the preparation of optical components. For example, potential applications are patterned polarization rotators for stereoscopic displays, optical data storage, polarization sensitive gratings or polarization sensitive recordings, and holograms for copy protection.[1–7] More recently, much attention is given towards local control of the alignment of liquid crystals in multidomain liquid crystal displays for the improvement of the viewing angle.[8–10]

In general, the liquid crystal (LC) orientation can be influenced via modification of the bulk LC orientation or, indirectly, via modification of the alignment layer. Modification of the transmission of liquid crystal layers between crossed polarizers via directly influencing the bulk orientation of liquid crystals has been shown to be possible using polarized light illumination of LC layers containing dyes.[3–5] The dye has to be anisotropic and photoisomerizable. Due to the absorption of light, the dye undergoes repeated trans to cis and cis to trans isomerizations.[5] During this process, the dye and the liquid crystals tend to reorient in a direction perpendicular to the polarization direction of the light.

Here we report a method for writing information in liquid crystalline polymer films. The method is based on the photochemical manipulation of the helical twisting power of chiral dopants in nematic liquid crystalline polymers. Opposed to the reorientation of anisotropic dyes, unpolarized light can be used and the dyes do not have to be liquid crystalline. Because the system is based on the modification of the structure of molecules, the patterns will be more suitable for hosts with low viscosities than the systems that are based on changing the orientation of molecules. It was previously shown that the helical twisting power of the photoisomerizable chiral menthone derivatives (referred to as NRM) strongly depends on the E/Z ratio.[11,12] The host chosen for the experiments is a nematic liquid crystalline polymer described by Portugall *et al.*[13] The structural formulas of the compounds are shown in Fig. 1.

II. EXPERIMENT

A. Materials

R811 was supplied by Merck (Poole, GB). (*E*)-(1*R*,4*R*) - 2 - (4 - (4 - hexyloxybenzoyloxy) phenyl - methene) menthan-3-on (NRM) and poly[4(6-acryloyloxyhexyloxy) benzoyloxy)benzonitrile] (polyCN) were synthesized according to previously published procedures.[8,10] The melting point of NRM was 96°. The molecular weight (M_n) of polyCN was 6100 g/mol and the polydispersity was 1.4 (relative to

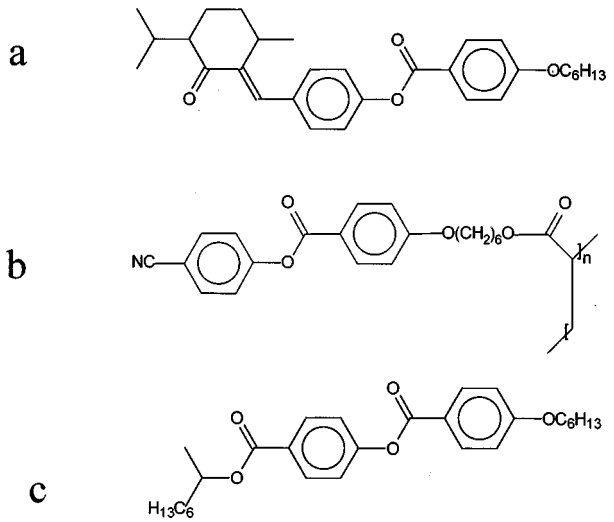

FIG. 1. Structural formulas: (a) NRM, (b) polyCN, (c) R811.

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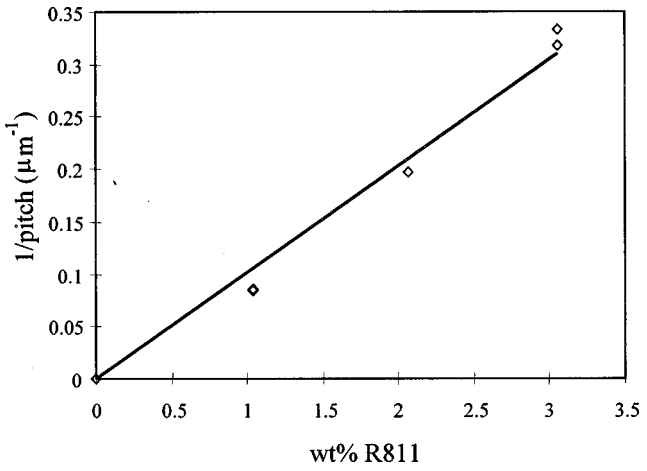

FIG. 2. Reciprocal pitch of R811 in polyCN as a function of concentration (each concentration two samples).

