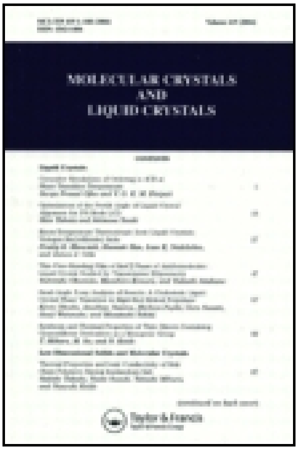

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Photo-Induced Alignment of LC Polymers by Photoorientation and Thermotropic Self-Organization

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Photo-Induced Alignment of LC Polymers by Photoorientation and Thermotropic Self-Organization

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Optical anisotropy is generated in films of photochromic LCPs upon irradiation with linearly polarized light. Annealing of these films above the glass transition temperature results in a significant amplification of the photo-induced anisotropy. The amplification takes place even in the case of copolymers with only 10% of azobenzene side groups and if only 7% of the saturation value of anisotropy are induced. Photoorientation and photoinduced alignment are restricted by thermal pretreatment and ageing at room temperature.

Keywords: photoorientation; photoisomerization; azobenzene; liquid crystalline polymers; thermotropic self-organization

1. INTRODUCTION

The defined preparation of anisotropic polymer films is of great importance for various fields of optical applications and for the photoalignment. Optical anisotropy is induced in films of photochromic polymers upon irradiation with linearly polarized light. The orientation process takes place via angular-dependent excitation, a number of EZ photoisomerization cycles and rotational diffusion within the steady state [1, 2]. In this way the photochromic side groups become oriented perpendicular to the electric field vector of the incident light. In amorphous and LC copolymers the process causes a co-operative orientation of the non-photochromic side groups as well [3-7].

Annealing of photooriented LCP films above Tg can result in a significant amplification of the anisotropy. The orientational order photogenerated in the glassy state acts as a directing force for the thermotropic self-organization resulting in a macroscopic alignment of the LC polymers [2-5]. The method combines the easy preparation of spin-coated films with the generation of the optical properties of LCs. So, very high values of birefringence up to 0.4 are developed. However, in the case of certain LC polymers the annealing procedure leads to a homeotropic order.

The aim of the study is to investigate the conditions for this „thermal development“ process of photochromic polymers. The dependence on the chemical composition of the LC polymers and the irradiation conditions will be discussed in order to optimise the photoinduced alignment process.

2. EXPERIMENTAL

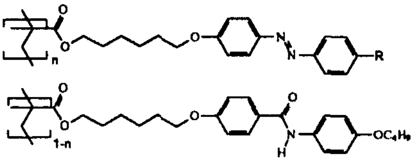

FIGURE 1: Structure of the polymers

	R	n	Phase transitions
C2/10	CN	0.10	G 63 S_{Ad} 166 I
C2/28		0.28	G 59 S_{Ad} 170 I
C2/50		0.50	G 52 S_{Ad} 168 I
C2/75		0.75	G 51 S_{Ad} 162 I
C2/90		0.90	G 48 S_{Ad} 162 I
C2/100		1.00	G 51 S_{Ad} 166 I
C3/25	OC_4H_9	0.25	G 71 S_{A1} 147 I
C5/25	C_6H_5	0.25	G 75 S_{A1} 166 I

TABLE 1: Properties of the investigated polymers

The synthesis of the monomers are reported in [5]. The polymers (Figure 1) were synthesized by radical polymerization adding 2 mol%

AIBN. The thermal properties (Table1) were characterized by means of polarization microscopy, DSC and X-ray diffraction.

Spin-coated films (2500rpm, 30s) were prepared from THF solutions (0.05mmol). The films were stored for at least one day. The irradiation was carried out using polarized light of an Ar^+ laser (Coherent) at 488nm (100mW/cm^2) and at 365nm (35mW/cm^2). A HBO lamp combined with different filters was used for the non-polarized irradiations. The time of exposure, the temperatures and the thermal pre-treatment of the films were varied. After the irradiation procedure the films were annealed at 20K above T_g for 1 to 3 days. The UV/Vis measurements were carried out using a diode array spectrometer (Polytec X-dap-04 V2.3).

3. RESULTS

3.1 Irradiation of Polymers at 488nm

The kinetic curve of the induction of dichroism (Figure 2) indicates that two processes are involved, a very efficient process and a slower one.

