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Structuring cholesteric polysiloxanes by photoinduced rotational diffusion

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Cholesteric polysiloxanes containing an azo dye were irradiated with linearly or circularly polarized laser light or with the unpolarized light from a HgXe lamp. Photoinduced rotational diffusion was observed leading to new textures with a completely different orientational distribution of the chromophoric and the mesogenic side chains. A broad variety of new structures was detected depending on the polarization state of the light, the helical arrangement of the azo dye and the optional application of an electrical d.c. field. The new structures were characterized by spectroscopy with polarized light. Co-operative reorientation of chromophoric and mesogenic side chains was proven. The formation of a Bragg grating upon short term irradiation with linearly polarized light was observed. Continued irradiation leads in most cases to a strongly birefringent texture with a high dichroic ratio of the azo dye resembling a planar nematic texture. With circularly polarized light or with unpolarized light, a uniaxial homeotropic texture appeared predominantly. The formation of the new textures occurred in the glassy state of the samples leading to new structures with good optical quality and an exceptionally good long-term stability.

1. Introduction

Liquid crystalline polymers (LCPs) containing an azo dye as a side chain have been intensively investigated for optical applications over the last few years. Of special interest was a possible use in the field of optical information storage [1-4], as these LCPs are photosensitive due to the chromophoric side chains. Upon irradiation, a pronounced change in the absorbance and index of refraction is observed and a reversible storage of the photoinduced modulation of optical properties in the glassy state of the LCPs could be demonstrated.

Holography represents a most promising method for optical information storage due to the extremely high storage capacity. Highly efficient holographic gratings have been generated in nematic polyacrylates [2, 3] and in cholesteric polysiloxanes [4], both containing an azo dye. The local processes leading to the pronounced modulation of the optical properties may either be investigated by holography itself, in the form of holographic grating experiments, in which two laser beams are superimposed [2-4] or by experiments in which only one laser beam or the beam of a conventional light source is used to irradiate the samples [5-13]. In these experiments, additional spectroscopy with polarized light yields angular dependent information about the photochemical process and the resulting modulation of the material properties. With this

method, different aspects of the basic processes can be investigated.

Here we will report the results of irradiation experiments and absorption spectroscopy with both polarized and unpolarized light. It was shown that photoinduced rotational diffusion is the fundamental process leading to the modulation of the optical properties in photochromic LCPs [5]. This effect was first described in [14]. Upon irradiation, the continuously absorbing and isomerizing azo dye molecules slowly change their orientation. This is the driving force of the process. It goes on until the molecular long axes of the molecules are completely reoriented, i.e. the absorption probability decreases to zero upon rotation of the transition dipole moment. The structures induced in this way depend on the alignment of the side chains of the LCPs before irradiation and especially on the polarization state of the actinic light. It will be shown that the photoinduced reorientation provides a very efficient way for the preparation of optically clear anisotropic samples.

We investigated the interaction of cholesteric polysiloxanes with unpolarized light, as well as with linearly and circularly polarized light, respectively. As the azo dye is aligned helically in the Grandjean texture, the interaction of polarized light with the aligned chromophore has to be considered in terms of photoselection phenomena, i.e. a selective excitation of a subset of dye molecules with an

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appropriate orientation [14]. Photoselection and rotational diffusion, as produced by polarized or unpolarized light, lead to a broad variety of new structures highlighting the extraordinary potential of cholesteric LCPs.

2. Experimental

2.1. Chemical composition and physical properties of the samples

All samples contain two different mesogenic side chains x and y (y_1 or y_2), a chromophoric side chain z (z_1 , z_2 or z_3) and cyclic tetramethyltetrasiloxane as shown in figure 1. Three different azo side groups derive from three azo dyes, namely *p*-ethoxyazobenzene (acronym: EAz),

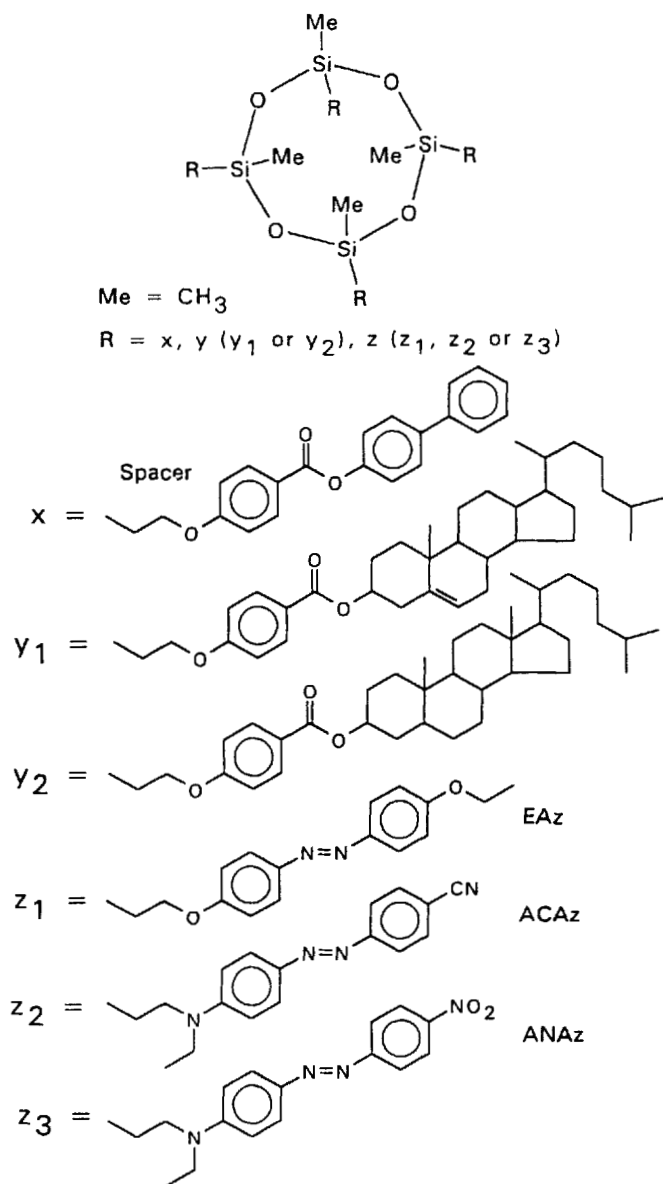


Figure 1. Structure of the backbone consisting of tetramethyltetrasiloxane and of the different side chains.

