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

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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].

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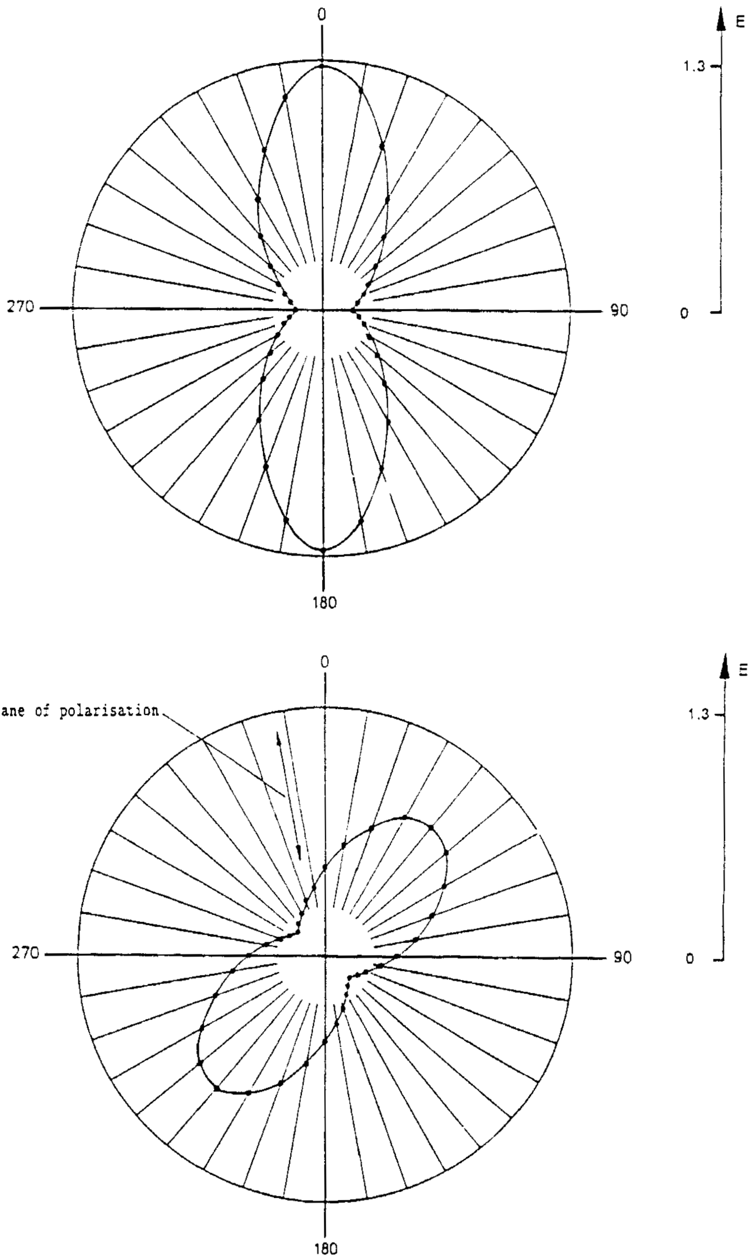


Figure 1. Absorption as a function of polarization at 360 nm of an azobenzene homopolymer [10] before and after irradiation with polarized light. The polarization of irradiating light was tilted 10° towards the director.

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 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 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

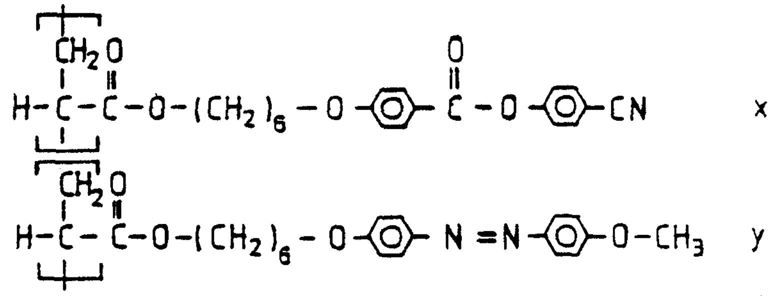


Figure 2. Copolymer used for the IR and UV dichroism experiments ($x=0{\cdot}5, y=0{\cdot}5$). Note the different substituents of the azobenzene and phenylbenzoate groups.

