Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Petri, A. , Bräuchle, Ch. , Leigeber, H. , Miller, A. , Weitzel, H. -P. and Kreuzer, F. -H.(1993) 'Cholesteric liquid crystalline siloxanes with azo dye. Generation of additional reflection bands with linearly polarized light', Liquid Crystals, 15: 1, 113 — 121
To link to this Article: DOI: 10.1080/02678299308027843
URL: http://dx.doi.org/10.1080/02678299308027843

Liquid Crystals, 1993, Vol. 15, No. 1, 113–121

Cholesteric liquid crystalline siloxanes with azo dye

Generation of additional reflection bands with linearly polarized light

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(*Received 4 January 1993; accepted 22 February 1993*)

Photosensitive cholesteric polysiloxanes, which contain an azo dye, were irradiated with linearly polarized light. The cholesteric samples were oriented in the Grandjean texture. Before irradiation they reflected circularly polarized light in the near infrared region. For perpendicular incidence, only one order of reflection was observed. Upon irradiation with linearly polarized light, which is absorbed by the azo dye, additional reflection bands appeared in the visible part of the spectrum. It turned out that the additional reflection is caused by a new Bragg type grating which shows higher reflection orders. The formation of the grating is based on the periodic deformation of the helical ordering of the molecules. The deformation is periodic, as due to photoselection, only dye molecules in equidistant layers with a suitable orientation absorb radiation. For low exposure, the grating reflects linearly polarized light. After continued irradiation, the reflection bands disappear almost completely. High birefringence, strongly dichroic dye absorption and the loss of the reflecting properties prove that a planar nematic texture has developed. The formation of this texture from the Grandjean texture is a new example for photoinduced rotational diffusion.

1. Introduction

Much attention has been paid to the properties of liquid crystalline polymers which contain an azo dye because of their potential for optical information storage [1–3]. In the storage process a high number of *trans–cis* isomerization steps leads to the reorientation of the long molecular axis of the dye molecules and of the surrounding mesogenic units. Irradiated and non-irradiated regions differ in the absorbance A and the index of refraction n. The new orientation of the molecules is frozen-in in the viscous glassy state, which makes the permanent storage of information possible. This process which is called photoinduced rotational diffusion was predicted by Michl and Thulstrup [4] and was first proved for nematic liquid crystalline polymers in [5]. Absorption spectroscopy showed that by irradiation with linearly polarized light the orientation of the azo dye molecules is changed until the transition dipole moment is oriented perpendicular to the polarization plane of the incident light. Somewhat later it

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was demonstrated with ^{13}C NMR [6] and FTIR spectroscopy [7] that the mesogenic molecules which do not absorb radiation are reoriented as well. The reorientation occurred above the glass transition temperature and for some materials also in the viscous glassy state. Holographic experiments with nematic liquid crystalline polymers showed that the photoinduced reorientation of molecules is usable for the formation of holograms [2]. We investigated cholesteric polysiloxanes, which contain *p*-ethoxyazobenzene as a photosensitive side group. Holographic grating experiments proved that cholesteric polysiloxanes are another class of promising materials for holographic information storage [3]. In these experiments grating efficiencies of about 70 per cent, with permanent storage over years, were achieved. The storage was reversible as the gratings could be erased completely when the polymers were heated to the glass transition temperature.

The holographic grating technique is a sensitive method used to determine photophysical and photochemical parameters as well as the mechanisms of hologram growth [8, 9]. However, grating experiments give no detailed information about the reorientation of the dye molecules. For this purpose it is of advantage to irradiate the samples with only one light beam and to investigate the samples spectroscopically. By irradiation with unpolarized light, cholesteric siloxanes were reoriented into a homeotropic nematic texture [10]. In this paper we concentrate on the interaction between photosensitive cholesteric polysiloxanes and linearly polarized light which is more complicated since several intermediate states appear until finally a planar nematic texture develops.

