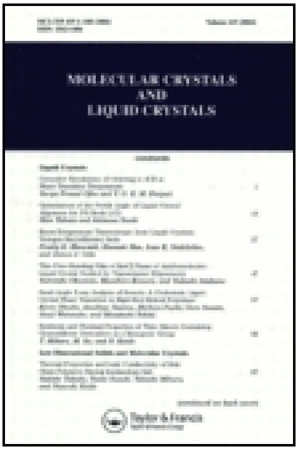

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Photoinduced Optical Anisotropy in Amorphous Films of Liquid Crystalline Polymers

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PHOTOINDUCED OPTICAL ANISOTROPY IN AMORPHOUS FILMS OF LIQUID CRYSTALLINE POLYMERS

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Abstract Amorphous, optically isotropic films of photochromic liquid crystalline copolymers have been prepared and irradiated with linearly polarized light. In this way high values of dichroism and birefringence have been induced.

Keywords: optical anisotropy, liquid crystal, copolymer, dichroism, birefringence, photochromic

INTRODUCTION

Recently much attention has been paid to the development of materials for optical data storage.[1] Liquid Crystalline Polymers (LCP's) are very promising for this purpose.[2,3] The optical properties of LCP films strongly depend on the molecular structure of the polymers and the supramolecular arrangement of their form anisotropic moieties. Their order and orientation may be modified by external fields or different light induced effects. In photochromic LCP's irradiation causes a change of the molecular form anisotropy of photochromic groups and in this way a modification of the supramolecular order.

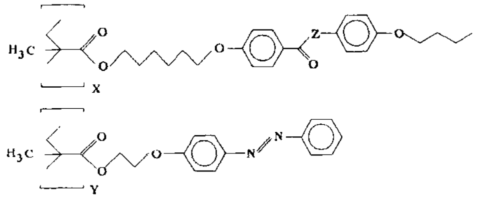
The use of linearly polarized light offers in principle a new way of photorecording.[4-6] Thus, upon irradiation of LCP films with azobenzene units in the side groups, an angular-dependent photoselection process occurs causing a reorientation of the photochromic moieties to a direction perpendicular to the electric vector of the actinic light.[7-11] However, for practical application it is necessary to orient the LCP's macroscopically, i.e. to prepare a non-scattering, uniformly aligned film. This often requires a complicated procedure. In some cases it is even impossible.

Optical anisotropy has also been induced by irradiating amorphous polymers containing photochromic moieties.[12] However, the values of induced birefringence are very small.[13,14] Recently, Shi et al. have induced higher values of birefringence in amorphous polyesters containing disperse red side groups and cinamoyl moieties in the backbone.[15]

The aim of our paper is to show, that the problems can also be solved by using amorphous films of photochromic LCP's. We have studied the light induced orientation of amorphous films formed by liquid crystalline copolymers containing azobenzene units. The kinetics of the molecular photoreaction and the reorientation processes in such films of different types of LCP's has been studied. The results are compared with those obtained from investigations of an uniformly aligned film of an identical polymer.

EXPERIMENTAL

The following polymers have been investigated.:

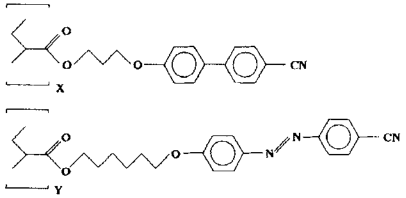


Polymer **1**

Z=NH; $y/(x+y)=0.3$; Tg=75°C;Tc=102°C

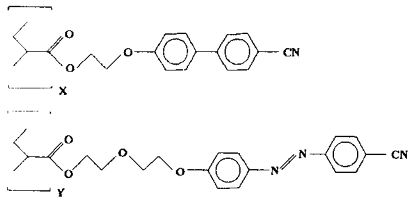
and **2**

Z=O; $y/(x+y)=0.5$; Tg=63°C;Tc=71°C



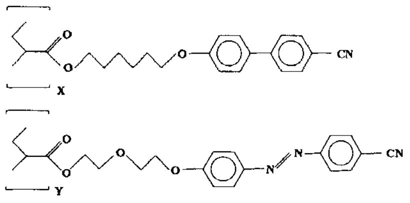
Polymer **3**

$y/(x+y)=0.2$; Tg=61°C;Tc=91°C



Polymer **4**

$y/(x+y)=0.2$; Tg=77°C;Tc=91°C



Polymer **5**

$y/(x+y)=0.6$; Tg=43°C;Tc=97°C

The synthesis of the polymers will be described elsewhere.[16,17]