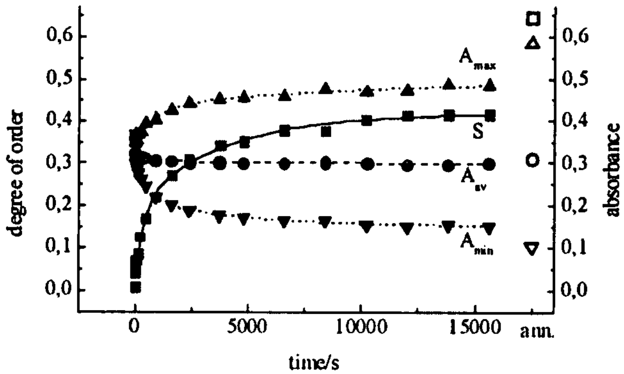

FIGURE 2: Time dependence of the photochemical induction of C2/28: ▲ absorbance perpendicular ▼ absorbance parallel ● average absorbance ■ degree of order; open symbols: state after annealing

The faster process is an angular-dependent photoselection process establishing the steady state of the EZ photoisomerization (angular-dependent bleaching). The slower process, which dominates on continued irradiation is related to the photoinduced orientation of the

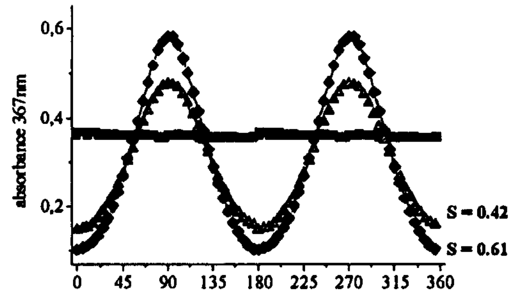

FIGURE 3: Angular dependent absorbance of C2/28: ■ initial state, ▲ after linearly polarized irradiation at 488nm and ● after annealing

photochromic side groups perpendicular to the electric field vector (photoorientation process). Figure 2 demonstrates that the absorbance parallel to the electric field vector of incident light decreases, while the absorbance perpendicular to E increases. In this way optical anisotropy is induced. The average absorbance is decreased reversibly caused by the first process. Comparing the virgin isotropic film with the photooriented film after the annealing, there is still a decrease of the average absorbance which is caused by a out-of-plane orientation

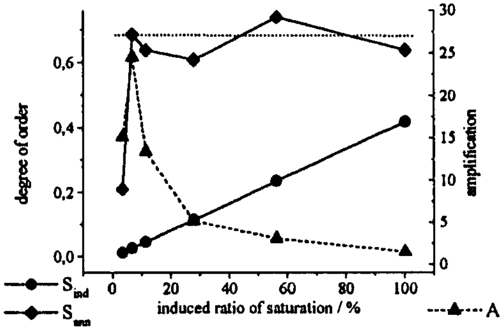

FIGURE 4: Photoorientation process of C2/28 films is stopped at different stages (3, 7, 11, 28, 56, 100%)

component. All investigated polymers show a comparable behavior.

The dichroism of the LCP films photoinduced below T_g can be amplified by thermotropic self-organization by annealing 20K above T_g

(Figure 3). The photo-generated order of the glassy state acts as aligning force. The annealing of samples, in which only a partial value of saturation is induced, results in almost the same values of dichroism (Figure 4). A maximum of amplification of a factor of about 25 was found for the photoinduction of only 7% of the saturation value.

Comparable values of dichroism after partially photochemical induction and annealing were found also in the case of the polymers with different substituents on the azobenzene side group as shown in Table 2.

	R	$S_{100\%\text{-ind}}$	$S_{100\%\text{-ann}}$	$S_{25\%\text{-ann}}$
C2/28	CN	0.42	0.61	0.65
C3/25	OC_4H_9	0.44	0.65	0.64
C5/25	C_6H_5	0.49	0.72	0.69

TABLE 2: Photochemically induced and thermotropically amplified order parameters detected by UV/Vis-spectroscopy

All polymers show a decrease of the average absorbance upon irradiation, caused by EZ-isomerization (Figure 5). Compared to the others, C2/28 with a cyano-substitutent, shows after irradiation an increase of the average absorbance by annealing. So, it seems that this polymer has the strongest tendency to establish an in-plane anisotropy. The highest values of anisotropy were detected in the case of polymer C5/25 containing a mesogenic azobenzene side group with three aromatic cores. In this case a degree of order of S = 0.88 was determined using a UV/Vis microscope spectrometer.