2. Experimental

The liquid crystalline polymers consist of a four-membered cyclic siloxane with the mesogenic side groups R_x and R_y and the azo dye side group R_z (see figure 1). The mesogenic units and the azo dye are connected to the siloxane backbone with a flexible oxypropylene spacer. For the experiments described in this paper, two different liquid crystalline polymers A and B were used (see table 1). In polymer A the molar ratio of the mesogenic unit R_x is reduced in order to increase the wavelength at which the sample reflects light. The synthesis is described elsewhere [11]. The samples were oriented between polyimide coated glass plates by mechanical shearing at about 410 K and annealing afterwards at 330–340 K. This simple treatment gives well-oriented samples (Grandjean texture) with good optical quality. The materials absorb light between 300 and 520 nm due to the azo dye.

The samples were irradiated with light from a Krypton-Ion Laser (Coherent Innova 100, $\lambda = 413$ nm, 482 nm) or broadband with light from a 200 W Hg-lamp (HBO 200 W). A water filter was used to avoid sample heating by the emitted infrared radiation. In both cases the light was linearly polarized. Linear polarization of the lamp light was achieved with a set of glass plates arranged in the beam at the Brewster angle. The irradiation intensity was kept between 10 and 250 mW cm^{-2}. The samples were mounted perpendicular to the propagation direction of the light.

Reflection spectroscopy was done using a Perkin–Elmer spectrometer (UV-Vis/NIR Lambda 19). Transmission spectroscopy was performed using a polarization microscope (Nikon Microphot FXA), which was supplied with a spectrometer (Photon Technologie GmbH, System OD5, wavelength range: 400–1500 nm). Spot selection was possible with different objectives and a continuously adjustable aperture (spot size $\approx 0{\cdot}01$ mm^2). In the microscope, the spectroscopy with polarized light was done with a fixed polarizer and by rotating the sample (see figure 2).

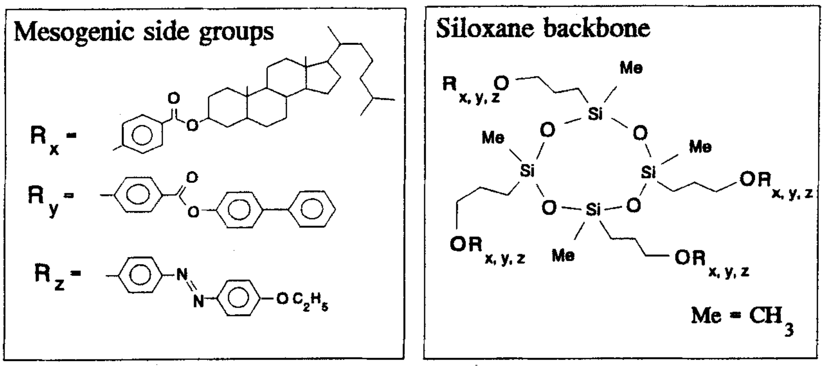


Figure 1. Structure of the mesogenic units R_x, R_y, the azo dye R_z and the cyclic siloxane backbone.

Table 1. Chemical composition and physical properties of the two polymers A and B under investigation.

	R_x	R_y	R_z	Transition temperatures/K	λ_r/nm
Polymer A	0·22	0·48	0·30	g 316 N* 450 I	1775
Polymer B	0·40	0·40	0·20	g 327 N* 466 I	1160

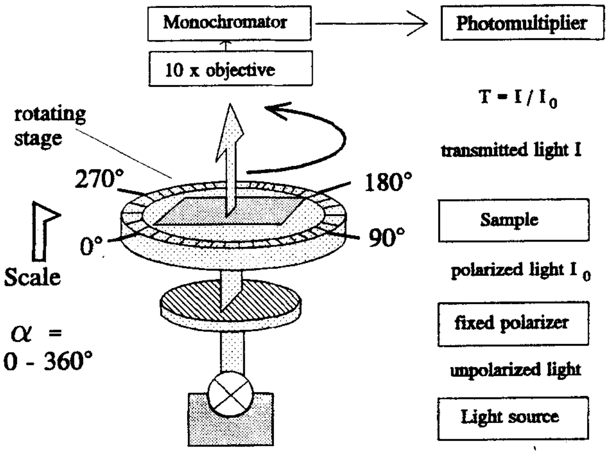


Figure 2. Experimental set up for the spectroscopic investigations in the polarization microscope.