The polymers have been sandwiched between two glass plates with a rubbed polyimide surface. The thickness of the films was 2μm. The films have been cooled down quickly from the isotropic melt to room temperature. In this way the polymers have been frozen-in in the amorphous state and optically clear films have been obtained.

A film of polymer **3** has also been oriented uniformly planar by slow cooling from the isotropic melt into the liquid crystalline state and annealing 1K below the clearing point.

The films have been irradiated with unpolarized light using a mercury lamp and filters (λ=365 nm; P=1.7 mW/cm^2 and λ=488 nm; P=0.44 mW/cm^2). The irradiation with linearly polarized light has been carried out with an Ar$^+$ laser (Coherent, λ=488 nm; P=40 ... 200 mW/cm^2). The light induced birefringence has been measured using a non-actinic laser beam (λ=632.8 nm).

The polarized UV/Vis spectra have been measured with a Lambda 19 spectrometer (Perkin Elmer) with polarizers, driven by a computer-controlled stepper. A similar polarizing device has been adapted to a RS 1 FTIR spectrometer (Mattson Instruments) to measure the polarized IR spectra.

RESULTS

Amorphous films of polymers **1**-**5** have been irradiated with linearly polarized light (λ=488 nm; P=40 mW/cm^2). Figures 1 and 2 show the polarized UV/Vis and FTIR spectra of polymer **3** measured in the isotropic initial state and in the anisotropic final state after irradiation (80 minutes) and thermal Z-E isomerization (48 hours).

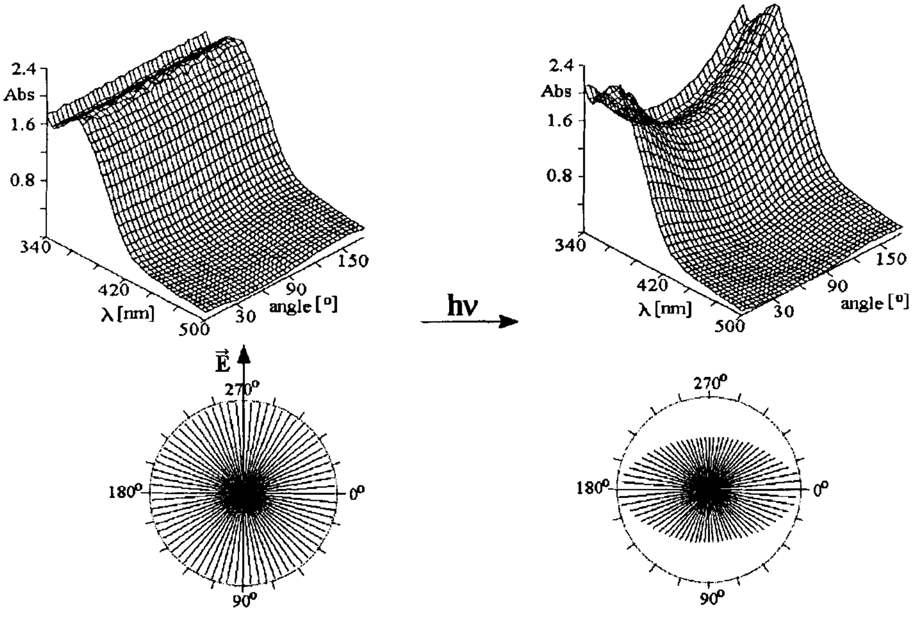


FIGURE 1 Polarized UV/Vis spectra and angular dependence of the absorbance at 380 nm of Polymer **3** in the initial state (optically isotropic; left side) and after irradiation and relaxation (dichroitic; right side)

The transition moment of the π–π* transition of the azobenzene group at 380 nm as well as that of the CN-stretching vibration at 2229 cm^{-1} are directed along the long molecular axis. The isotropic distribution of UV and IR absorbance in the initial state demonstrates that there is no preferred orientation of both side groups of the LCP.

