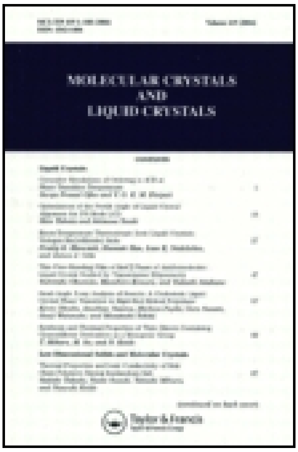

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Influence of Supramolecular Order on the Light-Induced Reorientation Process in Photochromic Side Group Polymers

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INFLUENCE OF SUPRAMOLECULAR ORDER ON THE LIGHT-INDUCED REORIENTATION PROCESS IN PHOTOCHROMIC SIDE GROUP POLYMERS

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Abstract A new approach for optical data storage is presented using amorphous films of photochromic polymers. Concerning the tendency to form supramolecular order these polymers are situated at the border between amorphous and Liquid Crystalline Polymers (LCP's). The light–induced reorientation of the photochromic azobenzene moieties by an angular–dependent photoselection process may cause a reorientation of the non–photochromic moieties. In this way an optical axis is generated in the initially amorphous films by a photochemically induced physical orientation process. The resulting values of optical anisotropy are close to those of aligned LCP films.

INTRODUCTION

Recently much attention has been paid to the development of photochromic polymers for optical data storage and processing. The effect of polarized light on photochromic molecules in inducing photochemically dichroism and birefringence has been well known in different matrices for several decades[1,2]. The interaction of photochromic polymers with polarized light offers a new method of orienting photochromic moieties and in this way to modify the optical properties of polymers. Angular–dependent photoselection on covalent bonded azobenzene moieties allows the efficient modification of the optical anisotropy in LCP's[3–7] as well as the generation of optical anisotropy in amorphous photochromic polymers[8–10]. However, the preparation of non–scattering, uniformly aligned films of LCP is a difficult procedure. On the other hand, the values of birefringence which have been induced in amorphous polymers are very small.

We have investigated the border between these two classical types of polymers to find materials which combine the easy handling of amorphous films with the high

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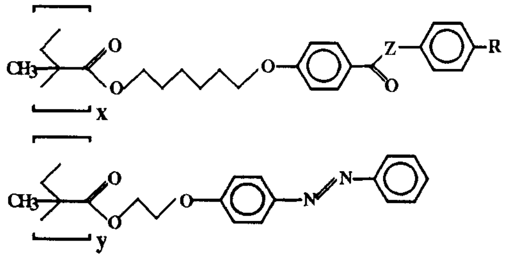
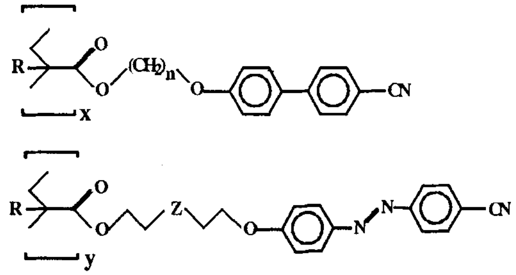
values and long-term stability of optical anisotropy that are characteristic of aligned LCP films. The aim of this paper is to show that this combination can be realized by two different approaches[11] either with LCP's from which amorphous films can be prepared[12] or with amorphous polymers which contain rod-like side groups[13]. Moreover, we discuss the influence of the tendency to form liquid crystalline order on the amount and the stability of the light-induced optical anisotropy.

EXPERIMENTAL

The structure and properties of some of the investigated polymers are shown in Figure 1. They were sandwiched between two glass plates forming films of 2μm thickness.



Polymer	I	II	III	IV
Z	NH	NH	NH	O
R	CN	OC_4H_9	OC_4H_9	OC_4H_9
y/(x+y)	0.24	0.3	0.4	0.5
T_g [°C]	97	75	79	63
T_c [°C]	-	102	-	78
$\Delta_t H$ [J/g]	-	1.32	-	1.6



Polymer	V	VI	VII	VIII
n	2	3	5	5
Z	O	$(CH_2)_2$	$(CH_2)_2$	$(CH_2)_2$
R	CH_3	H	H	H
y/(x+y)	0.6	0.2	0.2	0.4
T_g [°C]	77	61	38	38
Phases	-	s_A	s_A94n	s_A106n
T_c [°C]	-	95	103	113
$\Delta_t H$ [J/g]	-	0.2	4.4	4.3

FIGURE 1 Structure and glass transitions, T_g, of the polymers as well as clearing temperatures, T_c, and phase transition enthalpies, $\Delta_t H$ of the LCP's

Films of polymers were oriented uniformly planar by slow cooling from the isotropic melt and annealing in the liquid crystalline state. Optically amorphous films of the LCP's were prepared by supercooling the isotropic melt.