3. Results and discussion

3.1. *Formation of new reflection bands*

Cholesteric liquid crystals show unique optical properties because of the helical arrangement of the mesogenic molecules. The polarization plane of linearly polarized light is rotated due to the structural chirality of the liquid crystalline phase. In the region of the reflection band the light is separated into left- and right-circularly polarized light, from which, depending on the handedness of the helix, one component is completely reflected. The wavelength λ_r of the reflection band depends on the mean index of refraction $\bar{n}$ and the pitch p of the helix. For perpendicular incidence, only one order of reflection is observed.

$$\lambda_r = p\bar{n}. \tag{1}$$

Samples which consist of a five-membered siloxane ring and cholesteryl benzoate have a pitch between 270 and 500 nm. They exhibit bright colours, as they selectively reflect visible light between 400 and 750 nm. In this investigation, compounds with a four-membered siloxane ring and cholestanyl benzoate were used which show a reflection band in the infrared region (see figure 3(*a*)). When such a polymer, for example, A, was irradiated with linearly polarized light from the Hg-lamp ($\lambda = 320$–520 nm), reflection of visible light appeared. Reflection spectroscopy revealed the formation of several new reflection bands λ_m. Four orders of reflection ($m = 1$–4) were detected, from which two are in the visible part of the spectrum (see figure 3(*b*)).

The wavelengths of the different bands and the intensities of the reflection are summarized in table 2. Assuming that the reflection is a typical Bragg reflection and that the new bands are higher order reflections, we calculated the wavelengths of the different orders m with Bragg's law.

$$m\lambda_m = 2d\bar{n}\sin\theta. \tag{2}$$

Using half the pitch $p/2$ as grating constant d, Bragg's equation reduces for perpendicular incidence to

$$\lambda_m = \frac{\lambda_r}{m}. \tag{3}$$

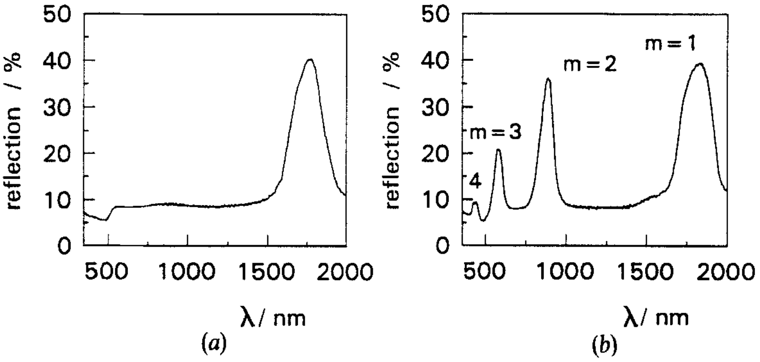


Figure 3. Reflection spectra of polymer A before (*a*) and after irradiation with linearly polarized light (*b*). Duration of irradiation with the Hg-lamp: 10 min, $I \approx 100\,\mathrm{mW\,cm^{-2}}$, from which $20\,\mathrm{mW\,cm^{-2}}$ were absorbed by the azo dye.

Table 2. Wavelengths and intensity of the four orders of reflection for polymer A—comparison of experimental and calculated values.

m	1	2	3	4
λ_m exp./nm	1840	885	580	440
λ_m calc./nm	1775	888	592	445
Reflection/per cent	32	27	12	3

With this formula the four orders of reflection were calculated. Calculated and experimental values are in good agreement. However, so far we have no explanation for the shift between λ_r and the first order reflection λ_1 at 1840 nm.