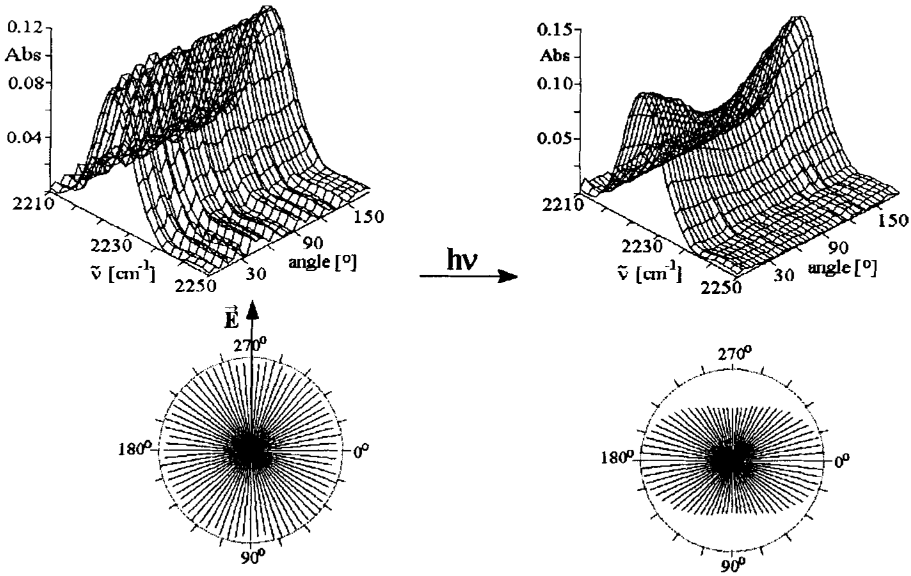


FIGURE 2 Polarized IR spectra and angular dependence of the integrated area of the CN stretching band of Polymer 3 in the initial state (optically isotropic; left side) and after polarized irradiation and relaxation (dichroitic; right side)

However, after polarized irradiation the long molecular axis of the photochromic as well as of the non-photochromic but strongly form anisotropic group are oriented perpendicular to the electric vector of the actinic light. A degree of order of about S=0.2 is detected by UV/Vis as well as by IR spectroscopy. The photochromic azobenzene groups have undergone reorientation due to angular-dependent photoselection process (figure 1). The accordance of the order parameters of azobenzene moieties and all cyano groups demonstrates that also the non-photochromic side groups have been reoriented in the same direction and to the same amount as the photochromic groups (figure 2). In the glassy state this is a surprising result which can be explained by a multistep co-operative nearest neighbour process within the steady state of the photoisomerization. The high values of dichroism demonstrate that the irradiation with linearly polarized light generates an orientational order in the initially amorphous film which is similar to the liquid crystalline order.

Concerning the dichroitic properties, the irradiation of a uniformly planar aligned film of LCP 3 results principally in the same final state. This process is shown in figure 3.

