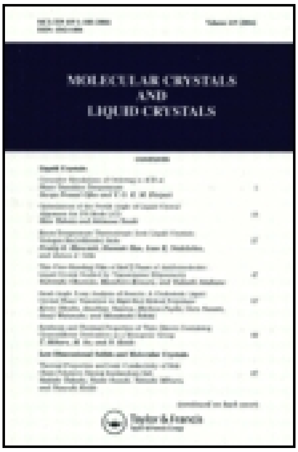

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Photoinduced Three-dimensional Structures in Amorphous and LC Polymers

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ABSTRACT

The 3D anisotropy generated by photoorientation of thin films of azobenzene containing polymers can be determined using waveguide spectroscopy [1-4]. Irradiation of the films in the glassy state of the polymers with polarized light resulted in almost perfectly oblate index ellipsoids. Recently [5], we have found, that in the case of LC polymers the anisotropy can be amplified by annealing. The investigation of a number of polymers shows, that various types of 3D orientations (biaxial and uniaxial, oblate and homeotropic) can be obtained by such a annealing procedure. The film interfaces seem to play a crucial role for the respective behaviour.

Keywords photoorientation; photoisomerization; azobenzene; liquid crystalline side chain polymer; waveguide spectroscopy; photoinduced anisotropy

INTRODUCTION

For industrial applications like displays and other optical devices it is necessary to have a well defined description of the anisotropy of thin films. This is of special interest in the cases, where the anisotropy is induced by irradiation with linearly polarized light. This photo-orientation process in azobenzene containing polymers takes place via repetition of angular-dependent excitation, a number of E/Z photoisomerisation cycles and rotational diffusion in the steady state. The three-dimensional structure of anisotropic polymer films of photochromic polymers formed by exposure to linearly polarized light is of great interest for the usage of such films for optical data storage or for the formation of optical components. The photoorientation of azobenzene containing polymers is a paradigm for the formation of such films and materials [5, 6]. This process results in an orientation of the chromophores perpendicular to the polarization direction of the actinic light.

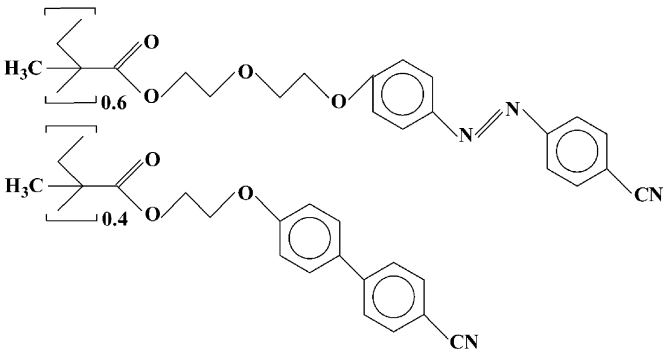
It was shown, that the photoinduced anisotropy of films made from liquid crystalline polymers can be further amplified by thermotropic self-organization, i. e. annealing in the liquid crystalline phase. The initial order and the history of the films have a strong influence on this second orientation process [5]. These studies were made for films of some hundred nm or below. We investigate here films with a thickness of at least 1 μm, which can be studied by the excitation of waveguide modes [1-4] using a wavelength of 632.8 nm. This technique allows us to measure the refractive index ellipsoid in all three spatial dimensions with a high accuracy.

EXPERIMENTAL

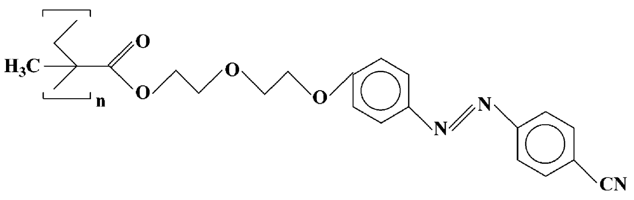
One amorphous and two liquid crystalline polymethylmethacrylates containing the 4-alkoxy-4’-cyanoazobenzene unit (P1 with 60 % azobenzene (T_g 77°C) and the homopolymer P2 (g 58°C s_A 115°C i)) or the 4-alkoxyazobenzene group (P3) with 30 % azobenzene group content: g 75°C s_A 102°C i) were used for the experiments.

Films with a thickness of 1.25 μm (P1), 1.7 μm (P2), and 4.1 μm (P3) were prepared by spin-coating on glass substrates using a solution of 100 mg (P1) or 20 mg (P2 and P3) of the liquid crystalline polymethylmethacrylates in 1 ml THF. From P3 an additional film of a thickness of 4.6 μm was prepared on a thin layer of rubbed polyimide.

Irradiation was in all cases performed at room temperature using the 488 nm line of an Ar^+ laser with power densities of 50 mW/cm² (P1



(P1)



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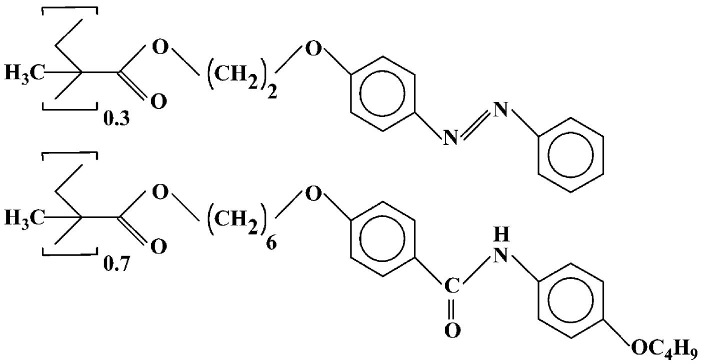

(P3)

and P3) or 90 mW/cm^2 (P2). The irradiation was carried out in normal incidence. During the irradiation the in-plane path length difference at the wavelength of 632.8 nm of the samples was measured as described in [7]. The irradiation was performed until saturation of the in-plane birefringence safely occurred (after 9-13 h). For some films the in-plane optical path length difference for ordinary and extraordinary light (632.8 nm) was determined using the Ehringhaus compensator method.