Irradiation with linearly polarized light was carried out with an argon laser (Coherent, λ=488 nm; P=800 W/sqm), measuring the induced birefringence at λ=632.8 nm.

The spectra were measured with a Lambda 19 UV/Vis spectrometer (Perkin Elmer) and a RS 1 FTIR spectrometer (Mattson Instruments), respectively. Both spectrometers were equipped with polarizers, driven by a computer-controlled stepper. The minimum and maximum absorbance yield the dichroic ratio, R=A[max]/A[min]. Analogous to the method known from nematic liquid crystals a spectroscopic degree of order, S=(R−1)/(R+2), was calculated to characterize the orientation.

RESULTS

Angular-dependent photoselection in polymers with azobenzene side groups

On irradiation the rod-like azobenzene moieties undergo E−Z isomerization and the steady state of the photoreaction is easily established. The generated Z isomers are characterized by a more crooked geometrical shape and a changed polarity. They modify their molecular environment, causing a change of the arrangement of the different moieties in the glassy state of amorphous films and a disturbance of the liquid crystalline order in aligned films. Moreover, in both types of films the supramolecular structure is strongly affected by the dynamics of the photostationary equilibrium.

The transition moment of the E azobenzene coincides with its long molecular axis. Thus, the probability of its excitation by linearly polarized light is proportional to the square cosine of the angle Φ between the long molecular axis and the electric field vector of the actinic light, i.e. moieties which are oriented parallel to the electric field vector are excited preferably whereas those with a perpendicular orientation do not undergo photoisomerization. The rotational diffusion processes which are involved in an E $\rightleftarrows$ Z isomerization cycle result in a change of site and orientation of the azobenzene side groups. If Φ is increased due to the changed orientation, the probability of repeated excitation will become smaller. Moieties which become oriented perpendicular cease to take part in the photoreaction. In this way, a large number of successive photoisomerization steps within the steady state result in a directed reorientation. Detecting this process by polarized spectroscopy, we show in the following paragraphs how the angular-dependent photoselection is influenced by the supramolecular order of the polymer films.

Reorientation in planar aligned LCP films

In the initial state of the experimental set-up the azobenzene moieties in a film of LCP **VI** are oriented in the 45^{0} direction of a laboratory frame. The actinic light is polarized along the 90^{0} direction ($\Phi=45^{0}$). During irradiation the angle between the maximum absorbance of the π-π^{*} transition of E azobenzene moieties and the electric field vector of the actinic light is continuously enlarged to a perpendicular orientation in the final state (see Fig. 2). Simultaneously the spectroscopic degree of order is decreased from 0.40 to 0.16 after thermal Z–E isomerization (see Fig. 3).

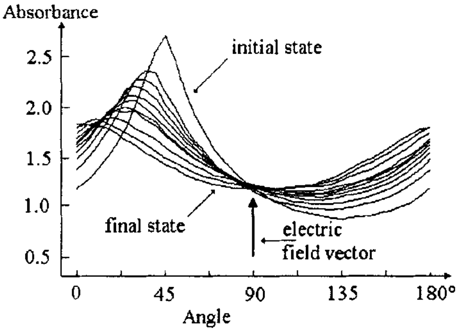
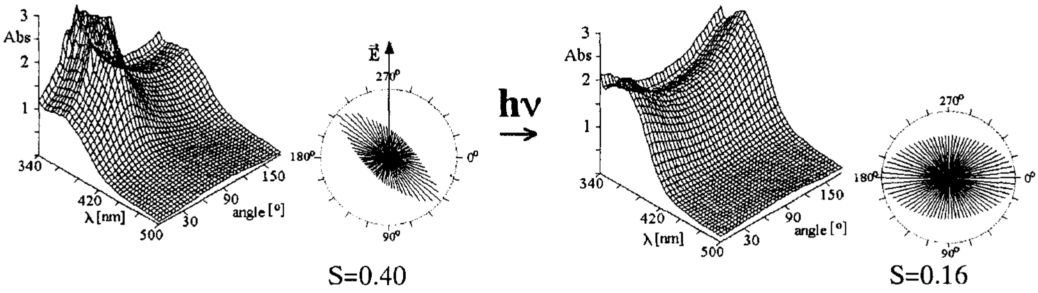


FIGURE 2 Change of absorbance at 378 nm and its angular dependence during polarized irradiation of a planar oriented film of LCP VI (λ_{irr}=488 nm).