The explanation of the experimental result is based on photoselection [4]. The absorption depends on the angle between the transition dipole moment and the oscillating electric field. Strong absorption occurs when both are oriented parallel; no absorption is found for perpendicular orientation. Figure 4 illustrates the situation for a cholesteric liquid crystalline polymer which contains an azo dye. Most important is the fact that the *trans* azo dye, which is mesogenic itself, fits perfectly into the liquid crystalline matrix and is helically arranged as well. Layers with strong absorption and no absorption alternate with a periodicity given by the pitch of the helix. The length of the bars in figure 4 give the component of the transition dipole moment, which is seen by a linearly polarized light wave incident in the plane of the paper. Due to the absorption, the index of refraction is changed in equidistant layers with a spacing of $p/2$ which explains the formation of the new reflection grating and the appearance of higher orders of reflection. Such an effect was discovered earlier in low molecular cholesteric liquid crystals in which higher order reflections were induced by means of an electric or a magnetic field [12, 13].

Several processes contribute to the modulation of the index of refraction. First, a single *trans–cis* isomerization step changes the index of refraction as the shape of the two isomers is different. The modulation is weak, but visible in the polarization microscope between crossed polarizers. Since the dye molecules relax thermally back to the thermodynamically stable *trans* state, the effect is only transient and no reflection bands develop. A permanent change of the index of refraction is, however, achieved by continued irradiation. As the $n\pi^*$ absorption bands of both isomers overlap, no photochemical bleaching occurs and the isomerizations take place in both directions as long as the sample is irradiated. With each isomerization step the long molecular axis of the dye molecules is rotated by a small angle. The rotation is complete when the long molecular axis is oriented perpendicular to the polarization plane of the light.

This reorientation was investigated by absorption spectroscopy with polarized light in the set up described in figure 2. The sample was rotated in steps of $\alpha = 15°$. For each sample orientation, an absorption spectrum between 400 and 700 nm was recorded. Before irradiation, no angular dependence of the dye absorption was detected because of the helical arrangement. Figure 5 (*a*) shows the induced dichroism

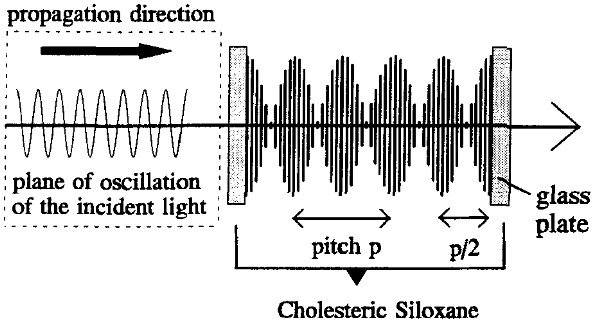
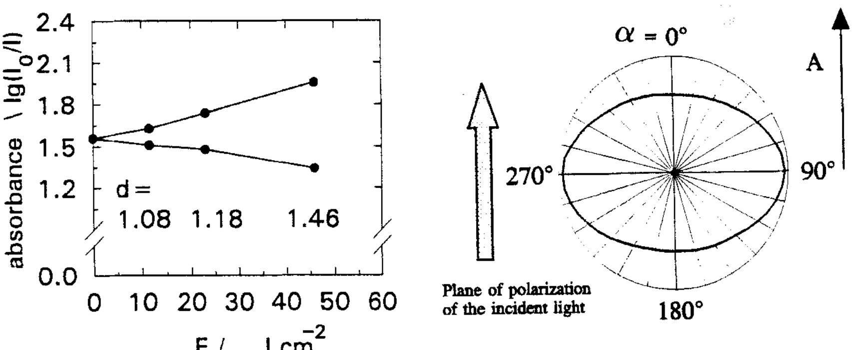
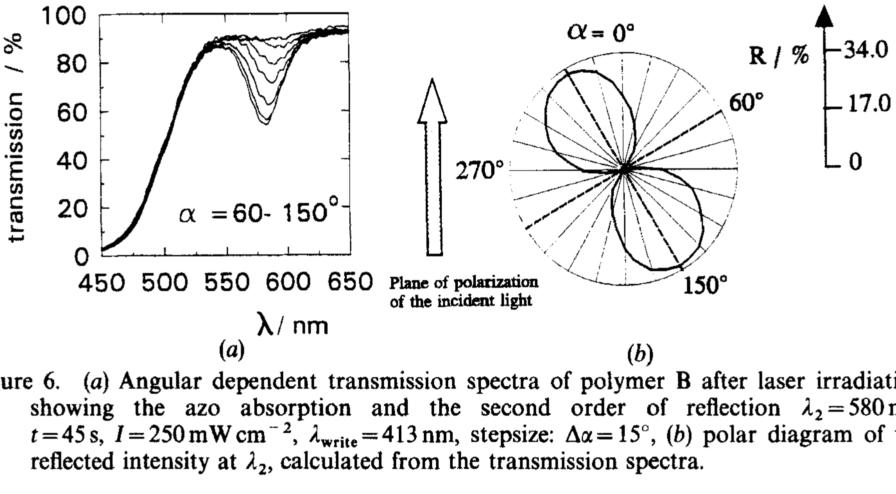