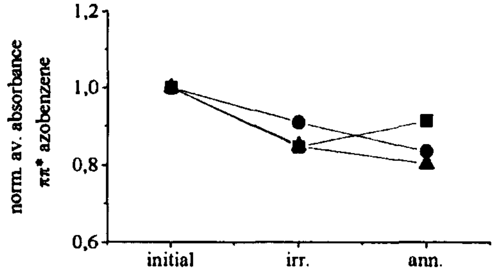

FIGURE 5: Progress of the average absorbance upon irradiation and annealing of the polymers ■ C2/28 ● C3/25 ▲ C5/25

As shown in Figure 6, the saturation value of photoinduced dichroism depends on the proportion of the azobenzene side groups in the copolymers. It increases up to a ratio of about 0.5, but higher azobenzene concentrations do not result in higher values. The induced dichroism of the photochromic azobenzene group (365nm) and that of the non-photochromic benzanilide group (280nm) are similar. This result demonstrates the co-operativity of the photoorientation process in the glassy state. The thermal amplification results in almost the same values of anisotropy in this series of copolymers. The highest absolute values and the maximum of amplification are observed for the polymers with low content of azobenzene side groups.

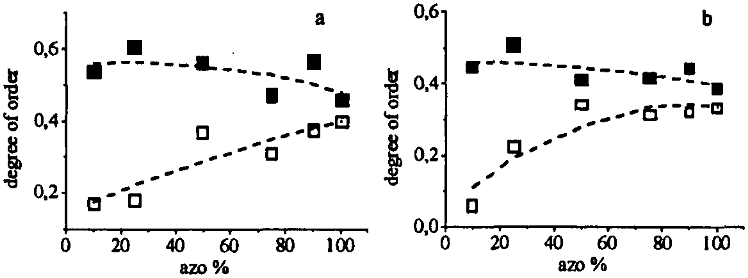

FIGURE 6: Dependence of the azobenzene content of C2-polymers on □ photoinduced and on ■ amplified order of
a: $\pi\pi^*$ transition of azobenzene at 365nm b: $\pi\pi^*$ transition of benzanilide at 280nm

3.2 Linearly Polarized UV Irradiation of Polymer C2/28

The linearly polarized UV irradiation (365nm) at room temperature results in a stronger decrease of the average absorbance compared to the

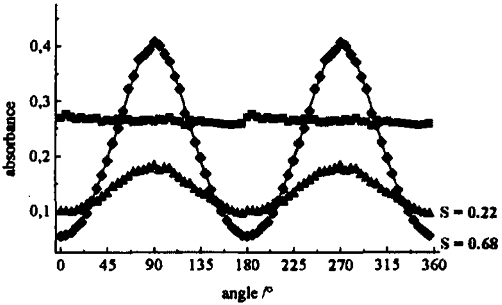

FIGURE 7: Angular dependent absorbance of polymer I ■ initial state, ▲ after linearly polarized irradiation for 15min at 365nm and ● after annealing

Vis-Irradiation. This is caused by a higher content of Z isomer in the steady state. Additionally, the photo-generated anisotropy was found to be lower as that observed for the Vis-Irradiation process. After the annealing procedure the dichroism was amplified to a value similar as obtained for the Vis-irradiated samples under the same conditions (Figure 7).

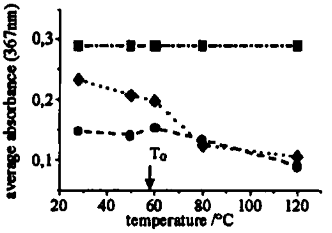

FIGURE 8a: Dependence of the av. absorbance at the $\pi\pi^*$ transition on the irradiation temperature

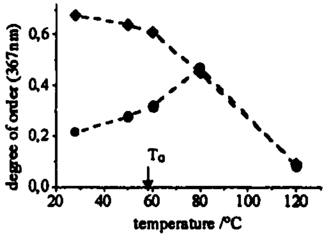

FIGURE 8b: Dependence of the degree of order at the $\pi\pi^*$ transition on the irradiation temperature

■ initial absorbance ● after irradiation ◆ after annealing

As shown in Figure 8b the induced degree of order shows a strong dependence on the irradiation temperature. The decrease of the anisotropy at higher temperature is accompanied with a decrease of the average absorbance of the film (Figure 8a). This behavior is caused by an increasing homeotropic orientation component of the smectic polymers.

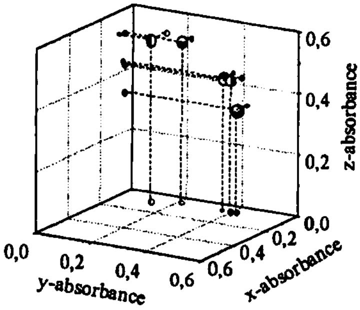

FIGURE 9: Vectors of absorbencies of the $\pi\pi^*$ transition after irradiation at different temperatures ● 28°C ◆ 50°C ● 60°C ● 80°C ◆ 120°C and annealing

The 3D spatial order can be described by a vector graph of the x-, y- and z-component of the absorbance (Figure 9). The z-component after the annealing procedure was calculated under the assumption that the spincoated film was isotropic: $A_z = A_{iso} - A_x - A_y$. The z-component of the absorbance increases significantly at higher temperatures.