S=0.40 S=0.16

FIGURE 3 Angular dependent UV/Vis spectra and absorbance at 378 nm of an oriented film of LCP VI before and after polarized irradiation (λ_{irr}=488 nm) and thermal Z–E relaxation; E indicates the direction of the electric field vector

However, the absorption of polarized light does not necessarily result in a reorientation via the angular-dependent photoselection process as described above. The azobenzene moieties of LCP VII are reoriented only through a very small angle (left part of Fig. 4). Moreover, the decrease of the order parameter is much smaller than in the case of LCP VI. The only difference in the structure of both polymers is the length of the alkyl spacer between the polymer backbone and the cyanobiphenyl moiety. The longer (and hence more flexible) spacer of LCP VII causes a lower glass transition temperature and a higher stability of the liquid crystalline phase (compare Fig. 1). For this reason a director reorientation by the photoselection process is strongly hindered.

If the disturbance of the initial liquid crystalline order caused by the photoisomerization is enlarged due to a higher content of photochromic moieties, the "reorienting power" of the polarized light is amplified. Thus, the photoselection process occurs in LCP VIII, a polymer with the same spacer length as LCP VII and a comparable stability of the liquid crystalline order but twice as much photochromic groups. However, the decrease of the degree of order as a result of the reorientation process is significantly smaller than for LCP VI because of the stronger stability of the liquid crystalline phase.

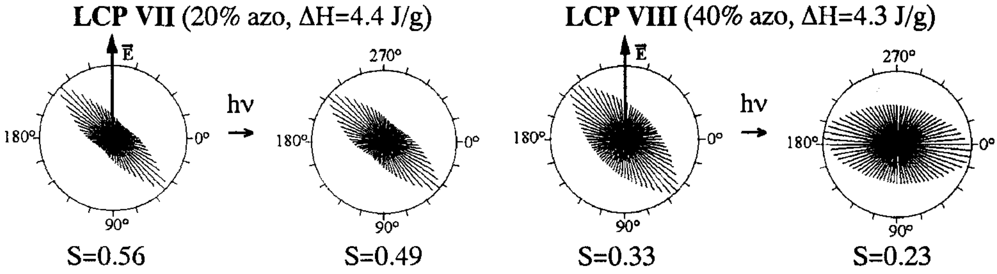


FIGURE 4 Angular dependence of the absorbance at 378 nm for LCP VII and LCP VIII before and after polarized irradiation (λ_{irr}=488 nm).

For a better understanding of the relation between the stability of the LC phase and the efficiency of the reorientation process we have irradiated planar oriented LCP films with unpolarized light at λ=365 nm. At this wavelength the content of the more polar and crooked Z isomers and hence the disturbance of the liquid crystalline order is much higher than at λ=488 nm. Thus, in polymers with low enthalpic stability and high T_g the E–Z photoisomerization and the following thermal Z–E relaxation result in a strong decrease of the order parameter of the azobenzene moieties (e.g. LCP VI), whereas in polymers with a strong tendency to form ordered structures a small increase of the order parameter is observed (e.g. LCP VII). In the latter case the dynamics in the steady state of the molecular photoreaction seems to allow a rearrangement of the rod-like side groups to a more perfect orientational order. After switching off the light, the polymer matrix which is now higher ordered than in the initial state forces the azobenzene moieties to a higher order when they relax to the E isomers.

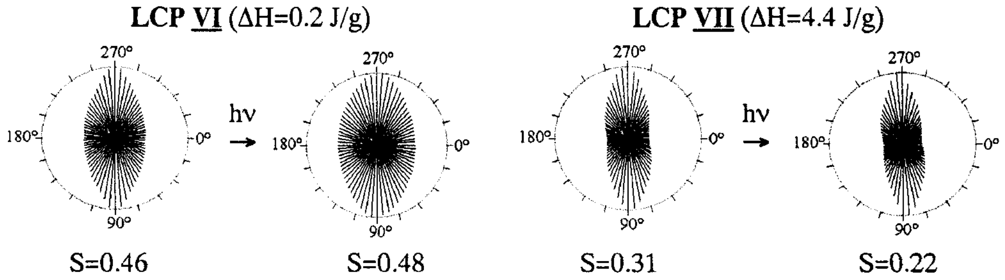


FIGURE 5 Angular dependent absorbance at 378 nm for LCP VI and LCP VII before and after unpolarized irradiation (λ_{irr}=365 nm) and thermal Z–E relaxation.

