Liquid Crystals

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

Holographic storage via the liquid crystal state: a success story

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To cite this Article Wendorff, J. H. , Anderle, Klaus , Birenheide, Richard , Werner, Martin J. A. and Wendorff, Joachim H.(2006) 'Holographic storage via the liquid crystal state: a success story', Liquid Crystals, 33: 11, 1419 — 1427

To link to this Article: DOI: 10.1080/02678290601119815

URL: http://dx.doi.org/10.1080/02678290601119815

Liquid Crystals, Vol. 33, Nos. 11–12, November–December 2006, 1419–1420

Holographic storage via the liquid crystal state: a success story

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A Commentary on the paper "Molecular addressing? Studies on light-induced reorientation in liquid crystalline side chain polymers", by K. Anderle, R. Birenheide, M. J. A. Werner and J.H. Wendorff. First published in *Liquid Crystals*, **9**, 691–699 (1991).

Azobenzene chromophores are subjected to isomerization cycles if irradiated with light of an appropriate range of wavelengths. The isomerization process does not only take place in low viscosity solutions but also in highly viscous polymer melts all the way up to the solid glassy state. A coupling between the isomerization process and molecular motions characteristic of the amorphous matrix is apparent. These facts were well known to us, of course, in 1985 as we started our investigations on azobenzene isomerization processes in liquid-crystalline environments. We were particularly interested in liquid-crystalline side chain polymers in which the azobenzene units were part of the side chains covalently linked to the polymer backbone.

Manfred Eich, a young Ph.D. student at that time, now a Professor of Physics at a university in Hamburg, was concerned at this time in my group at the Deutsches Kunststoff-Institut (DKI) in Darmstadt, Germany with the coupling between the kinetics of isomerization and the kinetics of the particular molecular motions occurring in such liquid-crystalline side-chain polymers. He decided to induce the isomerization processes in monodomain samples to take advantage of the anisotropic nature of the liquid-crystalline state and he decided to use linearly polarized light for the irradiation of the chromophores, for the same reason. Within a short time he made the rather unexpected but especially fascinating observation that linearly polarized light not only induced the isomerisation but caused, in addition, a reorientational motion of the molecular long axis of the chromophore. The finding was for planar monodomain samples that the long axes rotated away from the preferred direction along the director to a final orientation perpendicular to this direction if the polarization direction was selected to be along the director. This happened within the solid glassy state at temperatures well below the glass transition and the reoriented state was found to be stable after switching the writing light off.

It was at once apparent that such an effect might be exploited for optical information storage, not only for digital but also for holographic storage including polarization holographic storage. The problem was, however, that the laboratories at the DKI were not really equipped for optical investigations of this kind, in particular not for holographic studies. Fortunately, just at this time, German chemical companies became interested in the topic of optical information storage on the basis of functional polymers and the interest in liquid-crystalline polymers in general was also very strong at that time.

So within a short time a chemical company-university research project financed by the German Federal Ministry for Research and Development was on its way and this project allowed us to set up all the equipment needed not only to to perform holographic studies but also to hire new Ph.D. students. Klaus Anderle, Richard Birenheide as well as Martin Werner were among them. Due to their strong motivation and experimental skills they came up with the results concerning details of the molecular processes involved in holographic storage which were reported in the 1991 *Liquid Crystals* paper considered here and summarized in the abstract as follows:

"Polarized light leads to an effective reorientation of the optic axis in the glassy state of liquid-crystalline side chain polymers containing azobenzene mesogenic groups via a *trans*-*cis* and *cis*-*trans* isomerization. Using a combination of UV and IR dichroitic studies it is shown for copolymers consisting of chromophores (azobenzene) and non-chromophores (phenyl benzoate) that only the chromophores are reoriented by light as far as the glassy state is concerned. Individual chromophores are thus addressed by photoselection.

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2006 Taylor & Francis
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DOI: 10.1080/02678290601119815

Photoselection in the fluid nematic state, on the other hand, leads also to a reorientation of the non-chromophores."

This publication actually met with tremendous interest at an international level not only in academia but also in industrial laboratories. As a consequence industrial funding continued for nearly nine years, many students became interested in this topic and applied for Ph.D. projects in this area, many members of the group were invited to conferences worldwide, other groups became strongly interested in cooperations in this area contributing their own specific expertise. A short survey on relevant publications follows [1–27]. Furthermore, I was invited as a visiting scientist to the research laboratories of Philips in Eindhoven, The Netherlands in the area of optical storage and I spent more than half a year at Philips on a kind of sabbatical leave from the DKI. I enjoyed the industrial environment gaining a lot of experience during this time.