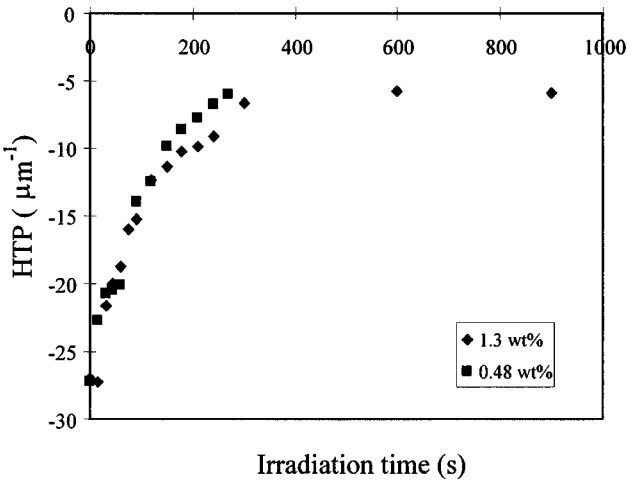

FIG. 3. Helical twisting power of NRM in polyCN as a function of irradiation time for two concentrations of NRM.

polystyrene standards). PolyCN showed a glass transition at 23 °C and a nematic to isotropic phase transition at 113 °C.

B. Methods

Polymer solutions in tetrahydrofuran were spincoated on glass substrates provided with rubbed polyimid alignment layers (AL1051, JSR, Japan). To produce well-aligned polymer films, the samples were equilibrated at 90 °C for 5 min. The thickness of the layers was determined using a Tencor alpha-step 200 profilemeter. Irradiation experiments were performed using a Karl Suss, MA6 irradiator containing a HgXe light source (wave length: 365 nm, intensity: 7 mW/cm^2). After irradiation, the samples were again equilibrated for 5 min at 90 °C.

Twist angles of the films were determined from the transmission of a HeNe laser through the twisted liquid crystal polymer film between two polarizers as a function of the azimuthal orientation of the retarder. An expression for the light transmission of a twisted liquid crystal layer as a function of the various optical parameters is given in the following equation:[14]

$$T=\left[\cos\beta\cos(\phi+\theta-\gamma)+\frac{\sin\beta}{\sqrt{1+\alpha^2}}\sin(\phi+\theta-\gamma)\right]^2 + \left(\frac{\alpha^2}{1+\alpha^2}\right)\sin^2\beta\cos^2(\phi-\theta-\gamma), \quad (1)$$

where

$$\alpha=\left(\frac{\Delta n d}{\phi\lambda}\right)\pi, \quad \beta=\phi\sqrt{1+\alpha^2}.$$

In this formula: T = transmission, ϕ = angle exit director minus angle input director (twist angle), d = thickness of the LC layer, Δn = birefringence, θ = angle polarizer minus angle input director, γ = angle analyzer minus angle input director, λ = wavelength. It can be derived that the transmission of a twisted retarder is at a maximum when the bisector of the angle between the director at the polyimid layer and the director at the air interface equals the bisector of the angle between the transmission axes of the two polarizers. Because the orientation of the director at the polyimide layer is determined by the rubbing direction, the twist angle can be determined easily.

The dispersion of the birefringence of polyCN is an important parameter. Using a spectrophotometer (Unicam 8700 UV/VIS spectrophotometer), the transmission as a function of wavelength of a uniaxially oriented polyCN films between crossed polarizers was measured. The birefringence could be calculated from the transmission using Eq. (1).