This experiment shows that not only the content of the photochromic groups and the wavelength of irradiation influence the disturbance of the liquid crystalline order which allows a director reorientation due to polarized irradiation, but the stability of the liquid crystalline phase has also to be taken into consideration. If it is strong and the disturbance due to photoisomerization is too weak to overcome the initial order, as in the case of LCP **VII**, the angular-dependent photoselection does not result in a reorientation.

Induction of anisotropy in amorphous films of LCP's

Besides having a more efficient director reorientation, polymers with a weak tendency to form LC phases show the advantage that they may be prepared as supercooled amorphous films. The polarized irradiation of such films results in the induction of optical anisotropy due to angular-dependent photoselection as it is shown for polymer **VI** in Figure 6. The initially isotropic distribution of the absorbance is changed and becomes very similar to that resulting from the polarized irradiation of an aligned film of the same polymer (compare Fig. 2), i.e. the maximum absorbance of E azobenzene moieties is in the direction perpendicular to the electric field vector of the actinic light.

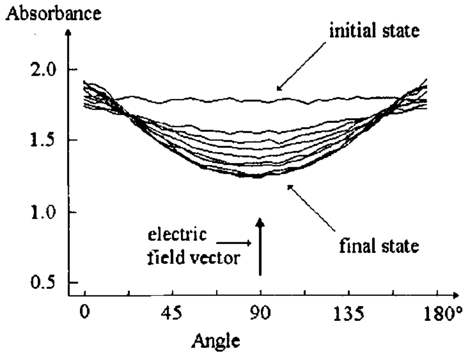


FIGURE 6 Change of absorbance at 378 nm and its angular dependence during the polarized irradiation of an amorphous film of LCP **VI** (λ_{irr}=488 nm).

The comparison of the results of both experiments, which is presented in Figure 7, shows more clearly that the polarized irradiation of the aligned and the amorphous film of polymer **VI** results in the same final state as far as the spectroscopic behaviour is concerned. This state is more easily established in the amorphous film, indicating again that ordered structures hinder the light-induced reorientation of photochromic side groups.

The fact, that in both cases the dichroic ratio in the final state is about the half of the value corresponding to the planar aligned film and the average absorbance is continuously decreased during the process, indicates that the light-induced order is qualitatively different from that of uniaxial liquid crystal. This phenomenon is under more detailed investigation now.

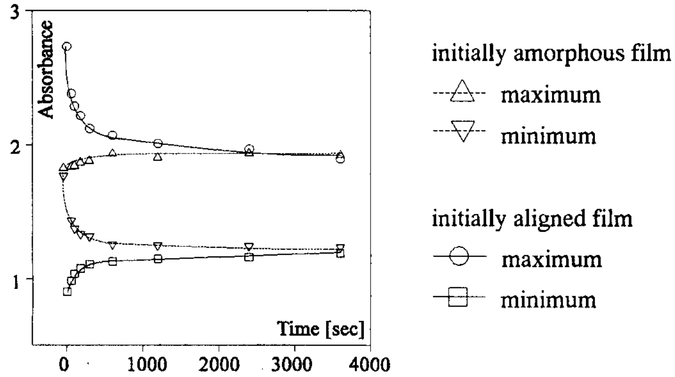


FIGURE 7 Change of maximum and minimum absorbance at 378 nm in the polarized UV/Vis spectra during polarized irradiation (λ_{irr}=488 nm) of two films of LCP VI with different initial states.

Figure 8 shows the angular distribution of the UV absorbance of the azobenzene chromophore at 378 nm and additionally that of the CN stretching vibration at 2229 cm^{-1} in the initial state and after polarized irradiation and relaxation.