Based on the results reported in *Liquid Crystals* we went on to learn more about the effect of the molecular dynamics of the polymer matrix [6, 15, 18, 20] as well as of the effect of other chromophore species able to isomerize on holographic storage [2, 9], we performed theoretical studies including Monte Carlo simulations to understand isomerization in anisotropic media in detail [2, 8, 9, 17], we investigated the differences in the storage processes taking place in liquid-crystalline, in frustrated liquid-crystalline and in amorphous environments [3, 5, 7], we studied again effects following storage in a non-equilibrium amorphous glass which on annealing turned liquid-crystalline [3, 5], again effects resulting from crystallization subsequent to the formation of the liquid-crystalline phase [1], holographic storage in discotic rather than calamitic systems [1, 4] and finally also the effect of the formation of light-induced surface modulations accompanying the writing-in of a grating pattern [1, 2, 3]. A side topic was the preparation of holographic optical elements such as Fresnel lenses or diffraction gratings based on isomerization in side-chain liquid-crystalline polymers [12, 19, 25].

All in all, this topic has been close to me for up to 20 years now. It has fascinated young students looking for a diploma or a Ph.D. thesis, and foreign students looking for a postdoctoral position for nearly two decades but it has also fascinated politicians such as, for instance, the Secretary of Research of the State of Hessen, which is important in terms of funding for the university.

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Liquid Crystals, Vol. 33, Nos. 11–12, November–December 2006, 1421–1427

Molecular addressing? Studies on light-induced reorientation in liquid-crystalline side chain polymers

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(*Received 21 June 1990; accepted 14 December 1990*)

Polarized light leads to an effective reorientation of the optic axis in the glassy state of liquid-crystalline side chain polymers containing azobenzene mesogenic groups, via a *trans–cis* and *cis–trans* isomerization. Using a combination of UV and IR dichroitic studies it is shown for copolymers consisting of chromophores (azobenzene) and non-chromophores (phenylbenzoate) that only the chromophores are reoriented by light as far as the glassy state is concerned. Individual chromophores are thus addressed by photoselection. Photoselection in the fluid nematic state, on the other hand, leads also to a reorientation of the non-chromophores.

1. Introduction

The laser addressing of liquid-crystalline side chain polymers for optical information storage has been the subject of numerous publications. Thermooptical recording techniques were introduced, employing a transparent monodomain film of a liquid-crystalline polymer which is locally heated by a focused laser beam up into its isotropic phase. Subsequent fast cooling results in scattering spots which can be detected optically [1–3]. As this involves a collective response (formation of scattering domains), the resolution of this method is restricted.

More recently, a new type of information storage in liquid-crystalline side chain polymers containing azobenzene mesogenic groups was reported by us. We were able to show (i) that a storage process can be performed in the solid glassy state via a *trans–cis–trans* isomerization cycle of the azobenzene units [4–9], and (ii) that this isomerization cycle causes a reorientation of the optic axis of the system. The result is a high quality phase object [10] (see figure 1). This process is, in principle, based on a combination of photoselection and a subsequent more or less random reorientational motion of the selected molecules [11, 12] as controlled by the local dynamics of the glassy state.

A similar yet not identical effect has recently been analysed theoretically [13, 14] for the case of azobenzene in matrices, which are not solid but viscous. The important difference is that brownian motions are allowed to occur in the latter case, which will, of course, affect the stability of the induced reorientation as well as the coupling between the reorienting molecules and those of the matrix. In addition, the treatment allowed only for small deviations from equilibrium, i.e. from an isotropic orientational distribution function [15].

We have proposed a different phenomenological description of this effect, which is able to account for all phenomena found for liquid-crystalline systems as well as for amorphous systems in the glassy state, and which allows us to calculate also changes of the orientational distribution far from the original [12]. This model was based on several assumptions.