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 $< 1\,\mu$m) on such a substrate. Annealing for 15 min in the viscous 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 $S=0{\cdot}71$.

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 $\Psi=10°$ 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

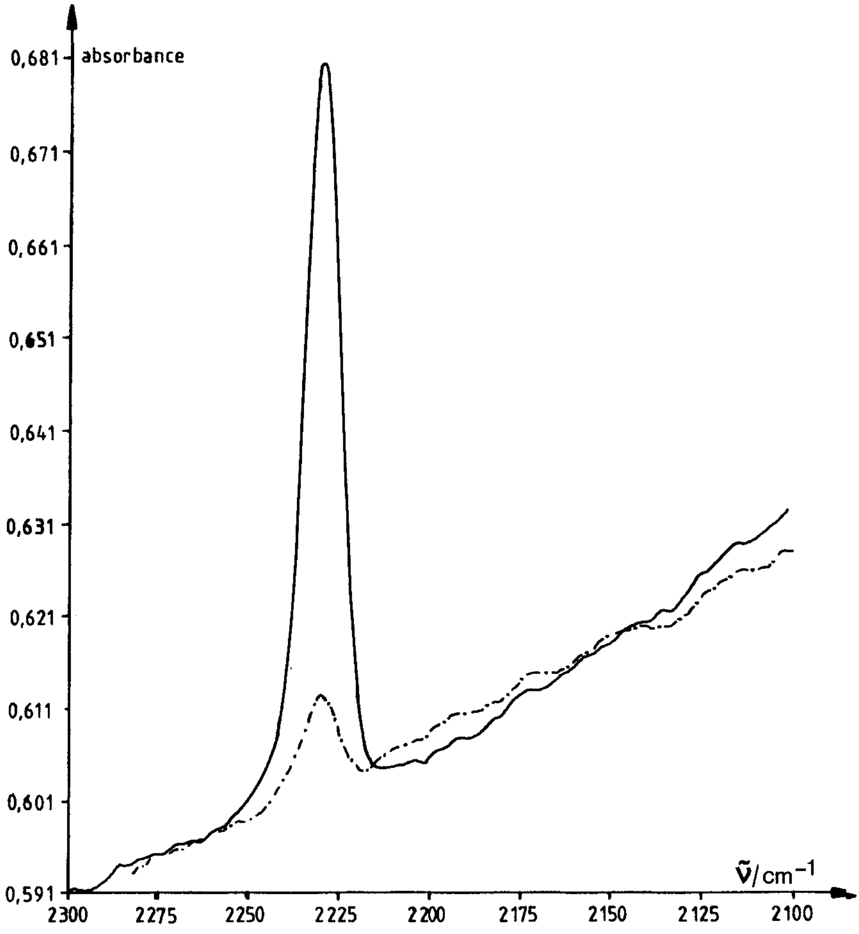


Figure 3. UR absorption spectra in the 2230 cm^{-1} region of the copolymer with light polarized parallel and perpendicular to the director.