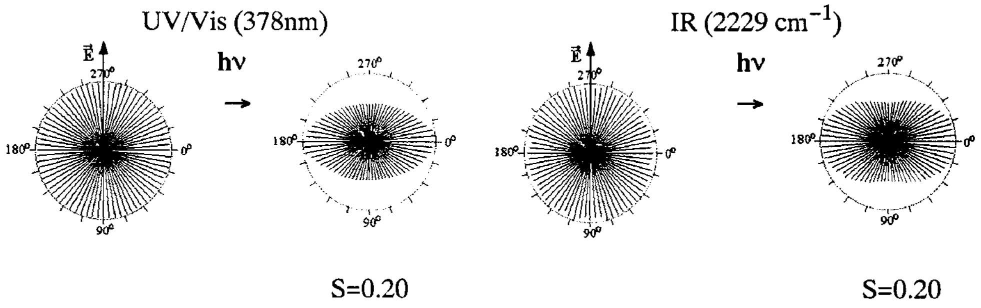


FIGURE 8 Angular dependent UV absorbance (azobenzene) and integrals of the CN band (both side groups) of an amorphous film of LCP VI in the initial state and after polarized irradiation

The spectroscopic degree of order is almost the same for both methods. From this fact it can be concluded that the non-photochromic moieties, which contributes 80% to the IR absorbance, have undergone reorientation in the same direction and to the same extent as the photochromic groups. This is a surprising result, because the process took place about 40 K below the glass transition.

Films of amorphous polymers

The structure of the amorphous polymers I and III is very similar to that of the LCP II. However, the tendency to selforganization is not strong enough to generate a thermotropic liquid crystalline phase. Nevertheless, the angular-dependent photoselection process causes a reorientation of the photochromic as well as of the non-photochromic side-groups (Fig. 9). Because the CN group is only attached to the non-photochromic moiety the light induced IR dichroism demonstrates that the cyanobenzanilide units are reoriented to the same amount as the azobenzene moieties due to a interactive effect within the glassy state of the polymer.

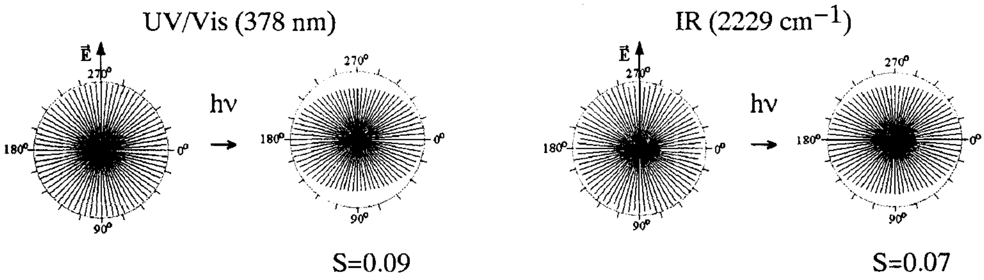


FIGURE 9 Angular dependence of UV absorbance (azobenzene) and CN band areas (benzanilide) of a film of the amorphous polymer I in the initial state and after polarized irradiation

The uniformly directed reorientation of the side groups results in an orientational order and thus in the outgrowth of an optical axis and the induction of birefringence in initially amorphous films.

Induction of birefringence

Values of birefringence as high as $\Delta n=0.08$ were induced by this process in some amorphous polymers of this type, i.e. one order of magnitude higher as that obtained in "classical" amorphous polymers in which the rod-like moiety is replaced by a methyl group. An even higher anisotropy was induced in amorphous films of LCP's, especially if the polarized irradiation is supported by a proper thermal treatment. The left part of Figure 10 shows the induction process for an amorphous film of the liquid crystalline polymer II and for the amorphous polymer III in the glassy state. In both cases the birefringence is continuously increased from $\Delta n=0$ to Δn_{max}. In the beginning the increase is faster in the amorphous polymer with 40% azobenzene side groups, whereas in the liquid crystalline polymer a higher value of Δn_{max} is induced over a longer period of irradiation, although it contains only 30% azobenzene moieties. After switching off the laser a small loss of birefringence was observed. The resulting values which were established within a few seconds are then stable for a very long time (up to several years).

The right part of Figure 10 shows the change of the light-induced birefringence with increasing temperature. The films were heated quickly to the corresponding temperature and stored for 30 minutes before the resulting birefringence was measured. The behaviour of the liquid crystalline and the amorphous polymers is completely different. In the amorphous polymer III Δn is continuously decreased becoming zero in the region of the glass transition (T_g=79°C).