Figure 4. Interaction of linearly polarized light with the azo dye in cholesteric liquid crystalline polymers. The length of the bars represents the component of the transition dipole moment, which is seen by the polarized light incident in the plane of the paper.



(*a*) (*b*)

Figure 5. (*a*) Angular dependence of the azo dye absorption for polymer B as a function of the exposure (J cm^{-2}). The highest and lowest value for $\lambda = 450$ nm are shown, from which the dichroic ratio *d* is calculated; (*b*) the ellipsoid in the polar diagram shows the angular dependence of the absorption after an exposure of 46·0 J cm^{-2}.



(*a*) (*b*)

Figure 6. (*a*) Angular dependent transmission spectra of polymer B after laser irradiation showing the azo absorption and the second order of reflection $\lambda_2 = 580$ nm, $t = 45$ s, $I = 250$ mW cm^{-2}, $\lambda_{write} = 413$ nm, stepsize: $\Delta\alpha = 15°$, (*b*) polar diagram of the reflected intensity at λ_2, calculated from the transmission spectra.

when polymer B was irradiated with linearly polarized laser light. The dichroic ratio *d*, which is defined as $A_{max}(\alpha_1)/A_{min}(\alpha_2)$, grows almost linearly with exposure. The angular dependent absorption of polymer B after an exposure of 46·0 J cm^{-2} is illustrated by the ellipsoid in figure 5 (*b*).

3.2. *Optical properties of the new reflection bands*

With increasing irradiation, the optical properties of the new reflection grating are changed. We analysed the spectra which had already been used to determine the azo dichroism. The second order of reflection of polymer B appears at $\lambda = 580$ nm. Figure 6 contains transmission spectra after an irradiation of 45 s with $I = 250$ mW cm^{-2} (laser radiation). The angular dependent spectra in figure 6 (*a*) were taken between $\alpha = 60$ and 150° in steps of 15°. The polar diagram in figure 6 (*b*) contains the angular dependent reflection, which was calculated from the transmission spectra. After low exposure the reflected light is linearly polarized. The reflection varies between 0 per cent at $\alpha = 60°$ and 33 per cent at $\alpha = 150°$. The rotation of the ellipsoid relative to the plane of polarization of the laser radiation probably results from the helical rotatory power, which is still present in the distorted cholesteric samples. For higher exposure the reflection is increased (see figure 7) and the state of polarization of the reflected light is changed. For the highest exposure of 46·0 J cm^{-2}, the reflected light is almost unpolarized. This is valid for the mid-point of the band at $\lambda = 580$ nm. Away from the mid-point, the light is still partly polarized.