4-*N*-ethylamino-4'-nitroazobenzene (ANAz) and 4-*N*-ethylamino-4'-cyanoazobenzene (ACAz) were used as chromophores. The amino group of ANAz and ACAz forms a part of the flexible amino ethyl propylene spacer linking the chromophores with the cyclic tetramethyltetrasiloxane backbone. EAz is connected to the backbone by an oxypropylene spacer. The synthesis has been described elsewhere [15, 16]. The composition of the samples and some important physical properties including the glass transition temperature, T_g , the maximum of the azo dye absorption band, λ_{max} , and the wavelength range of the reflection bands, λ_{ref} , are summarized in table 1. The concentrations refer to the molar amounts of the different monomers before their linkage to the backbone in a standard hydrosilylation reaction. When cholesteryl benzoate (y_1) is replaced by cholestanyl benzoate (y_2) the wavelength of the selective reflection λ_{ref} is shifted from the visible to the infrared part of the spectrum.

ITO cells ($d = 5 \mu\text{m}$) were filled with LCPs containing ANAz or ACAz chromophoric side groups at $\approx 410 \text{ K}$. These cells allow the additional application of an electric field during irradiation. Samples with EAz were prepared between polyimide coated glass plates or between CaF₂ plates at $\approx 410 \text{ K}$. The quality of the alignment of samples containing EAz was ameliorated by shearing the plates with respect to each other. Final annealing above T_g led generally to samples with good optical quality.

2.2. Experimental set-up

The samples were irradiated with the polychromatic light from a mercury-xenon lamp (HgXe, HBO 200 W) or with the monochromatic light from a krypton ion laser (Coherent, Innova 100) at $\lambda = 413, 482$ or 568 nm . Linearly or circularly polarized light was used for the laser experiments, while a series of object slides at the Brewster angle served to polarize the light from the HgXe lamp. Polarized absorption spectra were recorded using a polarization microscope (Nikon Mikrophot FXA) which was equipped with a spectrometer (System OD 5, Photon Technologie GmbH), allowing measurements in the wavelength range from 400 to 700 nm. The polarization of the spectroscopic light was achieved with a sheet polarizer. The size of the area examined was selected by means of a variable aperture in the tube of the microscope, thus making an investigation of small uniformly irradiated areas possible. For the recording of the spectra, the samples were rotated in steps of 10° or 15° on the rotating stage of the microscope. As the polarizer was mounted statically, an alteration of the intensity of the spectroscopic light by depolarization effects introduced by the monochromator and other optical elements was strongly reduced. Infrared spectra were recorded by an FTIR spectrometer (Bruker IFS 66) at a resolution of 2 cm^{-1} collecting 64 scans.

Table 1. Chemical composition and physical properties of the cholesteric polysiloxanes investigated: x and y are always used in equal amounts; λ_{\max} = wavelength of maximum absorption, T_g = glass transition temperature, λ_{ref} = selective cholesteric reflection, d = sample thickness.

Composition	$x/\text{mol } \%$	$y/\text{mol } \%$	$z/\text{mol } \%$	T_g/K	λ_{\max}/nm	$\lambda_{\text{ref}}/\text{nm}$	$d/\mu\text{m}$
x, y_2, z_1 (EAz)	35–45	35–45	30–10	328–336	360	1215–1000	6–12
x, y_1, z_2 (ACAz)	40–45	40–45	20–10	328–330	450	630–600	5
x, y_2, z_3 (ANAz)	40–47.5	40–47.5	20–5	328–332	490	960–1230	5

Both the actinic and spectroscopic light propagated, in all experiments, parallel to the helical axis (z axis) of the cholesteric samples. The definition of the coordinate system is given in figure 4.

3. Results

3.1. Principal aspects of photoinduced rotational diffusion

Until now, photoinduced rotational diffusion has only been observed in LCPs which contain an azo dye as chromophoric side chain. Thus this novel effect seems to be closely related to the *trans*–*cis*-isomerization of the azo dye. During the isomerization, the shape of the dye moieties changes from rod-like (*trans*-isomer) to bent (*cis*-isomer). The structural change and its effect on the surrounding mesogenic side chains is shown in a schematic way in the upper part of figure 2. As will be shown later, a strong coupling between the dye moieties and the mesogenic side chains may cause a slight reorientation of all side chains. The new orientation may then be frozen-in in the glassy state of the LCP. In this way a new structure can develop irreversibly in which the side chains have no memory about their initial orientation. This structure can

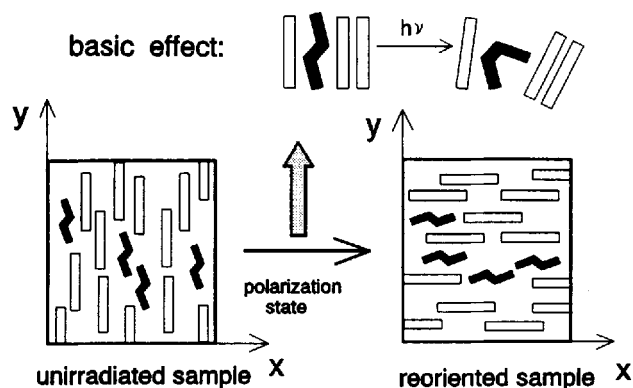


Figure 2. Change of the structure of an azo dye molecule by *trans*–*cis*-isomerization and its possible effect on the surrounding mesogenic units which are slightly reoriented. All molecules may be frozen-in in this new orientation. Finally the molecular long axes of all side chains are oriented in the x direction for actinic light polarized in the y direction. This effect is found in nematic polyacrylates and in cholesteric polysiloxanes.

further be modified with every photochemical isomerization step. Figure 2 displays the state of a sample observed before and after irradiation with linearly polarized light. In an idealized final state, all side chains will be oriented perpendicularly to the electrical field vector of the actinic light.

This effect was found in nematic polyacrylates [5–9] and in cholesteric polysiloxanes [10–13]. Since only special aspects of our work have been published [10–13] so far, we want to present here the full and detailed investigation of the photoinduced rotational diffusion in cholesteric polysiloxanes which includes the complete unwinding of the helical alignment of the side chains. The results and some experimental parameters are briefly summarized in table 2 to give an instructive survey of our work. A successful experiment according to the mechanism in figure 2 is characterized by a (+) denoting complete reorientation. Deviations were found only in two cases which will be discussed in § 5.

3.2. Rotational diffusion with unpolarized or circularly polarized light

Unpolarized or circularly polarized light is characterized by a constant value of the electric field vector in all

Table 2. Summary of the reorientational experiments; irradiation of samples containing EAz, ACAz or ANAz as chromophoric side chains with differently polarized light: krypton ion laser and HgXe lamp; (+) denotes a result according to the mechanism in figure 2, (–) denotes that only a partial reorientation or no reorientation was detected.