III. RESULTS AND DISCUSSION

Homogeneously aligned polymer films with uniform thickness up to 5 μm could be obtained by varying the conditions of the spincoating process. Directly after spinning the samples were amorphous. Good alignment was obtained after equilibration at temperatures above the glass transition. Twisted retarders could be obtained by adding a small amount of chiral dopant to the polymer. For the experiments described below the twist angles were smaller than 300°.

The twist angle (ϕ) is related to the pitch (P) and the thickness (d) via the relation: $P=360.d/\phi$. Figure 2 shows the expected linear relation between the reciprocal of the pitch of R811 in polyCN and the concentration. The helical twisting power (HTP) of the chiral dopant can be calculated from the pitch and the concentration (c in wt %) using the relation HTP$=100/(P.c)$. The average HTP of R811 was 9.5 μm^{-1}.

The HTP of NRM is dependent on the ultraviolet (UV) dose (Fig. 3). Without UV exposure, the HTP is -27 μm^{-1}. This value is somewhat higher than found previously in low molecular weight liquid crystal mixtures.[11,12] After UV irradiation and subsequent annealing, the properties of the films are different. The HTP of NRM decreases during UV exposure. Equilibrium is obtained after a UV dose of approximately 3 J/cm^2 (400 s exposure). Because the irradiation with 365 nm is relatively far from the absorption maximum of NRM (280 nm), it is expected that the required dose can be strongly reduced by reducing the wavelength for irradiation.

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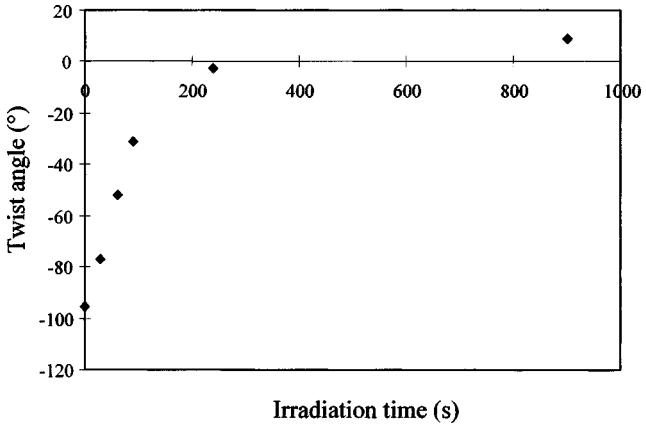

FIG. 4. Twist angle for a 2.5 μm thick film as a function of irradiation time. The composition is 0.292 wt % R811, 0.494 wt % NRM in polyCN.

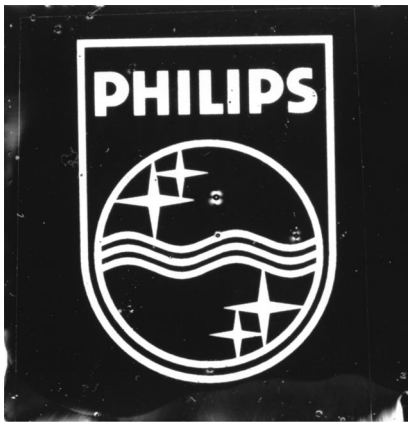

FIG. 6. Patterned LC layer between crossed polarizers. Philips logo.

No significant differences in trends between the two concentrations of NRM in polyCN can be observed. It has been previously shown that under these irradiation conditions the photostationary state of the irradiated product contains mainly the *Z* isomer.[11] This implies that the HTP of the *Z* isomer is at least five times lower than the HTP of the *E* isomer.

From these experiments, it is clear that for this system local modification of the twist angle by patternwise exposure to UV light is possible. Between crossed polarizers these variations in twist angle will show up as variations in light transmission. For patterns, a maximum contrast in light transmission between the exposed and the nonexposed area of the film between crossed polarizers is desired. In addition, the wavelength dependency of the transmission should be minimal. The light transmission of twisted retarders as a function of twist angle, wave length and retardation can be calculated from Eq. (1). It can be derived that, in order to obtain maximum transmission of green light (550 nm) for a twist angle of 90°, a retardation of 476 nm is required. From the transmission spectrum of nontwisted retarders, the birefringence of polyCN was calculated to be $\Delta n = 0.150$ $+ 120000/\lambda^2$. Using these values, the optimum layer thickness can be estimated to be 2.5 μm.