Further development of the reflection bands for higher exposure was investigated with polymer B and the Hg-lamp as light source. The spectra were taken in the reflection spectrometer with unpolarized light. The highest reflectivity was reached after 17 min (see figure 8 (*a*)). During four more hours of irradiation, the reflection bands disappeared almost completely. From the angular dependent absorption spectra, a dichroic ratio of $d = 5{\cdot}8$ at $\lambda = 450$ nm was calculated. Observed between crossed polarizers, the sample appeared strongly birefringent. The loss of the reflecting properties, the birefringence and the dichroic absorption indicate that a state has been reached in which all dye molecules are oriented perpendicular to the polarization plane of the light. According to the polar diagram, the sample resembles a planar nematic

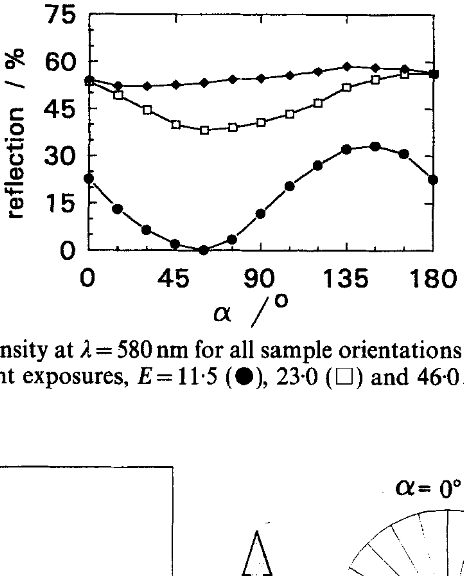
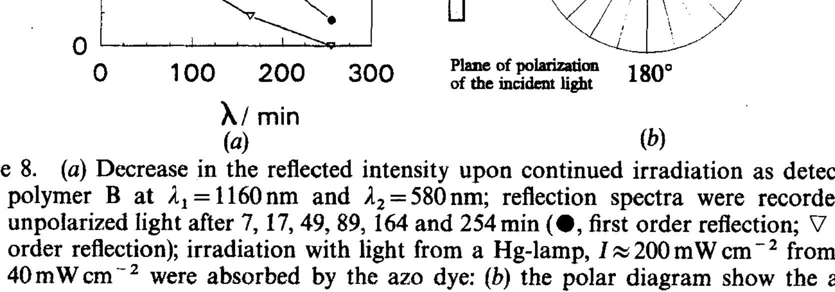


Figure 7. Reflected intensity at $\lambda = 580$ nm for all sample orientations between 0 and 180° and three different exposures, $E = 11{\cdot}5$ (●), 23·0 (□) and 46·0 J cm^{-2} (◆).



(*a*) (*b*)

Figure 8. (*a*) Decrease in the reflected intensity upon continued irradiation as detected for polymer B at $\lambda_1 = 1160$ nm and $\lambda_2 = 580$ nm; reflection spectra were recorded with unpolarized light after 7, 17, 49, 89, 164 and 254 min (●, first order reflection; ▽ second order reflection); irradiation with light from a Hg-lamp, $I \approx 200$ mW cm^{-2} from which 40 mW cm^{-2} were absorbed by the azo dye: (*b*) the polar diagram show the angular dependent absorption at $\lambda = 410$ nm after the reorientation is completed.