	Light source			
	Laser		HgXe lamp	
	λ/nm			
	413,482,568		320–600	
Azo dye	Polarization			
	Linearly	Circularly	Linearly	Unpolarized
EAz	–	–	+	+
ACAz	+	+	+	+
ANAz	+	+	+	+

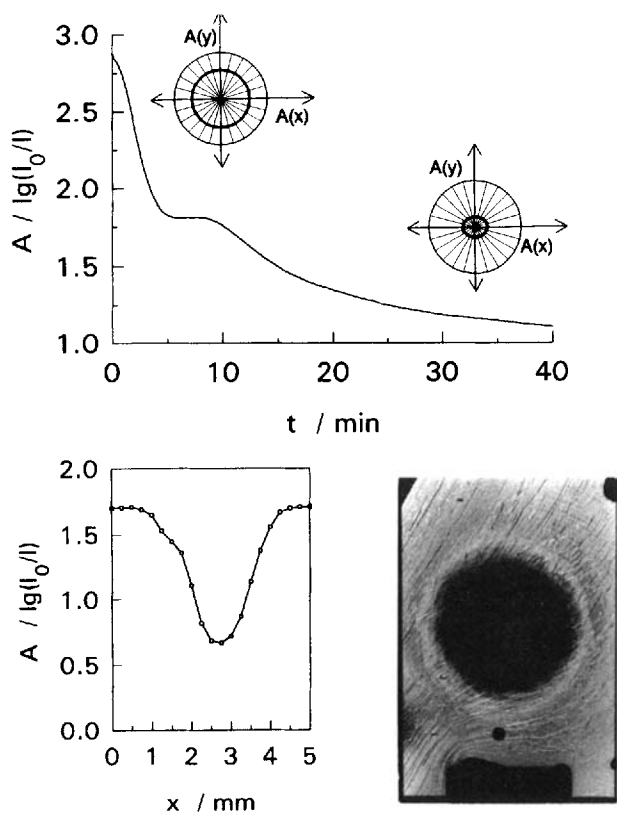


Figure 3. Irradiation and bleaching of a sample with 10 mol % ANAz with circularly polarized laser light at $\lambda = 482$ nm; $I = 1.0$ W cm $^{-2}$, $T = 328$ K, upper diagram: change of the absorbance $A(t)$ during continued exposure to laser light at 482 nm; the polar diagrams display the angular dependent absorbance of ANAz at 450 nm; lower part: a profile of the absorbance $A(x)$ through the irradiated spot, recorded in steps of 0.25 mm, reflects the gaussian intensity distribution of the laser beam and the microscope photograph shows the irradiated spot between crossed polarizers, $\phi \approx 3$ mm.

directions perpendicular to the propagation direction. If such a light beam is propagating along the helical axis, a constant value of the absorption probability for all dye molecules is found independent of their orientation. Clearly under this condition, light induced rotational diffusion occurs until the azo dye is reoriented in the direction of the helical axis, resulting in a strong decrease of the absorption probability. This rotational motion which is combined with the bleaching of the sample in the direction of the propagating light can be monitored by the detection of the time and exposure dependent increase of the transmitted light intensity.

This behaviour is reported in figure 3. A sample with 10 mol % ANAz is bleached by a circularly polarized laser beam at 482 nm. The bleaching effect is caused completely by rotational diffusion and not by a photochemical bleaching which can be shown to occur much faster. Heating of the sample below T_g helped to accelerate the

reorientation. However, the elevated temperature is not principally necessary for a successful reorientation, as the same results were obtained at room temperature. The little shoulder appearing after 10 min occurs probably due to the birefringence of the sample in this state of the reorientation causing a partial reflection of the laser light.

To characterize the reoriented spot, the orientational distribution of the azo dye was investigated by spectroscopy with linearly polarized light in the polarization microscope spectrometer before and after the reorientation. The values $A(x)$ and $A(y)$ and values at intermediate angles were measured at 550 nm and displayed in the two polar diagrams in figure 3. The axes in the polar diagrams correspond to the axes defined in figure 4(a) for the Grandjean texture. Due to the helical alignment of the dye molecules, the absorbance is large and independent of the angle before the irradiation (left polar diagram). As expected from the mechanism of light induced rotational diffusion described above, the absorption is again angularly independent in the irradiated spot, but is much smaller. This is shown in the second polar diagram in figure 3. It clearly indicates that after illumination the dye molecules are oriented in a small cone along the z -direction.

Figure 3 also contains a microscope photograph of the irradiated spot taken between crossed polarizers. The spot appears black, which is consistent with a uniaxial orientation of the side chains parallel to the z axis. Tilting the sample leads to a brightening and proves, together with the very low value of the absorbance, that a sample with a uniaxial orientational distribution of the azo dye molecules has developed. Finally the absorbance profile $A(x)$, which was taken across the spot in steps of 0.25 mm, is consistent with the gaussian intensity distribution in the laser beam.

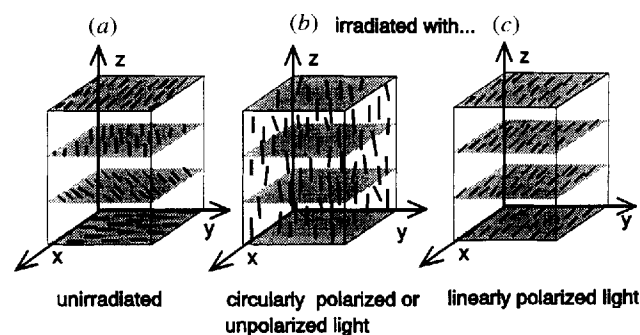


Figure 4. Textures of the unirradiated sample and possible structures of the reoriented samples: (a) Grandjean texture, (b) homeotropic texture after irradiation with unpolarized or circularly polarized light, (c) planar nematic texture after irradiation with linearly polarized light; the grey shaded layers in (b) and (c) were not removed in order to emphasize the relation to the initial structure (a).

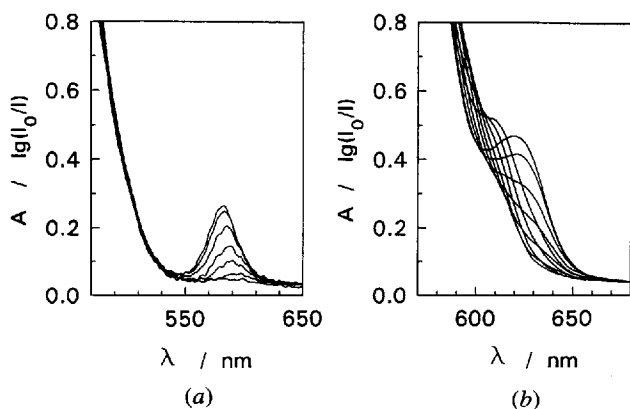


Figure 5. The additional reflection bands of second order of the Bragg grating developed upon irradiation with linearly polarized light are investigated with linearly polarized light. The angular dependence is shown in steps of 15° from 0° to 90° . Two samples containing (a) 20 mol % EAz or (b) 5 mol % ANAz were irradiated at 413 nm and 482 nm, respectively; Exposure: sample with EAz $\approx 10 \text{ J cm}^{-2}$, sample with ANAz $\approx 200 \text{ J cm}^{-2}$.