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

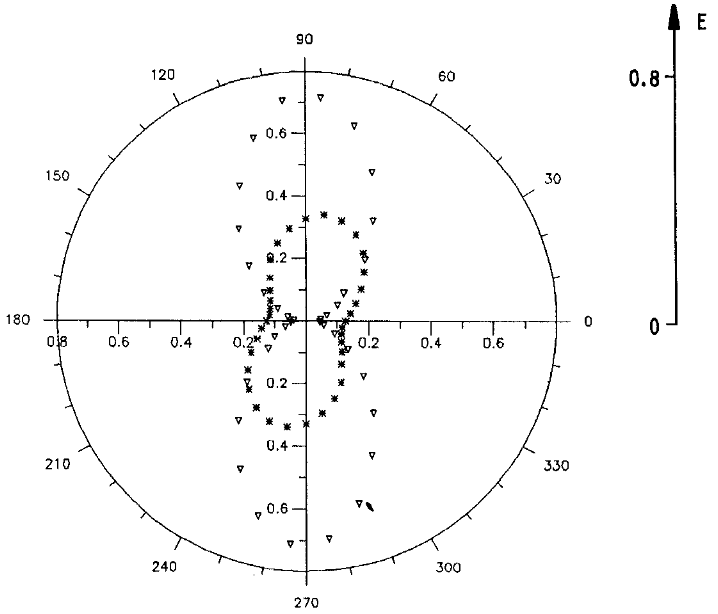


Figure 4. UV absorption of the copolymer at 360 nm before and after irradiation with polarized light of 488·0 nm. The absorption is shown as a function of the polarization of the measuring (360 nm) light. The irradiating light was tilted 10° with respect to the director.

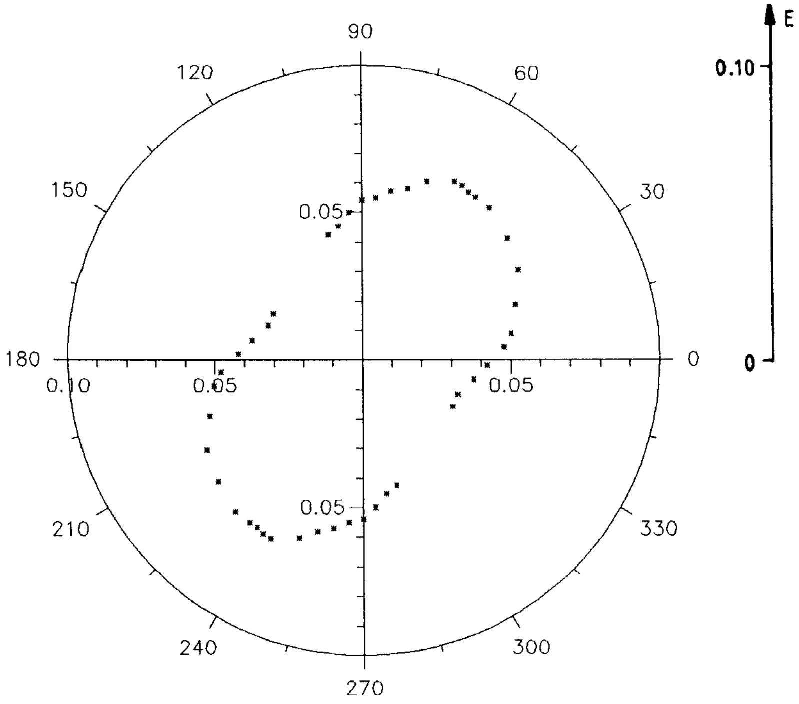
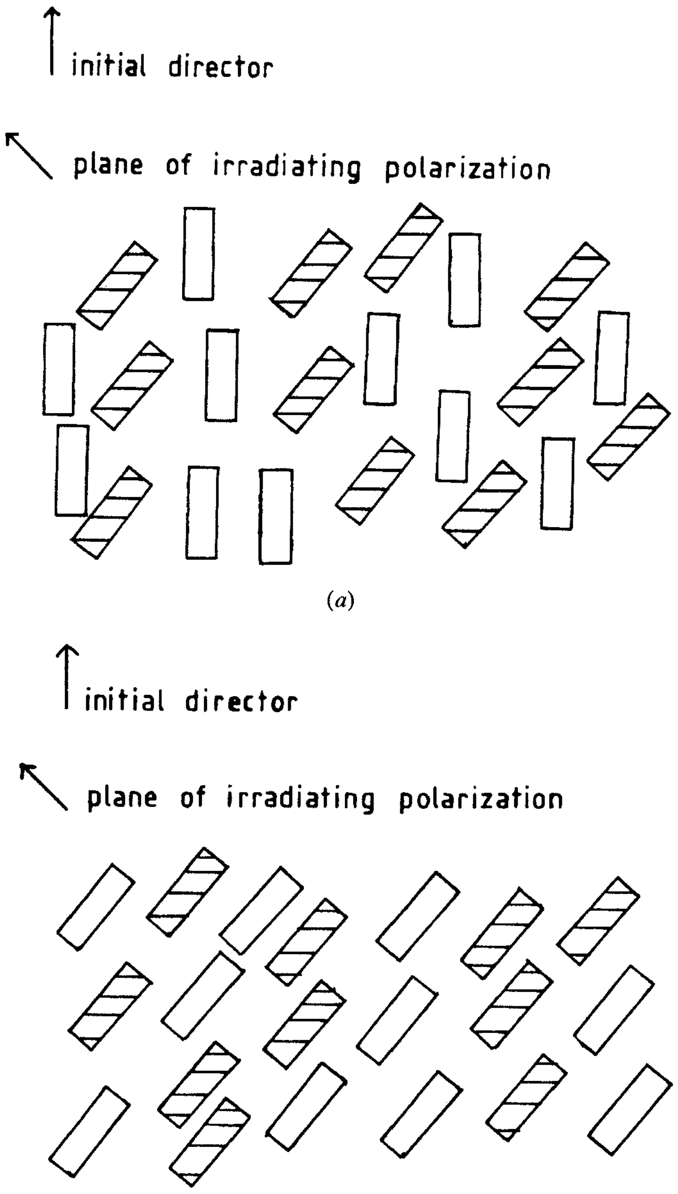