For a black state, a nontwisted retarder is required with its optic axis parallel or perpendicular to the polarizer axis. From Fig. 3 it is clear that after irradiation the twisting power of the *Z* isomer of the menthone derivative is not zero. Addition of a nonphotosensitive chiral dopant with opposite twisting sense is required to compensate the residual twisting power. R811 was used for this purpose.

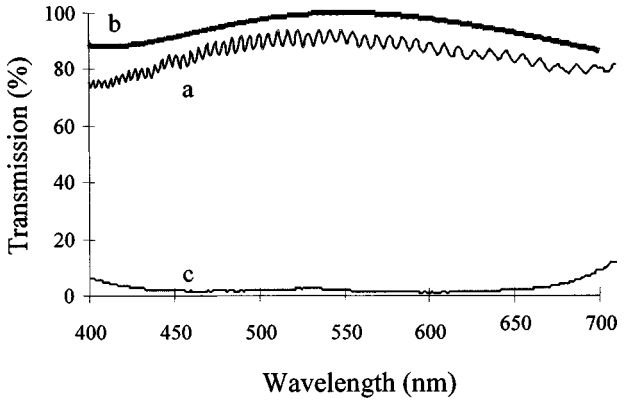

FIG. 5. Transmission as a function of wavelength of the polymer films between crossed polarizers: (a) measured transmission for an unexposed polymer sample, (b) calculated transmission for a sample with 90° twist, (c) measured transmission for a sample exposed for 900 s. (The calculated transmission for a sample with 0° twist angle is zero for all wavelengths.)

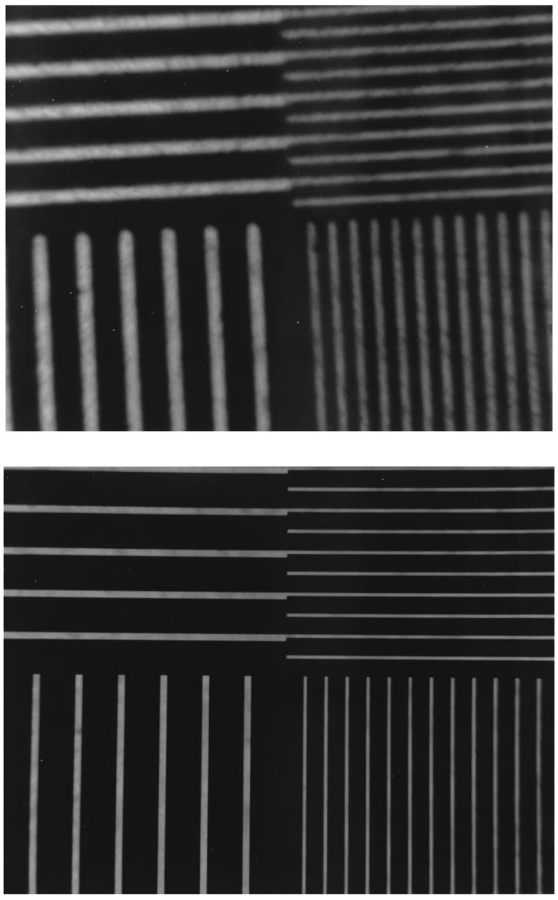

FIG. 7. Patterns obtained with a striped mask. (a) Patterned LC layer between crossed polarizers. (b) Micrograph of the original line mask. Sizes of the lines 30 and 15 μm.