The resulting uniaxial phase is in accordance with the structure (b) in figure 4. This structure appeared generally when the unpolarized light of the HgXe lamp was used. With circularly polarized light, ANAz and ACAz gave the same result. Samples with EAz showed almost no reaction upon irradiation with circularly polarized laser light. This will be discussed in more detail in § 5.

3.3. Rotational diffusion with linearly polarized light

The reorientation with linearly polarized light is more complicated in comparison with circularly polarized light. First of all, photoselection has to be considered. Photoselection means that only a subset of chromophores with an appropriate orientation of the transition dipole moment absorbs radiation [14]. In this case the direction of the rotational motion had to be considered, as there are two independent directions in which the reorientation may take place.

For linearly polarized light propagating parallel to the helical axis, photoselection causes rotational diffusion in equidistant layers with a period of $p/2$ (p = pitch), thus producing a periodic modulation of the optical properties and the formation of a superstructure on top of the helical structure. The layers of this superstructure can be viewed as a Bragg grating which, in contrast to the unirradiated samples with only one reflection band λ_{ref} , exhibits several orders of reflection at λ_{ref}/n with $n = 2, 3$ and 4 [10–12]. When the additional reflection bands appear in the visible part of the spectrum, bright reflection displays with a very good contrast ratio are formed upon irradiation with linearly polarized light through a photo mask. Figure 5 shows the second order reflection band as measured with

polarized light in the microscope spectrometer in two samples containing EAz and ANAz, respectively, after exposure to laser light at 413 or 482 nm. After a short irradiation of the sample containing EAz, the reflected light is linearly polarized. This is shown by the seven absorption spectra taken with polarized light in steps of 15° over the range from 0° to 90° with the microscope spectrometer. After a higher exposure, for example, 25 J cm^{-2} , the reflection is independent of the polarization state of the incident light. This may for example be seen in figure 9(b) (upper diagram), wherein the angular dependent spectra differ remarkably from the spectra taken after a low exposure. In this example the total absorption amounts to 780 J cm^{-2} . However, the essential features of these spectra already appear after an exposure of only 20 to 30 J cm^{-2} .

By way of contrast, samples with ANAz show an angular dependent reflection of linearly polarized light even after very high exposures, for example, 200 J cm^{-2} in figure 5(b). We assume that the differences between EAz and ANAz at high exposures result from the very high absorbance of ANAz at 482 nm which limits the number of equidistant layers which contribute to the new reflection grating.

The Bragg grating only represents an intermediate situation in the continuing destruction of the cholesteric helix. Using a sample with 10 mol % ACAz as a further representative example, figure 6 shows the complete bleaching process, as described above for circularly polarized light, monitored by detecting the increasing transmittance of the laser beam at 482 nm. Despite the fact that the little shoulder in $A(t)$ is absent, a comparable decrease of the absorbance is detected, as with circularly polarized light in the example of figure 3. The absence of

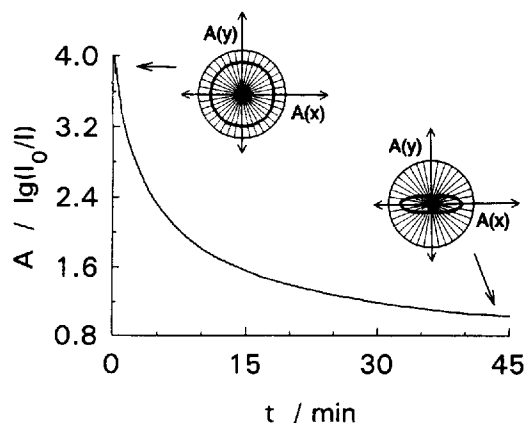


Figure 6. Decrease of the absorbance in a sample containing 10 mol % ACAz upon irradiation with linearly polarized laser light in the y direction with $\lambda = 482 \text{ nm}$; $I = 1.5 \text{ W cm}^{-2}$, $T = 325 \text{ K}$; the polar diagrams of the initial and the final state display the angular dependent absorbance of linearly polarized light at 525 nm.

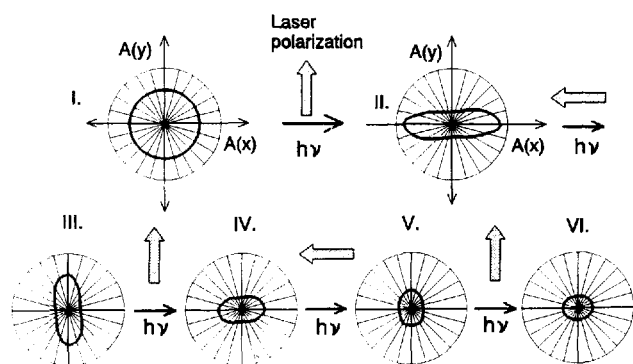


Figure 7. Angular dependent absorption $A(\theta)$ at 550 nm of a sample with 10 mol % ANAz before and after irradiation with linearly polarized laser light at $\lambda = 482$ nm; $T = 296$ K; upper diagram: polar diagrams before I, and after the first exposure II.; lower diagram: the change of the angular dependent absorbance during four irradiation steps and alternately using x and y polarized laser light is displayed in the polar diagrams III. to VI.

the reflection band at the end of the irradiation process proves the complete destruction of the helical structure. Further, the nematic structure becomes apparent upon observing the sample between crossed polarizers in the microscope. The irradiated spot is strongly birefringent.

The anisotropic properties were additionally detected by means of polarization spectroscopy. The corresponding polar diagrams are shown in figure 6. Surprisingly the decrease of $A(y)$ is not fully accompanied by a corresponding increase of $A(x)$. This allows one to conclude that an exclusive reorientation of the azo dye in the xy -plane, leading to an ideal uniaxial structure like in figure 4(c), did not occur. We further investigated this point concerning the distribution of the chromophoric side chains with respect to the z and the x axis upon irradiation with y polarized light in the following measurement.

A sample with 10 mol % ANAz was first reoriented with linearly polarized light (I \rightarrow II in figure 7). This time, a relatively high increase of $A(x)$ was detected. The experimental value of $A(x)$ is relatively close to the theoretical value for a planar nematic texture which is easily calculated from the absorbance of the azo dye in the Grandjean texture. Hence in this experiment, the reorientation led to a texture closely resembling the texture in figure 4(c). The orientational distribution may be described as quasi-planar. However, it is clear from this experiment and the experiment described before that there are some variations in the degree of reorientation in the xy plane. The sample was then exposed four times to a laser beam switching the polarization direction from one experiment to the next as shown in figure 7. The result of the spectroscopic investigation with polarized light after every reorientation step is shown in figure 7 in the polar diagrams III \rightarrow VI. From the shape of the ellipsoids it can

be seen easily that the molecules are more and more reoriented in the z direction. These four additional exposures were sufficient to create an orientation distribution almost identical to the distribution obtained with circularly polarized light. Thus multiple switching of the direction of linearly polarized laser light has the same effect as a single irradiation with circularly polarized light.