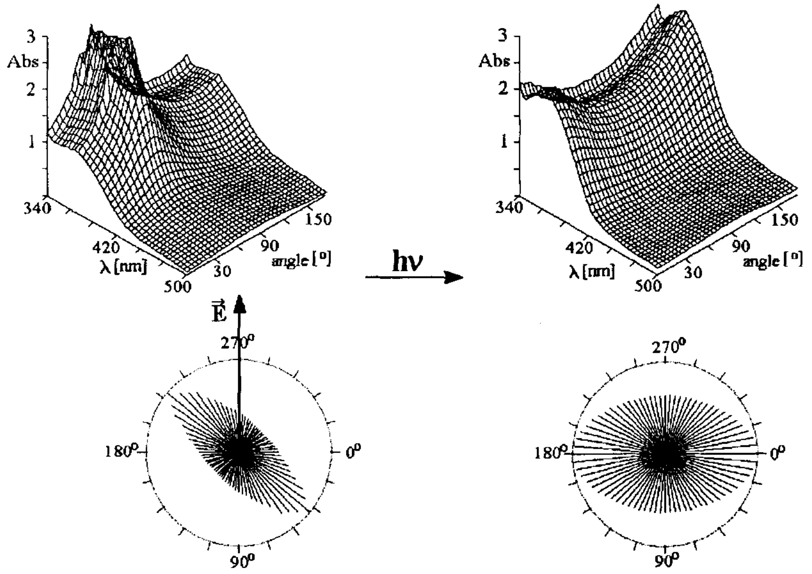


FIGURE 3 Polarized UV/Vis spectra and angular dependence of the absorbance at 380 nm of an uniformly planar oriented film of Polymer 3 in the initial state (left side) and after polarized irradiation and relaxation (right side)

A planar film of polymer 3 has been irradiated with linearly polarized light. In the initial state the electric vector of the actinic light formed an angle of 45° to the director orientation of the LCP. In this case the absorbance of actinic light is quite similar to that of the amorphous film. After irradiation and relaxation the optical axis has been rotated by 45°. Thus, in the final state the optical axis of the LCP film is oriented perpendicular to the electric vector of the laser beam. The degree of order after irradiation (S=0.16) is much lower than in the initial state (S=0.4) and even slightly lower than that obtained from irradiation of amorphous films of the same polymer. This fact implicates that the reorientation process disturbs the liquid crystalline order. On the other hand it is restricted by this order. Recently, we have reported that the reorientation process due to photoselection is completely surpressed in a polymer with a similar structure but a stronger tendency to form a liquid crystalline phase.[18]

To study the reorientation process more detailed, the kinetics of the molecular photoreaction as well as that of the supramolecular rearrangement has been investigated during irradiation and relaxation. Figure 4 shows the kinetics of the light induced E-Z isomerization upon a non-polarized irradiation at 365 and 488 nm and the following thermal Z-E relaxation of the azobenzene moieties of polymer 3. The photostationary equilibrium between the E and Z isomers is easily established whereas the reorientation process due to angular-dependent photoselection within the steady state takes place in a much longer period of irradiation (see figure 5).

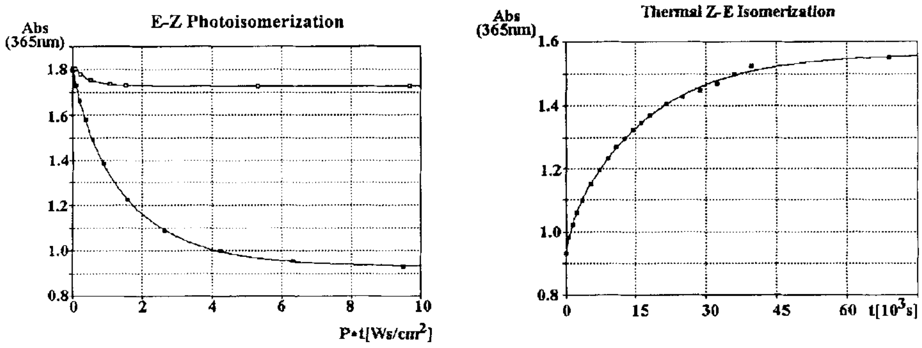


FIGURE 4 Absorbance at 380 nm due to E-Z photoisomerization during irradiation (▪ λ=365 nm; ▫ λ=488 nm; unpolarized light) and increase of absorbance due to thermal E-Z isomerization at room temperature after irradiation (λ=365 nm)

Completely different kinetics of the molecular processes on the one hand and the change of supramolecular order on the other hand is also observed during the relaxation after irradiation. Upon switching off the laser, the birefringence slightly decreases to a stable value within a few seconds (see figure 5). However, the thermal Z-E relaxation to the initial configuration of the azobenzene side groups takes place in a period of more than 30 hours.