1. The molecules are held in a glassy matrix. As a result there is no brownian motion or any other effect which drives the molecules back to their original orientational distribution function after having changed their orientation under the influence of an isomerization process.
2. Only those molecular groups can change their orientation which undergo an isomerization cycle. In other words, only the axis of the chromophores should be reoriented in a copolymer consisting of isomerizable chromophores (azobenzene) and non-chromophores. This assumption implies consequently that we should be able to address single molecules: molecules react without influencing their surrounding, i.e. the matrix.
3. The reorientation is the effect of the local mobility within the glassy state, as controlled by free

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ISSN 0267-8292 print/ISSN 1366-5855 online
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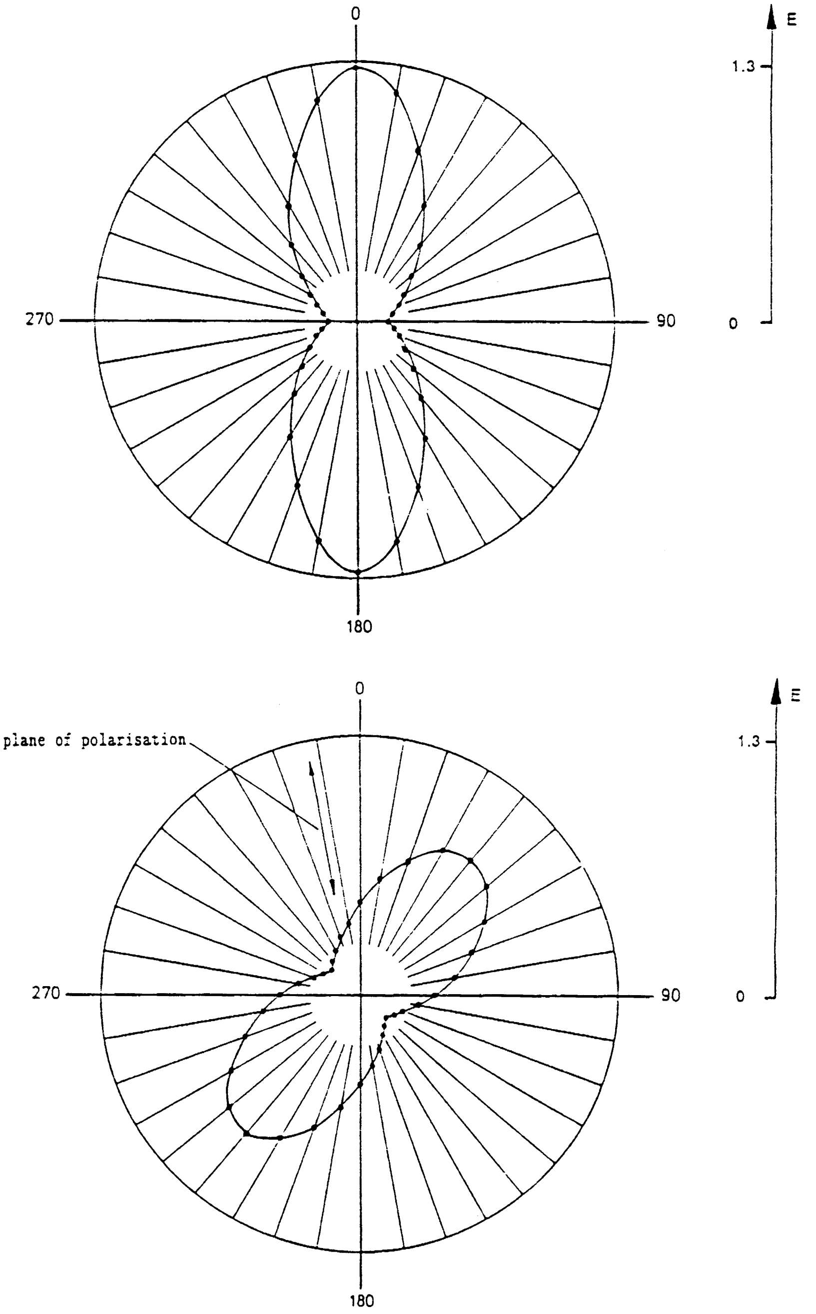

Figure 1. Absorption as a function of polarization at 360 nm of an azobenzene homopolymer [10] before and after irradiation with polarized light. The polarization of irradiating light was tilted 10° towards the director.

volume fluctuations [16, 17] and a partial or complete memory loss of the molecules undergoing isomerization cycles as far as their original orientation is concerned.