During the reorientation, the laser beam is slightly depolarized due to the birefringence of the distorted helix. Probably this depolarization is one of the reasons why a perfectly planar nematic texture was never formed, as depolarized light will always cause a reorientation into the z direction. However, there seems to be a strong tendency for an initial reorientation in the xy plane in the first reorientational step (I \rightarrow II) leading to a quasi-planar texture.

For the samples which were reoriented with linearly polarized light, the order parameter was determined from $A(x)$ and $A(y)$ according to [14, 17]. This calculation is only strictly valid for a perfectly planar nematic texture which did not always fully develop in our experiments. As the difference between the experimental $A(x)$ and the calculated value for a planar nematic sample was mostly rather small however, the resulting order parameter should characterize the reoriented sample relatively well. According to [14], the order parameter may also be calculated from the absorbances of the Grandjean texture and the photoinduced homeotropic texture. This method is advantageous, as the final state is well defined and the spectroscopic investigation may be carried out with unpolarized spectroscopic light.

Independent of the method used, we generally obtained order parameters between 0.5 and 0.6. These values are in the typical range of LCPs which are oriented by mechanical shearing or by means of an electrical field, which supports light induced orientational diffusion as an appropriate new tool for the orientation of LCPs containing an azo dye moiety in the side chain.

4. Infrared spectroscopic investigation of the cooperative reorientation of the mesogenic side chains

The cooperative reorientation of the mesogenic side chains during the reorientation of the chromophoric side chains with circularly polarized laser light has so far only been proven by investigating the reoriented samples between crossed polarizers. The observed extinction is only possible when the mesogenic side chains are also reoriented. If there was a partial, possibly distorted, helix built up by immobile mesogenic side chains, there should still be some optical rotation leading to a certain transmittance through the crossed polarizers.

Therefore an infrared-spectroscopic investigation was conducted before and after irradiation of the samples in

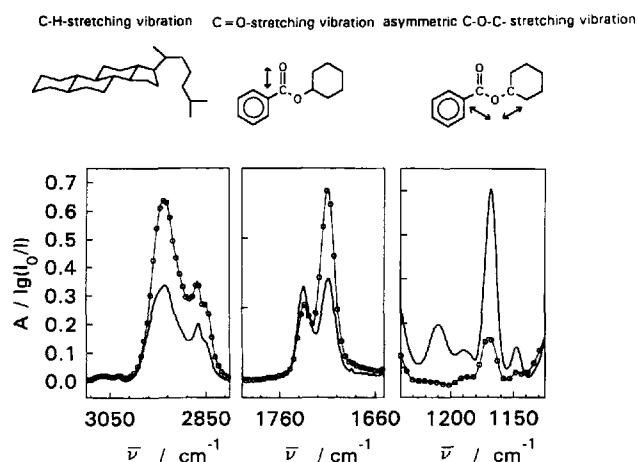


Figure 8. Infrared spectra of a cholesteric polysiloxane with 25 mol % EAz before and after reorientation with unpolarized light from a HgXe lamp; unirradiated sample: (—), reoriented sample (O—O).

order to get further evidence for the co-operative motion of the mesogenic side chains.

A sample with 25 mol % EAz was prepared between CaF_2 plates and was then reoriented with unpolarized light from the HgXe lamp. Due to the symmetry of the initial and the final texture, the full set of spectroscopic information is obtained. FTIR spectra of the monomeric compounds were recorded in order to relate the different absorption bands to vibrational modes of the cholesteric LCP being investigated. According to figure 8, the spectra of the initial and final states differ markedly. For some bands, a decreasing or an increasing intensity was detected, while others displayed constant intensity. The different effects of the reorientation on the intensity of the bands correspond to the different orientations of the vibrational transition dipole moments relative to the molecular long axis.

Figure 8 contains three partial spectra displaying interesting features of the experiment. An intense absorbance between 2800 and 3000 cm^{-1} comes almost exclusively from the aliphatic C–H stretching vibration of cholesterol. The increasing intensity is reproducible and proves, although not quantitatively, that the side chain containing cholesterol is reoriented during the irradiation. As the carbon atoms are sp^3 hybridized, there is no preferred orientation of the C–H bonds which explains why the change of the absorption intensity is not so pronounced as the change of the absorption of the azo dye in which the transition dipole moment is oriented parallel to the molecular long axis.

Both mesogenic side chains differ from the chromophoric side chain by the benzoate group. Typical vibrational modes of this group should therefore allow discrimination between the mesogenic and the chro-

mophoric side chains. The C=O stretching vibration, appearing at different wavenumbers for the mesogenic side chains, changed non-uniformly as depicted in the central spectrum. For the cholestanyl benzoate ($\bar{\nu} = 1735\text{ cm}^{-1}$), the intensity drops by a small amount. However, for biphenyl benzoate ($\bar{\nu} = 1710\text{ cm}^{-1}$), a distinct increase is registered. With this vibrational band only the reorientation of the biphenyl component in the cooperative motion may be proven. Probably the non-uniform change of the intensity originates from the different orientation of the C=O bond relative to the molecular long axis in the mesogenic side chains.

The band at 1165 cm^{-1} is caused by the asymmetric C–O–C stretching vibration of the benzoate group [18] and is found in both mesogenic side chains at almost the same wavenumber. The C–O–C bond, which aligns fairly well with the molecular long axis, is thus the best group for the investigation of the cooperative motion of the mesogenic side chains. Indeed the intensity of this band dropped to approximately 20 per cent of its initial value, which is a similar decrease on comparison with the values found for the chromophoric side chain. The FTIR spectra therefore prove the cooperative reorientation of the mesogenic side chain. The same results were obtained for a sample with only 10 mol % of the azo dye, thus demonstrating that even with a relatively low concentration of the azo dye, a complete cooperative reorientation takes place.

5. Peculiarities in the reorientation of samples with EAz under irradiation with linearly polarized laser light

All effects discussed so far were also found in samples containing EAz, as long as the irradiation was carried out with the polychromatic light from a HgXe lamp. Surprisingly, different results were obtained as soon as linearly or circularly polarized laser light was used. The experiments with the HgXe lamp show that photoinduced rotational diffusion is principally possible in samples containing EAz chromophoric side chains. Neither the structure of the azo dye, the thermal *cis*–*trans*-relaxation nor the less dipolar character in comparison with ANAz or ACAz may thus explain the surprising behaviour with laser light. Also the isomerization mechanism, i.e. an isomerization through rotation ($\pi\pi^*$ excitation) or inversion ($n\pi^*$ excitation) may be disregarded as a reason for the deviating behaviour, since in polymers and LCPs the inversion mechanism is generally favoured independent of the $\pi\pi^*$ or $n\pi^*$ excitation, because of the limited free volume favouring the inversion [19]. The independence of the different results from the isomerization mechanism is further evident from the formation of the Bragg grating, together with a dichroic azo dye absorption upon irradiation with monochromatic laser light [10]. This