Figure 5. Polar diagram of the absorbance of the copolymer at 2230 cm^{-1} after irradiation with 488·0 nm at 40°C and polarization at 350°. The initial director was along 0°.



(*a*)

(*b*)

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.

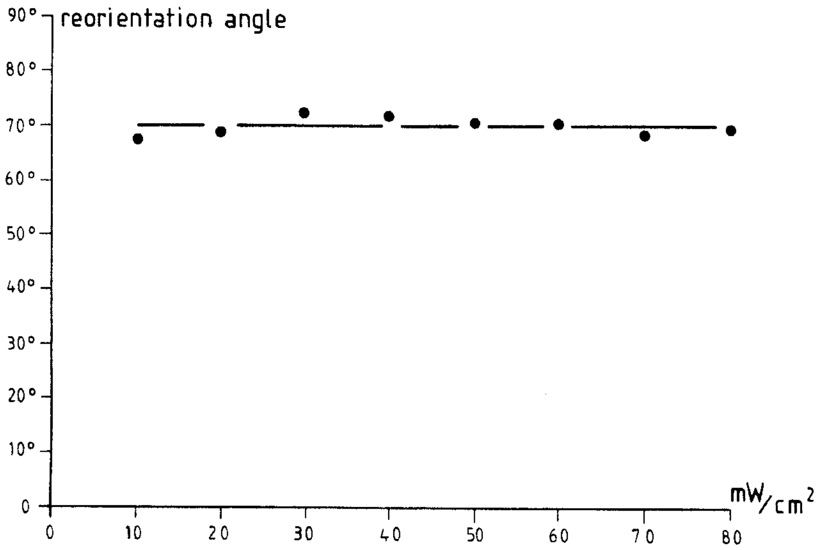


Figure 7. Angle of reorientation as a function of the intensity of the irradiating light. The irradiating energy was held constant at 72 J/cm^{-2}, i.e. the illumination time was varied in an appropriate manner. The polarization of the incident light was tilted 10° with respect to the director.

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.

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