(4) The molecules are subjected to the isomerization cycle and the corresponding reorientational motion unless the transition dipole moment is perpendicular to the polarization direction of the light. The final orientational state is one in which all chromophores fulfill this requirement.

Despite these strong assumptions, the predictions of the resulting equations agree quite well with our experimental results. This was a motivation for us to try to test these assumptions experimentally. For this purpose we have studied the effect of photoselection on the

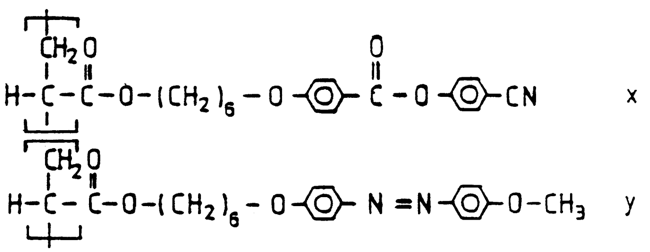

Figure 2. Copolymer used for the IR and UV dichroism experiments (x=0.5, y=0.5). Note the different substituents of the azobenzene and phenylbenzoate groups.

reorientation of the molecules in the glassy state on the one hand and in the fluid nematic state on the other hand. The expectation is that the assumptions (1) and (2) are no longer fulfilled for photoselection in the viscous state [18]. IR dichroism experiments were chosen as the experimental technique. The basic concept of the experiment was to use a nematic side chain copolymer with one co-monomer being sensitive to light and the other being unable either to absorb light of the desired wavelength or to perform an isomerization upon irradiation (see figure 2). This polymer has a glass transition temperature of 30°C and a transition from the nematic into the isotropic phase at 110°C. The reorientation of the molecules was detected by UV-VIS dichroism for the light-sensitive molecules and IR dichroism measurements of the CN stretching band were used to detect motions of the light-insensitive molecules. As the azobenzene unit contains no CN group we are able to detect motions of the phenylbenzoate groups only. Photoselection was done at room temperature, i.e. in the glassy state, and at temperatures of 40°C and 50°C, i.e. in the fluid nematic state.

2. Experimental

The synthesis of the polymer has been described elsewhere [19, 20]. In order to obtain homogenous liquid-crystalline side chain polymer monodomain films of high optical quality, polymide coated and subsequently rubbed glass plates or silicon wafers were prepared [8]. The side chain polymers were coated from dilute solution (5 per cent by weight, thickness <1 μm) on such a substrate. Annealing for 15 min in the viscous

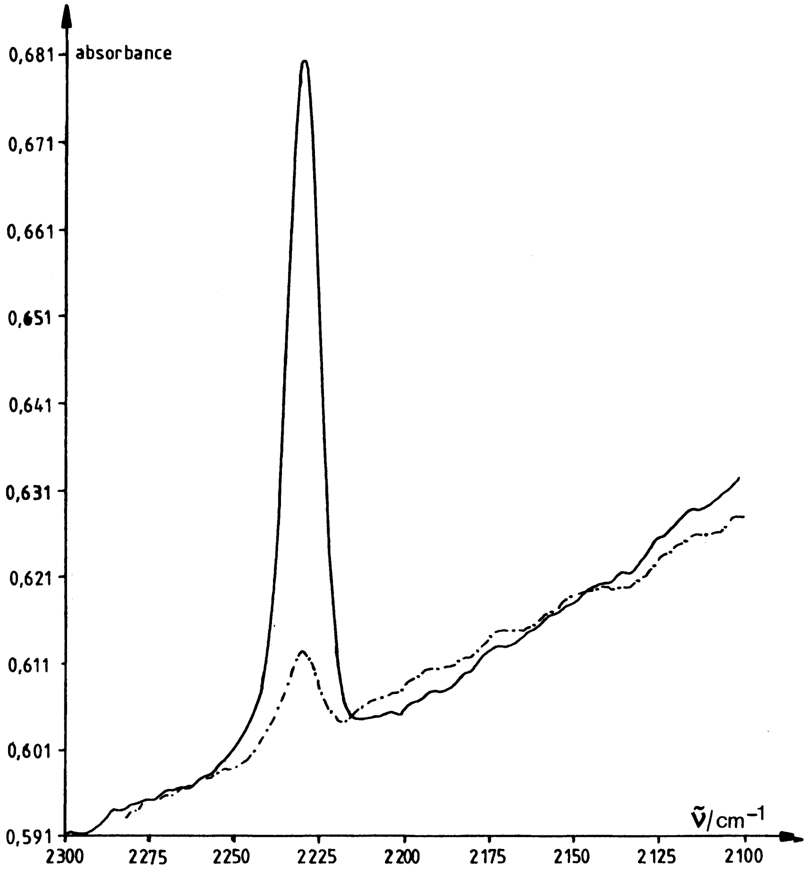

Figure 3. UR absorption spectra in the 2230 cm^{-1} region of the copolymer with light polarized parallel and perpendicular to the director.