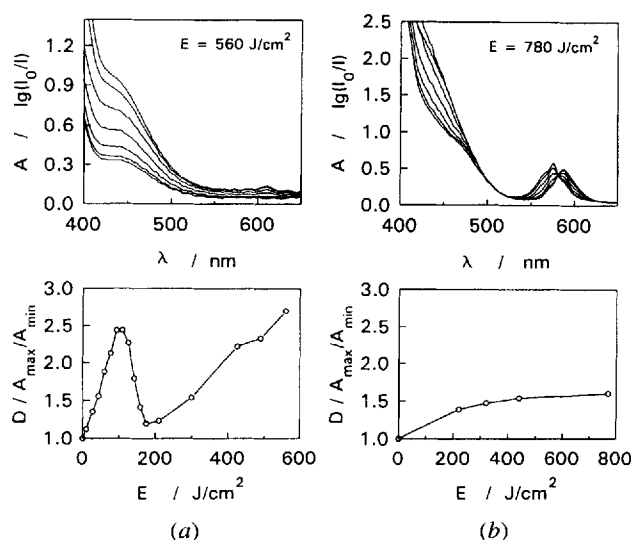


Figure 9. Upper diagrams: Angular dependent absorption spectra recorded with linearly polarized light in steps of 15° . (a) Sample with 30 mol% EAz, irradiated with linearly polarized polychromatic light from a HgXe lamp, $E = 560 \text{ J cm}^{-2}$; (b) sample with 25 mol% EAz, irradiated with monochromatic light from a laser at 482 nm, $E = 780 \text{ J cm}^{-2}$; both groups of polarized spectra represent final states. Lower diagrams: irradiation dependent dichroism of the azo dye at $\lambda = 450 \text{ nm}$ for both samples.

clearly proves that rotational diffusion takes place at least in the beginning of the laser beam irradiation.

A time resolved measurement of the photoinduced reorientation with a laser beam or the HgXe lamp, measuring the angular dependent absorbance with polarized light at different times of irradiation served to demonstrate and investigate the surprising behaviour of cholesteric polysiloxanes containing EAz. The upper diagrams in figure 9 contain angular dependent polarized absorption spectra, in steps of 15° , of the final states, after a total exposure of 560 J cm^{-2} ((a) = HgXe irradiation) and 780 J cm^{-2} ((b) = laser irradiation), respectively. The dichroic ratio at $\lambda = 450 \text{ nm}$ of these final states and its development during the irradiation is shown in the diagrams below.

The polarized spectra after laser irradiation indicate that an unwinding of the helix, as found with HgXe irradiation, did not take place with the laser. An intensive second order reflection of the Bragg grating is still visible which occurs, as mentioned above, in cholesteric samples with a distorted helix. The structure of the reflection band has changed in a very distinct way compared with the short term laser irradiation as shown in figure 5 (a). Instead of only one linearly polarized reflection band, now two bands appear. These bands still reflect linearly polarized light, but the polarization direction changes from one band to the other by 90° . Another obvious difference between the left and the right spectrum in figure 9 is the comparably low

dichroic ratio at $\lambda = 450 \text{ nm}$, despite the even higher exposure by the laser irradiation. Upon laser irradiation, the dichroic ratio D quickly rose to approach an upper limit of approximately 1.6. Polychromatic irradiation with the HgXe lamp, however, causes a much faster increase, with a dichroic ratio as high as 2.5. The unexpected intermediate drop to 1.1 motivated a closer examination at the course of the photoinduced reorientation. The reason for the low intermediate value is obvious when the polar diagrams after every single irradiation step are taken into consideration. For a clearer demonstration, figure 10 contains polar diagrams which are reduced to $A(\text{max})$ and $A(\text{min})$, whereby $A(\text{max})$ is normalized to the diameter of the circle. The white arrow indicates the polarization direction of the lamp light.

The dichroism grows until an exposure of 110 J cm^{-2} is reached, as can be seen from the decreasing length of the thin bar representing $A(\text{min})$. Light polarization direction and the direction which is bleached do not coincide because of the optical rotation of the actinic light in the distorted helix. The bleaching direction however appears to be constant, which reflects a constant optical rotation by an obviously only slightly distorted helix.

Between 125 and 180 J cm^{-2} , the dichroic ratio slowly drops to approximately 1.1. Exactly during this time, the orientation of the ellipsoid is regularly turned clockwise,

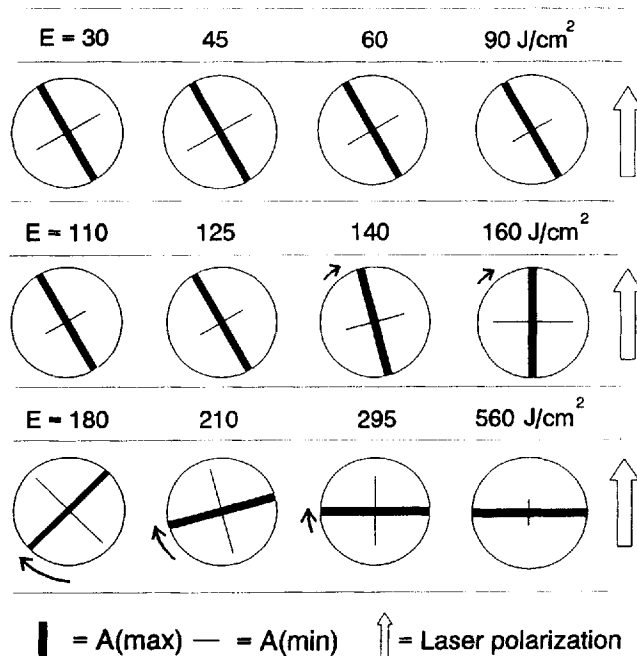


Figure 10. Polar diagrams containing the angular dependent absorbances at 450 nm after different exposures to linearly polarized, polychromatic light (HgXe lamp); the polar diagrams are reduced to $A(\text{max})$ and $A(\text{min})$, whereby $A(\text{max})$ is normalized to the diameter of the circle; the arrow indicates the polarization direction of the lamp light.

which indicates an increasing distortion of the helix due to the continued reorientation of the side chains. The decreasing dichroic ratio no longer reflects the true distribution of the molecular long axes of the chromophores as there is no meaningful mechanism through which linearly polarized light should be able to evoke such a distribution of the azo dye. Obviously, in this period the distorted helix leads to pronounced birefringence effects. While in the beginning ($0\text{--}110\text{ J cm}^{-2}$) the optical rotation of light is the only effect of the anisotropic matrix, the transmitted light is strongly depolarized in this second phase due to an alignment of the mesogens which resembles less and less the initial helix. A quantitative evaluation of the dichroism is impossible due to the depolarization in this strongly distorted state. The depolarization effect is much better seen in the original polarized absorption spectra which are not displayed here. Perpendicular to the polarization direction of the actinic light, the spectral features are as usual. However, parallel to this direction, the shape strongly deviates from that of typical azo dye spectra. A local maximum is found around 450 nm where the birefringence leads to a decreasing transmittance.