3.3 Non-Polarized UV Irradiation of Polymer C2/28

Non-polarized UV irradiation experiments show a strong dependence on the irradiation temperature. The steady states at different temperatures were almost similar up to the glass transition. Obviously, the power density was high enough to compensate the increasing rate of the thermal ZE isomerization. At temperatures above T_G the absorbance decreases during the thermal ZE isomerization too. This behavior has to be explained with an establishing of a homeotropic orientation. This was demonstrated for the final state of irradiation at 103°C by absorption measurements of the 45° tilted sample. Moreover, a subsequent annealing at 90°C for 2 days results in an amplification of the homeotropic order (Figure 10).

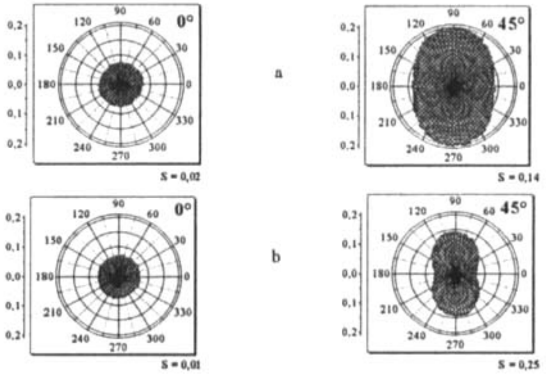

FIGURE 10: Angular dependent absorbance of C2/28 (a) Induction of anisotropy by non-polarized irradiation at 103°C and (b) thermotropic amplifying of anisotropy in normal (0°) and tilted (45°) position

3.4 Behavior on Ageing and Annealing

The spectra of the polymer films are not significantly effected by ageing. In a film of C5/25 only a small change of the average absorbance at 0° and 45° angle of incidence was observed (Figure 11).

The other polymers behave in almost the same manner. As seen in Table 3, after ageing the photochemical induction of 25% saturation anisotropy works in the same manner as for freshly prepared samples.

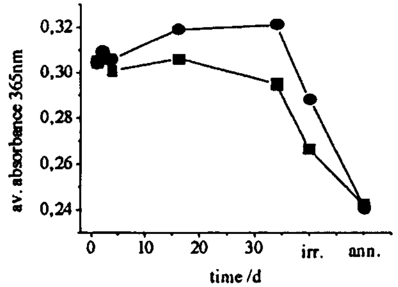

FIGURE 11: Changing of av. absorbencies of C5/25 by ageing, irradiation and annealing at ■ 0°(normal) and ● 45° (tilted) position

Nevertheless, the thermotropic amplification leads to lower values after ageing. The effect is smallest for C2/28, the polymer with the least bulky substituent

	C2/28			C3/25		C5/25	
Ageing /d	63	34	1	34	1	34	1
S_{ind}	0.08	0.1	0.12	0.08	0.1	0.12	0.15
S_{ann}	0.46	0.65	0.61	0.32	0.52	0.4	0.69

TABLE 3: Photochemically induced and thermally amplified order of aged films

	C3/25	C5/25
S_{ind}	0.02	0.04
S_{ann}	0	0

TABLE 4: Photochemically induced and thermally amplified order of pre-annealed films

To overcome any restriction by aggregation, the C3/25 and C5/25 films were pre-treated with non-polarized UV light. But this treatment results in homeotropic alignment of the films after amplification. Moreover, it was observed for films of polymer C3/25 and C5/25 that a pre-annealing leads to a decrease of the average absorbance at 0° and 45°. The photochemically induced ordering process is restricted and the thermal amplification is prevented (Table 4). This behavior should be caused by a decrease of free volume in the film due to ageing or annealing.

4. CONCLUSIONS

Optical anisotropy is generated in films of photochromic LCP upon irradiation with linearly polarized light. The photochromic azobenzene side groups become oriented perpendicular to the electric field vector of the incident light. In films of copolymers this causes a co-operative orientation of the non-photochromic side groups in the same direction and to a comparable degree of order.

Annealing of such photo-oriented LCP films above the glass transition temperature results in a significant amplification of the photo-induced anisotropy up to a degree of order of 0.88. The orientational order generated in the glassy state acts as an initializing force for the thermotropic self-organization resulting in a macroscopic alignment of the LC polymer. However, in the case of UV irradiation at higher temperature the annealing procedure leads to a homeotropic order.

The amplification takes place even in the case of copolymers with only 10% of azobenzene side groups and if only 7% of the saturation value of anisotropy is induced. Photoorientation and photoinduced alignment are restricted by thermal pretreatment and ageing at room temperature.

This photo-induced "command" effect in the bulk caused by the combination of the both principles of ordering, photoorientation and thermotropic self-organization, represents a new method to align photochromic LC polymers.

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