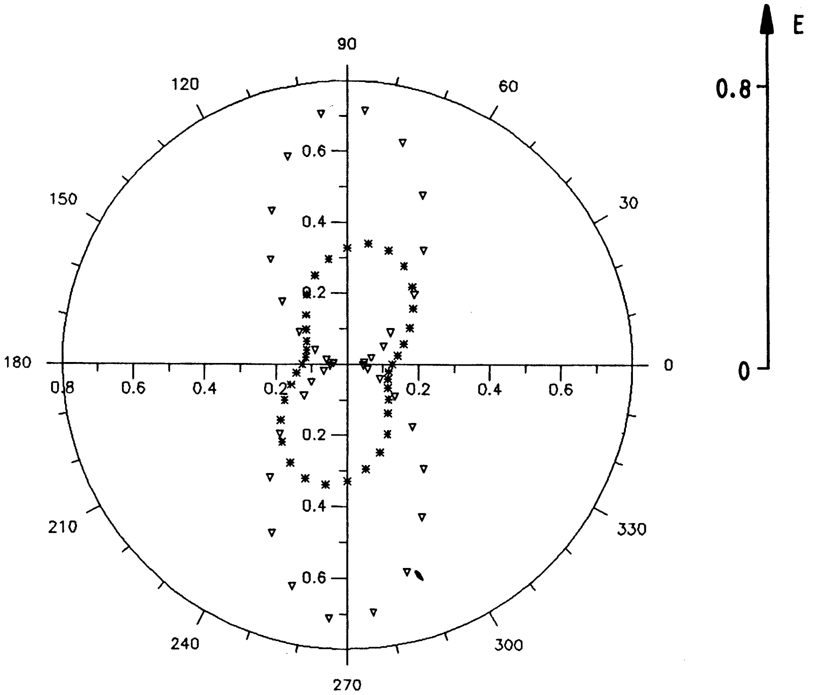

Figure 4. UV absorption of the copolymer at 360 nm before and after irradiation with polarized light of 488.0 nm. The absorption is shown as a function of the polarization of the measuring (360 nm) light. The irradiating light was tilted 10° with respect to the director.

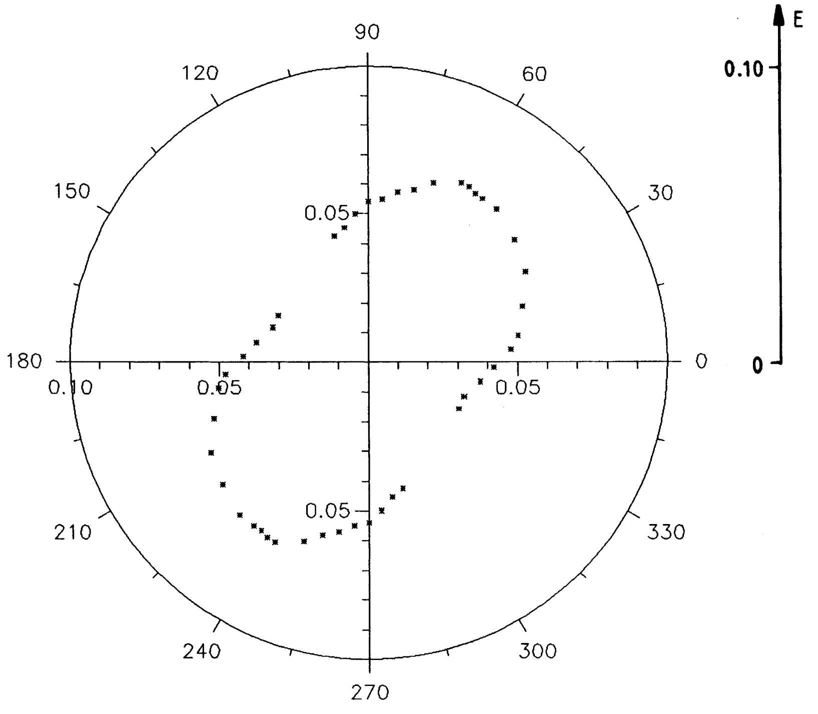

Figure 5. Polar diagram of the absorbance of the copolymer at 2230 cm^{-1} after irradiation with 488.0 nm at 40°C and polarization at 350°. The initial director was along 0°.