We suggest that this local and angular dependent increase of the absorbance, which is caused by the birefringence, causes a passivation of the sample when monochromatic laser light falling into the reflected wavelength range is used. With polychromatic light, the same effect occurs as can be seen from the polar diagrams in figure 10. However, in this case there is a wavelength range outside the strongly depolarized section remaining linearly polarized. Despite the depolarization effects, the photoinduced rotational diffusion is pushed ahead by the remaining polarized light.

After an exposure of 210 J cm^{-2} the conditions change again. Now the helical unwinding is almost finished and the influence of the birefringence is reduced to directions oblique to the molecular long axes. Parallel and perpendicular to the optical axis, there are no birefringent effects at all, allowing for an exact quantitative determination of the dichroic ratio. As the initial optical rotation has disappeared, the direction which is bleached coincides with the polarization direction of the lamp light.

We do not know why a similar effect is not observed in samples with ANAz or ACAz. An influence of the much higher absorbance in comparison with samples containing EAz was excluded by a successful photoinduced reorientation of a sample with ANAz at 568 nm. Under these conditions the optical density is comparable to the optical density of samples with EAz at 482 nm.

5.1. Temperature and electric field effects

An important material property exercising an influence on the dynamic properties of LCPs is the sample viscosity.

The speed of all processes which include a mass transport is governed by the viscosity and depends on the sample temperature. Therefore the question arises as to how the actual temperature and the glass transition temperature T_g (measured as an averaged value from DTA curves for heating and cooling) influence the formation and the stability of photoinduced structures. The reorientations in figure 3 and figure 6 had been carried out just below T_g . Taking possible laser beam heating into account, a rise of the temperature above T_g seemed to be very likely and could suggest that a heating into the liquid crystalline phase is necessary for a successful photoinduced reorientation. We proved, however, that the reorientation already occurs in the glassy state well below T_g . For this the rise of the sample temperature was determined with an infrared camera. This camera registers the black body radiation of the heated spot. With calibration measurements it was possible to determine the laser induced rise of the sample temperature by means of the infrared radiation. For a laser intensity of 0.32 W cm^{-2} ($\lambda = 488\text{ nm}$), an increase of the sample temperature of less than 10° was evaluated after an irradiation time of 60 s. After this time, an equilibrium between sample heating and heat dissipation in the sample was reached and no further temperature increase could be observed. As samples were successfully reoriented starting at room temperature with an intensity as low as 0.01 W cm^{-2} , there is no doubt that the reorientation also takes place at about 35° below T_g .

Above T_g the reoriented side chains slowly relaxed back into the Grandjean texture. Nevertheless a successful reorientation was still possible at temperatures just above T_g as long as the speed of the photoinduced processes was higher than the rate of the viscosity dependent relaxation. At even higher temperatures ($T \approx T_g + 20^\circ$) with a markedly increased relaxation rate, an electric d.c. field helped to stabilize the photoinduced reorientation of dipolar azo dyes like ANAz or ACAz. It is important to mention that well-tempered samples could not be noticeably reoriented by an electric field ($E = 22\text{ MV m}^{-1}$) at this temperature in the absence of light. When the light was turned on under these conditions (electrical field and heat), a quick reorientation took place, showing that the reorientation was still photoinduced. However, every reorientation step had to be stabilized by the field to avoid a quick relaxation. This process might be called 'field-assisted photoinduced rotational diffusion'.

At temperatures not much above T_g , the thermal relaxation of completely reoriented samples led to strongly scattering samples built up of microdomains. However, at $T = 410\text{ K}$, an optically clear sample in the Grandjean texture reappeared without any additional shearing. Therefore the reorientation is an irreversible process below T_g and a totally reversible process at, for example, $T = 410\text{ K}$.

5.2. Cold poling mechanism

Only recently we discovered another field- and light-dependent phenomenon called ‘cold poling’ which is described in [12, 13] and shall be mentioned only shortly. Upon irradiation of samples containing the dipolar azo dye moieties ANAz or ACAz with circularly polarized light at room temperature in the glassy state under the influence of an electric d.c. field, a non-centrosymmetric structure developed. The non-centrosymmetric structure was detected by second harmonic generation showing a high doubling efficiency. The underlying process of ‘cold poling’ is a photoinduced reorientation of the azo dye moieties at room temperature, as described in § 3.2 of this paper. However, the additional electric field has induced the non-centrosymmetric orientation of the dipolar molecules, because a non-centrosymmetric structure was not achieved without the field. No poling at all was observed when the sample was exposed to an electric field at room temperature without irradiation with visible light. Since this new poling mechanism took place at room temperature in the glassy state—in contrast to the other poling mechanisms like d.c. or Corona poling which require a temperature rise to about T_g —this poling mechanism was called ‘cold poling’. The main advantages of this new poling mechanism are the long term stability of the non-centrosymmetric structure in comparison with, for example, Corona poling, and the now discovered gating effect, where only the simultaneous application of light and field leads to the formation of a non-centrosymmetric structure. With this gating effect, a microstructuring by the combined application of a photo mask and an electric field is possible, as sketched in figure 11. This leads to well-defined areas with non-linear optical properties. This is especially interesting for practical applications like producing non-linear wave-guiding structures.

5.3. Influence of the dye concentration

The photoinduced rotational diffusion was demonstrated with samples containing 10, 25 or 30 mol % of one of the three azo dyes. Further experiments showed that the results are generally valid for all samples containing between 10 and 30 mol % of an azo dye. Samples with 5 mol % ANAz may be reoriented at 482 nm, where the extinction coefficient ϵ is especially high. The photosensitivity of the samples is proportional to the dye concentration. However, a quantitative determination of the photosensitivity is difficult in the set-up used here for the investigation of the photoinduced rotational diffusion. Quantitative and more accurate data can be obtained by holographic grating experiments, in which the speed of the formation of a grating is measured for a given light intensity. According to these experiments the photosensitivity increases by a factor of 10 when the dye concen-

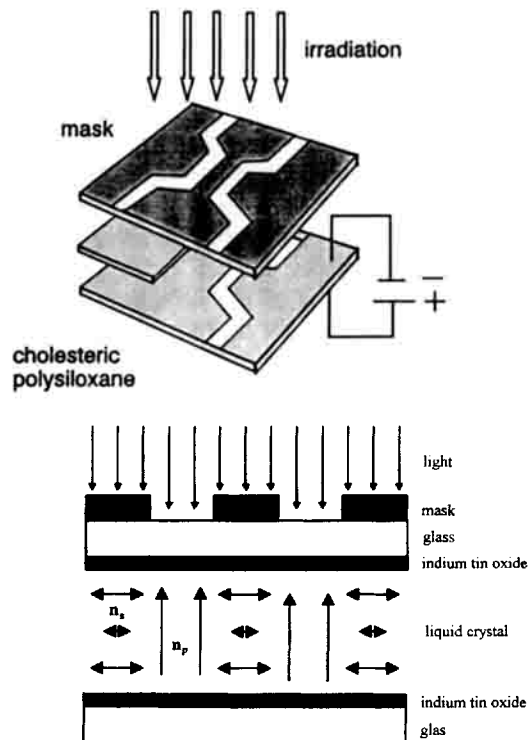


Figure 11. Generation of microstructures with the gating effect. The electric field is applied to the whole sample, whereas local poling is only achieved in the illuminated area through the mask. In this area, non-centrosymmetric homeotropic orientation with a higher index of refraction is achieved compared to the cholesteric phase in the other parts of the sample.

tration is raised from 10 to 30 mol %. These holographic grating experiments will be described in more detail elsewhere [20].