During and after irradiation of the amorphous films the increase of birefringence due to the generated laser induced orientational order has been measured on-line. In figure 5 the process is shown for polymer 3.

In comparison to the establishing of the photostationary equilibrium (see figure 4) much more energy is necessary to achieve the amount of reorientation of the side groups corresponding to the high values of dichroism (figure 1 and 2) and birefringence (figure 5 and table 1). The induction process of birefringence takes place mainly within the steady state of the molecular photoreaction. A large number of angular-dependent isomerization steps results in an uniformly directed reorientation of the side groups. This process yields the emerging of an optical axis and in this way the increasing of birefringence.

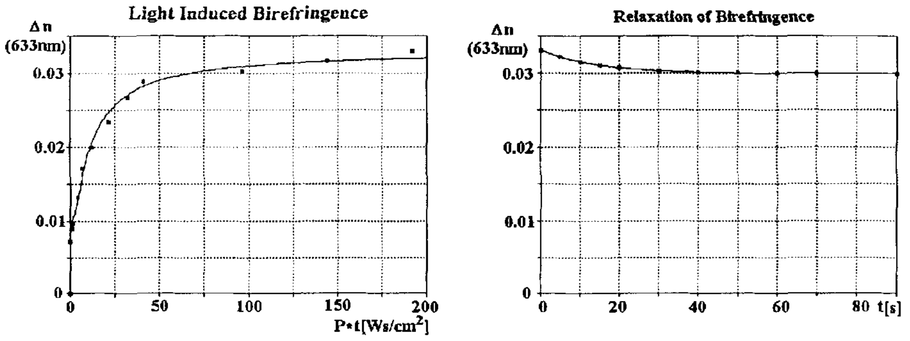


FIGURE 5 Increase of birefringence due to light induced reorientation (λ=488 nm; P=40 mW/cm^2) and decrease of birefringence after switching off the laser

After switching off the laser the birefringence falls down to a stable value within a few seconds. Generally, this relaxation process is smaller for polymers with high glass temperatures. Table 1 shows the values of stable birefringence for the investigated polymers.

TABLE 1 Stable values of light induced birefringence in amorphous films after irradiation (λ=488 nm; P=200 mW/cm^2) and relaxation

Polymer	1	2	3	4	5
Δn_{stab}	0.0312	0.0330	0.0350	0.058	0.11

In case of polymer 5 the induced birefringence is in the order of magnitude of uniformly aligned liquid crystalline polymers. Up to now such high values have not been induced in amorphous films of photochromic copolymers.

The resulting birefringent films are completely transparent, i.e. non-scattering. We have found that LCP's with especially strong interactions between the side groups and extremely high viscosity (e.g. polymer 1) can not be oriented to non-scattering monodomain films, neither by carefully annealing in a strong magnetic field of 7 T nor by the use of electric fields. In such cases the orientation by polarized irradiation starting from an amorphous film has turned out to be the only method to obtain optically anisotropic and transparent films.

DISCUSSION

Optical anisotropy is induced in amorphous films of liquid crystalline polymers in the glassy state via the following steps illustrated schematically in figure 6:

1. Angular-dependent absorption

The absorption of linearly polarized light by the photochromic moieties is proportional to the square of the cosine of the angle ω between the electric vector of actinic light and the transition moment, which coincides with the long molecular axis of the azobenzene moiety. Thus, the smaller the angle ω, the greater is the probability that the respective moiety will be excited.

2. Repeated $E \rightleftharpoons Z$ photoisomerization steps

In the wavelength-dependent steady state which is easily established, the azobenzene units undergo E-Z and Z-E photoisomerization as well as thermal Z-E isomerization. After an isomerization cycle the long molecular axis of the E isomer will have a different site and orientation, because the photochemical switching between the rod-like E isomer and the crocked Z isomer causes a perturbation of the molecular environment.