state at temperatures close to the nematic–isotropic transition temperature yielded defect free monodomain films. The samples were then illuminated with a Lexel 95-4 argon laser operating at 488.0 mW/cm. For the absorption spectroscopy studies in the UV range a Perkin-Elmer UV-VIS 554 spectrometer was used. In order to perform measurements for different angles between the polarization plane and the nematic director, two synchronously operating Glan prisms were mounted in the sample beam path and in the reference beam path respectively. The experiments in the IR range were performed with a Nicolet 60SX FTIR spectrometer in transmission. The incident beam was polarized by means of a grating polarizer working in the IR range. The CN stretching band at about 2230 cm^{-1} was used for the dichroism experiment.

3. Results and discussion

3.1. *Photoselection in the glassy state*

Figure 3 shows the IR absorption spectra obtained for the copolymer for polarization parallel and perpendicular to the nematic director. The spectra measured at ambient temperature are shown. The analysis of the magnitude of the absorption parallel and perpendicular to the director yields the orientational order parameter S [21]

$$S=\frac{A_{\parallel}-A_{\perp}}{A_{\parallel}+2A_{\perp}}.$$

This represents the appropriate formula since the C–N stretching band is characterized by a transition moment which is, to a good approximation, parallel to the long axis of the phenylbenzoate unit. As a result the order parameter can be determined from figure 3 by calculating the absorbance of the CN band as the difference between the maximum and the base of the appropriate peak. The particular value obtained for this polymer is $S=0.71$.

Figure 4 shows the variation which is induced in the distribution of the azobenzene units due to illumination with light from the argon laser having its polarization tilted by $\Psi=10^\circ$ relative to the nematic director. The illumination was performed at room temperature below the glass transition temperature. The intensity used is not able to increase the temperature above the glass temperatures [18]. The spectroscopic measurements were performed at room temperature after the thermal *cis–trans* back relaxation was completed. The experimental finding is that the local optic axis which controls the anisotropy of the extinction has been reoriented by a discrete angle ϕ of 12°. The analysis of figure 4 yields an order parameter S defined for the new direction of 0.40. The degree of order has thus been decreased considerably compared to the unilluminated sample. The same experiment was performed on the samples coated on silicon wafers. All experiments carried out on the CN stretching band yielded no change neither in orientation nor in order parameter. As a result the experimental finding is that light insensitive phenylbenzoate units do not change their orientation to a measurable amount.

From these results we can conclude that upon irradiation in the glassy state only those molecules can change their orientation which are isomerized by the incident light (see figure 6(*a*)). This agrees with assumption 2 and verifies assumption 1 to a certain extent. Furthermore we find that the reorientation process in those systems is totally a local process if the irradiation is performed in the glassy state. This is in agreement with the very high resolution obtained in those systems (up to 5000 l/mm). Since there is no coupling of a selected molecule to the surrounding, we