6. Summary

Cholesteric polysiloxanes containing an azo dye moiety in a side chain were successfully reoriented by irradiation with light which is absorbed by the azo dye. Well-defined new structures were formed during the photoinduced rotational diffusion.

Rotational diffusion was detected for samples which contain EAz, ACAz or ANAz as chromophoric side groups. The significant modulation of the optical properties, combined with the well-defined orientation of the side chains, offers the possibility of using light as a tool for the formation of samples with a desired local distribution of the rod-like molecules.

With linearly polarized light, photoselection led to the excitation and rotational diffusion of a subset of appropriately oriented chromophores which form a new Bragg grating. This shows several orders of reflection in contrast

to the initial cholesteric reflection. After continued irradiation, all reflection bands disappear, and a strongly birefringent, dichroic sample with a dichroic ratio of up to 7.0 was obtained. In the initial reorientation step, the predominant reorientation in the nematic layers takes place in the xy plane. By multiple switching of the polarization direction of linearly polarized laser light, it was shown that the molecular long axis was increasingly reoriented into the z direction, finally leading to a homeotropic texture.

A homeotropic texture can also be prepared directly with circularly polarized or unpolarized light. All reorientations took place in the glassy state of the cholesteric polysiloxane, but were also possible at T_g or above T_g if a supporting electric d.c. field was applied. The simultaneous application of circularly polarized light or unpolarized light and an electric d.c. field at room temperature led to the formation of non-centrosymmetric structures in samples containing ANAz or ACAz, an effect which may be used in non-linear optical applications. A gating effect allows the creation of microstructures with non-linear properties when a photomask defines the area which is reoriented by the light.

The mesogenic side chains which do not absorb radiation are co-operatively reoriented as shown by both polarization studies and infrared spectroscopy.

A surprisingly different behaviour was found when samples with EAZ were reoriented with linearly or circularly polarized laser light. Only the formation of the Bragg grating with a relatively small dichroic ratio of the azo dye was possible with linearly polarized laser light. We assume that due to the reorientation and the formation of a distorted helix, the birefringence causes a depolarization and reflection of the laser light which passivates the sample. A complete reorientation was again detected as soon as the linearly polarized polychromatic light from a HgXe lamp was used. Under these conditions only partial depolarization occurred because of the dispersion relation, leaving enough light polarized to push the reorientation ahead.

The light induced structures showed excellent long term stability at room temperature. Above T_g , the relaxation of the side chains back into a helical alignment resulted in a strongly scattering sample after several hours. At $T = 410$ K, the Grandjean texture with good optical quality appeared again without any mechanical shearing.

For all samples with dye concentrations between 10 and 30 mol %, the same products with comparable order parameters were obtained. By including the effects of polarized light, of photoselection and of an electric field, a broad variety of new structures are possible

which may be interesting with regard to practical applications.

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References

- [1] MCARDLE, V. B., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Blackie), Chap. 13.
- [2] EICH, M., WENDORFF, J. H., RECK, B., and RINGSORF, H., 1987, *Makromolek. Chem. rap. Commun.*, **8**, 59.
- [3] EICH, M., and WENDORFF, J. H., 1987, *Makromolek. Chem., Macromolek. Commun.*, **8**, 467.
- [4] ORTLER, R., BRÄUCHLE, CH., MILLER, A., and RIEPL, G., 1989, *Makromolek. Chem. rap. Commun.*, **10**, 189.
- [5] ANDERLE, K., BIRENHEIDE, R., EICH, M., and WENDORFF, J. H., 1989, *Makromolek. Chem. rap., Commun.*, **10**, 477.
- [6] ANDERLE, K., BIRENHEIDE, R., WERNER, M. J. A., and WENDORFF, J. H., 1991, *Liq. Crystals*, **9**, 691.
- [7] WIESNER, U., REYNOLDS, N., BOEFFEL, C., and SPIESS, H. W., 1991, *Makromolek. Chem. rap. Commun.*, **12**, 457.
- [8] WIESNER, U., REYNOLDS, N., BOEFFEL, C., and SPIESS, H. W., 1992, *Liq. Crystals*, **11**, 251.
- [9] ENDRES, B., KRIEG, M., OMEIS, J., and RAU, N., 1990, *Die Angew. Makromolek. Chem.*, **183**, 103.
- [10] PETRI, A., BRÄUCHLE, CH., LEIGEBER, H., MILLER, A., WEITZEL, H.-P., and KREUZER, F.-H., 1993, *Liq. Crystals*, **15**, 113.
- [11] EP 92119475.9-, (12.1.1993), Consortium für elektrochemische Industrie GmbH.
- [12] PETRI, A., KUMMER, S., ANNESER, H., FEINER, F., and BRÄUCHLE, CH., 1993, *Ber. Bunsenges. phys. Chem.*, **97**, 1281.
- [13] ANNESER, H., FEINER, F., PETRI, A., BRÄUCHLE, CH., LEIGEBER, H., WEITZEL, H.-P., KREUZER, F.-H., HAAK, O., and BOLDT, P., 1993, *Adv. Mater.*, **5**, 556.
- [14] MICHL, J., and THULSTRUP, E. W., 1986, *Spectroscopy with Polarized Light* (Verlag Chemie).
- [15] EP 0060335 (16.03.81), Consortium für elektrochemische Industrie GmbH.
- [16] DOF 3940148A1 (5.12.89), Consortium für elektrochemische Industrie GmbH.
- [17] MAIER, W., and SAUPE, A., 1959, *Z. Naturf. (a)*, **14**, 882.
- [18] GÜNZLER, H., and BÖCK, H., 1983, *Infrarotspektroskopie*, (Verlag Chemie), 2nd edition, p. 223.
- [19] RAU, H., and LÜDDECKE, E., 1982, *J. Am. chem. Soc.*, **104**, 1616.
- [20] PETRI, A., and BRÄUCHLE, C., in preparation.