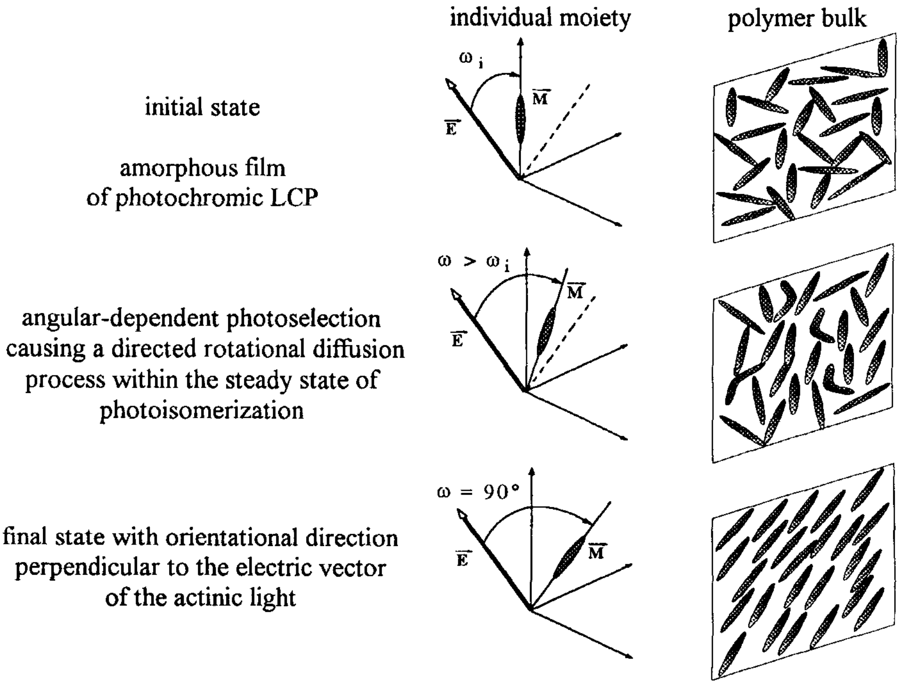


FIGURE 6 Scheme of the reorientation process due to angular-dependent photoselection in an amorphous film of a photochromic Liquid Crystalline Polymer

The probability that an individual azobenzene unit is excited again will be decreased if the angle ω has become greater, and vice versa.

3. Reorientation of the axis of the photochromic moieties

Repetitions of steps 1 and 2 within the steady state of photoisomerization result in a successive reorientation of the photochromic moieties via photoinduced rotational diffusion steps. Only the moieties which are oriented perpendicularly to the electric vector do not undergo the molecular photoreaction, thus cease to take part in the reorientation process.

4. Reorientation of the other mesogenic side groups

The reorientation of the photochromic moieties may cause a continuous reorientation of non-photochromic but rod-like side groups .

Thus, angular-dependent photoselection in amorphous LCP films is characterized as a **photochemically induced, directed, co-operative physical reorientation process** of photochromic groups as well as of the non-photochromic but mesogenic moieties.

This effect offers new possibilities for orientation of polymers and for optical data storage with respect to storage density and reversibility. The induced optical anisotropy can be modified continuously and reversibly by rotating the plane of polarization of the laser beam in relation to the film. In the glassy state of LCP's the written information is stable for years and may be erased thermally or by light

CONCLUSION

The main feature of this new approach in photochemistry is the fact that the irradiation does not result in a stable product of photoreaction but in a directed dynamics causing a photochemically induced directed, continuous, co-operative physical reorientation process. The angular-dependent photoselection process via a large number of single E-Z and Z-E photoisomerization steps of the azobenzene moieties generates an orientational order in the initially amorphous film. On the molecular level the initial state of the chromophore is restored. However the orientation of the side groups, i.e. the supramolecular structure has changed in a strongly defined way.

High values of optical anisotropy have been induced photochemically because the new preparation technique of LCP's yields films which combine three very important features: At first, the desired initial state, i.e. a macroscopically uniform, optically isotropic, non-scattering film is easily to prepare. At second, a high content of moieties with a strong form anisotropy and a high molecular polarizibility will cause high values of optical anisotropy, if they are uniformly oriented by light. At third, a light induced uniform orientation is enabled by the co-operativity of the reorientation process.

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