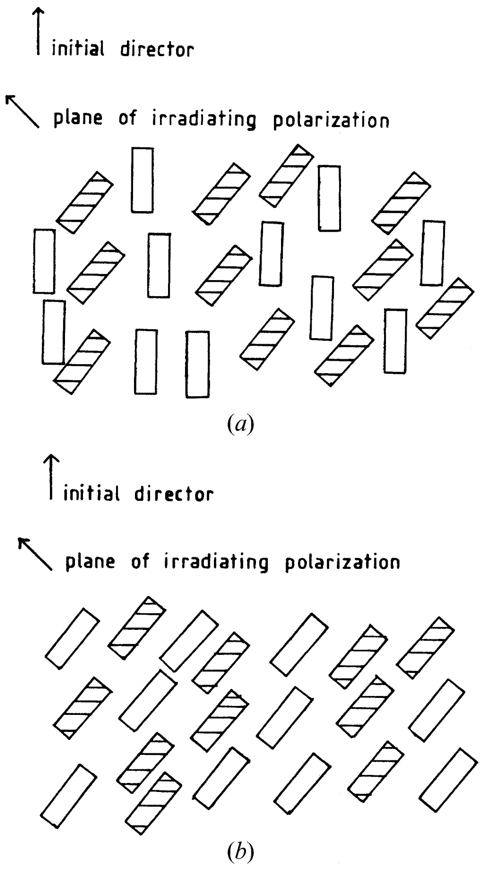

Figure 6. Schematic representation of the storage process in a copolymer on a molecular level (*a*) in the glassy state, (*b*) in the fluid nematic state. In the stationary state the photoselected molecules should have an orientation 90° towards the polarization of the incident light.

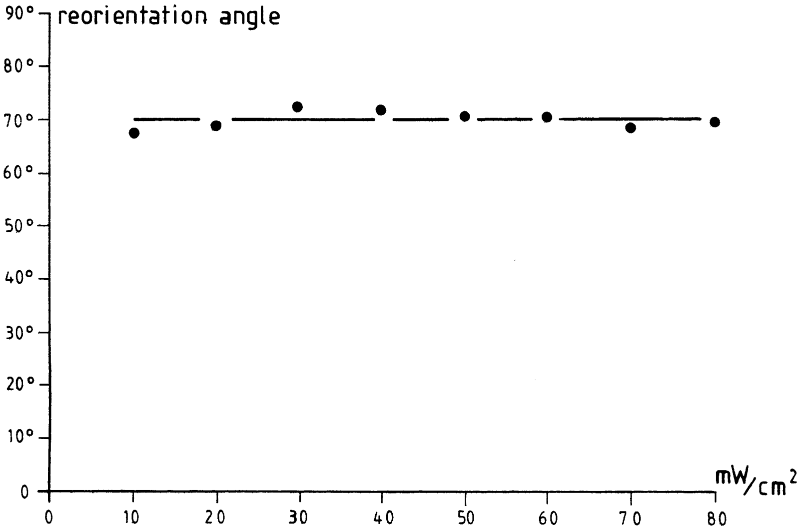

Figure 7. Angle of reorientation as a function of the intensity of the irradiating light. The irradiating energy was held constant at 72 J/cm^{-2}, i.e. the illumination time was varied in an appropriate manner. The polarization of the incident light was tilted 10° with respect to the director.

conclude that we should be able to address the system on a molecular level, i.e. a single molecule.

Another result which is in accord with these results is the finding that the magnitude of reorientation depends only on the energy brought into the system by the incident light and not on its intensity (see figure 7). The phenomenological theory predicts this behaviour if the assumptions hold.

4. Photoselection in the nematic fluid state

Figure 5 shows the polar diagram of the CN stretching band after irradiation of the azobenzene units due to illumination with light from the argon laser having its polarization tilted by Ψ of 10° relative to the nematic director. The illumination was performed at 40°C, i.e. above the glass transition temperature. The spectroscopic measurement was performed at room temperature after the thermal *cis–trans* back relaxation was completed. The experimental finding is that the local optic axis which controls the anistropy of the extinction at 2230 cm^{-1} has been reoriented by a discrete angle. As one can see the order parameter of the non-chromophoric mesogens has been decreased considerably to 0.25. The same experiment carried out at 360 nm in the UV experiment leads to similar results as in the IR experiment, beside the fact that we find an order parameter of the azobenzene of about 0.5. Under the same conditions of irradiation, the change of the optic axis is about the same for the chromophores and the non-chromophores.

From these results we can conclude that upon irradiation in the viscous nematic state both the dye molecules as well as their surrounding can change their orientation. This shows that assumptions (1) and (2) are no longer valid above the glass transition temperature.

5. Conclusions

From these results we can conclude that we should be able to address single molecules in the glassy state (see figure 6 (*a*)) and that there is a collective process in the fluid nematic state (see figure 6 (*b*)), when photoselected rotational diffusion in a liquid-crystalline side chain polymer takes place.

Acknowledgements

We gratefully acknowledge the financial support of the BMFT (Bundesministerium fur Forschung und Technologie). We thank Dr. Rau, Röhm GmbH, Darmstadt, for providing us with the sample.

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