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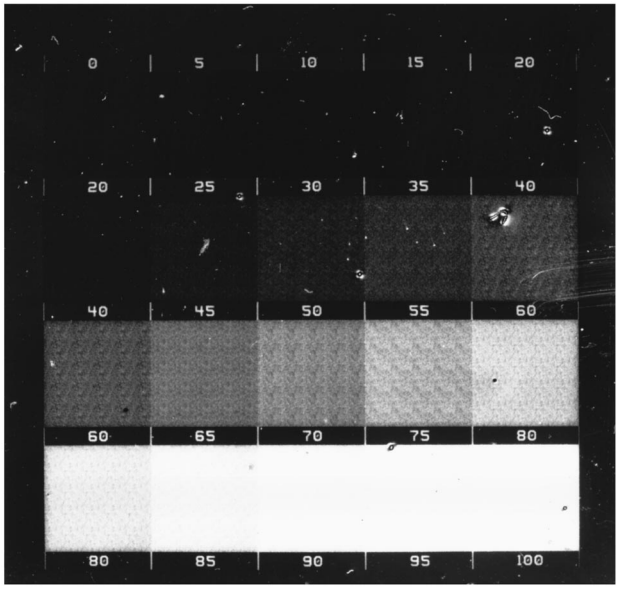

FIG. 8. Gray scale patterns recorded in LC films. The light intensities were varied using a chromium-patterned mask. The percentage below each square indicates the fraction of the mask area that is transmissive for UV light. The UV transmission of the squares varied between 0% and 100%. The total UV exposure was 900 s.

In Fig. 4, the measured twist angles in a 2.5 μm thick film obtained with a mixture of 0.292 wt % R811 and 0.494 wt % NRM in polyCN are shown. The twist angle before irradiation is close to the desired 90°, while after 300 s of irradiation, the twist angle is close to zero. In order to decrease the twist angle for long-term irradiation, the dopant concentrations were slightly modified to 0.274 wt % R811 and 0.635 wt % NRM. Using this dopant composition, the twist angle of a 2.5 μm thick layer was $-80°$ before illumination and $+5°$ after 900 s of irradiation. This composition was used for making patterned films. The transmission as a function of wavelength for both the unexposed sample and the sample exposed to UV light for 900 s were measured using a spectrophotometer. The results are shown in Fig. 5.

The transmission as a function of wavelength for the unexposed sample is high and is close to the calculated value for 90° twist angles. The dependence of the transmission on the wavelength is small. This indicates that the color of the unexposed areas of the samples between crossed polarizers will be close to white. The transmission of the black state is low as expected. The contrast of the samples between crossed polarizers is higher than 20.

Structured films could be easily obtained using masks. For example, in Fig. 6, the Philips logo is shown. The boundaries of the recorded structures are sharp. In Fig. 7, a mask with small stripes is reproduced in the layer. The lines are well reproduced in the layers. However, some broadening of the lines can be observed. This broadening can be either due to diffraction of UV light at the edges of the mask or to diffusion of the dopants during equilibration of the sample. Better equipment for illumination can minimize the first effect. The latter effect can be minimized by incorporation of the dopants in the polymer chain.[12] It is expected that micrometer resolution is possible. The LC films patterned with thin lines could be used to diffract laser light (results not shown). A second application is polarization encoded stereoscopic displays.[1,2]

(a)

(b)

FIG. 9. Reproduction of a negative of a photograph: (a) crossed polarizers, (b) parallel polarizers. UV exposure: 450 s.

Gray scale production is possible by using intermediate exposure times. In Fig. 8, micrographs are shown of an LC layer exposed to different light intensities. It is clear that the UV dose can be used to determine the transmission of the LC layer between crossed polarizers. The UV exposure of the sample was too long to obtain intensity differences between the darker gray scales. The fact that UV dose can be used to make gray scales is a major difference between this method and the method that is based on the reorientation of dyes in

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polarized light. In that case, the gray scales have to be produced by changing the polarization direction of the light.[10]

A complex pattern containing gray scales was recorded in the polymer film using a negative of a photograph. Compared to the patterns shown in Fig. 7, the UV exposure was shortened. The results are shown in Fig. 9. It is clear that the reproduction of the figure in the layer is very good. Using parallel polarizers the inverse picture is visible. Such layers may find application in copy protection of bank notes and credit cards.

It can be concluded that the presented system offers many possibilities for recording of complex patterns in liquid crystalline media.

ACKNOWLEDGMENT

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