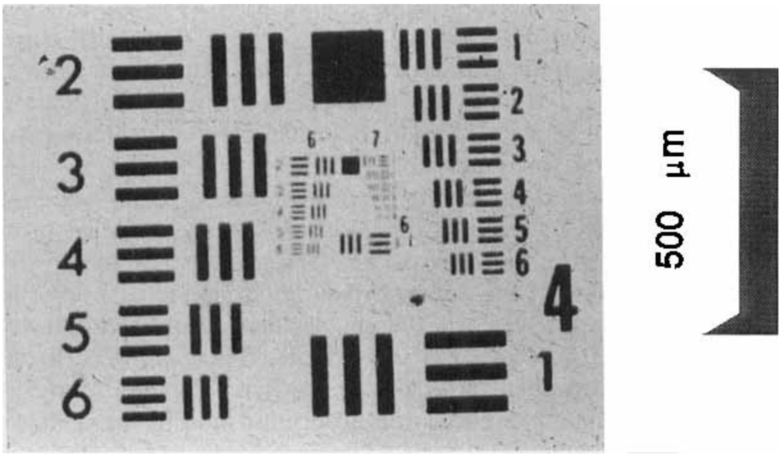


Figure 9. Image of the USAF test pattern, photo taken in the polarization microscope; sample between two polarizers after an exposure of 10 J cm^{-2}

liquid crystal with the optical axis perpendicular to the polarization plane of the light (see figure 8 (*b*)). For this sample, we calculated a Saupe order parameter S of 0·61 [14]. The unwinding of the helix leads to a constant index of refraction in the propagation direction of the light beam. Without the periodic modulation of the index of refraction, the reflecting properties of the sample disappeared. The loss of the reflecting properties proves that the mesogenic units, which build up the helical system, were reoriented as well. The unwinding of the helix is a new example of photoinduced rotational diffusion of an azo dye and a cooperative reorientation of the surrounding matrix.

4. Applications

We investigated the storage properties of the cholesteric polysiloxanes with respect to the physical processes discussed in the last chapter. An image of the USAF test pattern was recorded in a sample with high resolution and high long term stability. To avoid a reduction of the resolution by diffraction, the sample was prepared between a glass plate and a thin polymer film, which was removed from the sample after the orientation was completed. The close contact between the sample and the test pattern which then was possible reduced the resolution limitation by diffraction extremely well. However, in the smallest details of the image, diffraction still was present. We used these diffraction fringes and not the details of the pattern itself to determine the resolution limit. The resolution comes to approximately 1 μm but is probably still higher. As long as the image is kept in the dark and at room temperature, no fading of the optical quality is observed. For low exposure, a pure phase object was obtained which is only visible between crossed polarizers due to the weak modulation of the index of refraction in the irradiated region. The photo (see figure 9) was taken in the polarization microscope after an exposure of approximately 10 J cm^{-2} laser radiation. After longer exposure the new reflection bands appear. The image is then visible by eye and stable over years.

5. Conclusion

We modified the optical properties of photosensitive cholesteric siloxanes by irradiation with linearly polarized light. A Bragg-type grating develops, which reflects light in several orders. The wavelengths of the higher harmonics were calculated with Bragg's law using half a helix pitch as the grating period. The formation of the grating is based on the photochemical *trans–cis* isomerization and the subsequent reorientation of the dye molecules. Due to photoselection the absorption and consequently the deformation of the helix are modulated periodically. The reorientation of the dye molecules causes a pronounced change of the index of refraction. The mesogenic units are reoriented as well and contribute to the modulation of the index of refraction. Initially the reflected light is linearly polarized. Upon further irradiation the reflection disappears completely as the helix is unwound. The loss of the reflecting properties, the strong birefringence and the dichroic absorption of the azo dye indicate that a phase has developed which resembles a planar nematic phase. The unwinding of the helix by irradiation with linearly polarized light is a new example of photoinduced rotational diffusion. In the final state all molecules are arranged perpendicular to the polarization plane of the incident light. The image of a test pattern was recorded with high resolution and high long term stability. Initially, the image is only visible between crossed polarizers. After higher exposure it is visible by eye because of the increasing reflection of visible light.

Part of this work was supported by the BMFT (Project 03 M 4059).

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