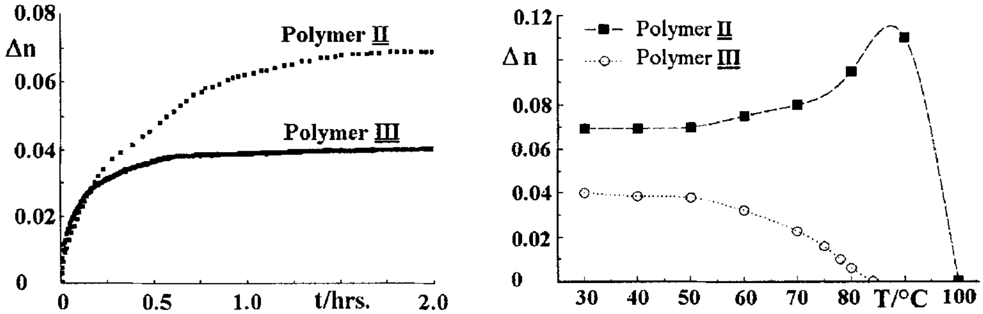


FIGURE 10 Increase of birefringence in amorphous films of polymers II and III during polarized irradiation (λ_{irr}=488 nm, P=800 W/sqm, T=30°C) and change of the induced birefringence upon increasing the temperature

In contrast, the birefringence grows with temperature in LCP II and breaks down only at the clearing temperature. In the visco-elastic state (T_g=75°C) the increase is especially strong. In principle, the resulting maximum value of $\Delta n > 0.11$ is also established at T=80°C, but because of the high viscosity of the polymer it takes a much longer time as at T=90°C. The film is completely transparent after the process. Obviously, the light induced initial orientation is strong enough to force the side groups of the polymer to an orientation which is similar to an ordinary monodomain. LCP II can not be aligned by the "classical" methods, i.e. careful annealing in cells with an orienting polyimide surface or the application of a magnetic field. Thus, the photoselection process can be used as a new method to orient liquid crystalline polymers.

DISCUSSION

Optical anisotropy is induced in non-scattering, isotropic films of photochromic LCP and amorphous polymers with rod-like side groups combining the easy handling of amorphous films with the strong optical anisotropy characteristic for aligned LCP films.

Irradiating such films with linearly polarized light causes a reorientation of the photochromic moieties to a direction perpendicular to the electric field vector of the actinic light via a great number of photoisomerization steps and directed rotational diffusion. Surprisingly, the photoselection process within a polymer having only a minority of azobenzene moieties causes a reorientation of non-photochromic side groups and in the generation of an optical axis. Thus, the angular-dependent photoselection in such polymers is characterized as a photochemically induced, directed physical reorientation process in the glassy state. The results demonstrate that liquid crystallinity is not a necessary condition for highly birefringent polymer films. Thus, the high values of Δn achieved by the light-induced process in the investigated amorphous polymers are caused by a high anisotropy of the molecular polarizibilty of all side groups and their uniform orientation.

In aligned LCP films a competition between two principles of order takes place – the selforganization of mesogenic side groups and the photoselection process stimulated by the ordered light. Thus, the initial order of the LCP film may restrict the ordering tendency of the linearly polarized light in polymers with a high enthalpic stability of the liquid crystalline phase. However, in case of polymers with low enthalpic stability of the LC phase the disturbance caused by the photoreaction can overcome the primary order. In such cases the photoselection process will result in an efficient reorientation of the side groups and thus in a rotation of the optical axis of the film.

Amorphous films of LCP´s are more easily to prepare and the light-induced reorientation processes are not restricted by a an initially existing order. Moreover, the selforganization of mesogenic moieties in the visco-elastic state amplifies the light-induced optical anisotropy. The orientational order generated by the angular-dependent photoselection acts as initializing force in the process of establishing the liquid crystalline phase, causing a more perfect alignment at temperatures above the glass transition. This is a new method to align polymers. It will be especially useful if neither surface interactions nor strong magnetic fields yield an uniform alignment.

Consequently we have studied LCP´s with low enthalpic stability which can be frozen-in to amorphous films and amorphous polymers with rod-like side groups. In films of such polymers the induced optical anisotropy can be modified continuously by a variation of the exposured energy and reversibly by changing the polarization of laser beam. Written information is stable for years in the glassy state of the polymers. Erasing of information and restoring the initial state of can be done by heating the polymer film above T_g (amorphous polymers) or above T_c and quick cooling (amorphous films of LCP´s), respectively. The angular-dependent photoselection process in such polymers offers new possibilities for the orientation of polymers and for optical data storage.

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