Polarized UV-VIS measurements were carried out with a diode-array spectrometer (Polytec XDAP V2.3) to determine the in-plane order of the films. A computer-driven stepper with a polarizer was used for investigations with polarized light. The spectroscopic order parameter (S) of the entire polymer film was calculated as $S = (A_{max} - A_{min}) / (A_{max} + 2A_{min})$.

The three-dimensional refractive indices were determined by waveguide spectroscopy using a He-Ne laser (632.8 nm). The x direction is the direction of polarization of the light used to irradiate the samples, the z direction is the film normal and the y direction is the direction in the plane of the film perpendicular to x. The coupling of the laser light into the films was achieved using a 90° prism made from LaSF N9 (Schott) with a refractive index of 1.84489. The refractive index of the Corning glass substrates was determined with an Abbe refractometer to be 1.5045.

RESULTS AND DISCUSSION

The UV spectrum of the initial state of the film made from the amorphous polymer P1 is shown in Fig. 1. We can clearly distinguish between the $\pi\pi^*$ at lower and the $n\pi^*$ band at higher wavelengths. Both bands are due to the azobenzene chromophore. Data below 390 nm could not be determined for the films under investigation, because the absorbance was too high.

Linearly polarized irradiation for 12 h gave an order parameter S measured at 467 nm of 0.13 (Fig. 2 a). The orientation of the chromophores is preferentially perpendicular to the polarization direction of the electric field vector of the actinic light, because the transition moment of the azobenzene moieties is oriented approximately along their long axis. This orientation is erased by heating above the glass transition temperature of the amorphous polymer (Fig. 2 b).

The results of the waveguide experiments for P1 are shown in Table 1. As the long axis of the chromophores is also the direction of the highest polarizabiliy the refractive indices in the three directions of space show the mean orientation of the chromophores. The fresh film and the heated film are nearly isotropic. The in-plane directions x and y seem to be slightly preferred. Irradiation with linearly polarized light results in a decrease of n_x (parallel to the polarization) and an increase in n_y and n_z.

The photooriented film is almost perfectly oblate, i. e. the chromophores orient equally strongly into all directions perpendicular to the polarization direction of the actinic light. This is seen by stating that $n_x < n_y \approx n_z$.

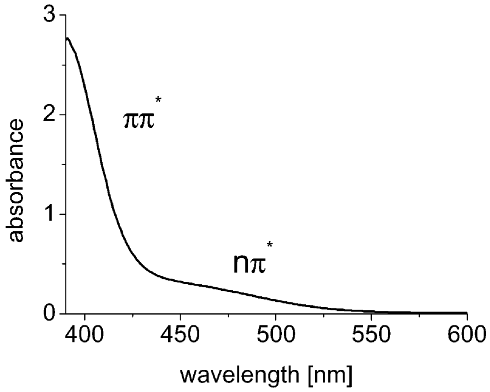

FIGURE 1: Polarized UV/VIS spectrum of a 1.25 µm film of P1 (initial state).

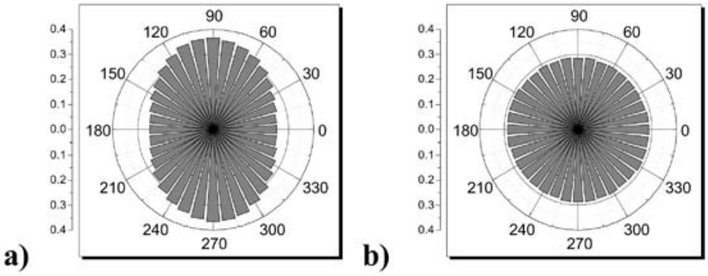

FIGURE 2: Polarized absorbance of a P1 film measured at 467 nm, a) irradiated film (50 mW/cm², 12 h), b) annealed film (90 °C, 4 h)

The initial states of the films made from the liquid crystalline polymers P2 and P3 are almost perfectly isotropic, too. The film made from P2 is slightly out-of-plane oriented in accordance with previous observations [8]. The film made from P3 spin-coated onto a previously deposited layer of polyimide and rubbed in the y-direction did not show a detectable preferential orientation, either.

TABLE 1: 3D refractive indices and thickness (d) of a film made from P1 measured by waveguide spectroscopy. Experimental conditions see Fig. 2.

	n_x	n_y	n_z	d (μm)	
Fresh	1.637	n. d.	1.628	1.25	isotropic
irradiated	1.601	1.659	1.658	1.16	oblate
annealed	1.644	1.644	1.640	1.15	isotropic

These films were photooriented until saturation of the birefringence occurred, as can be seen in Fig. 3. The results from the waveguide spectroscopy show in all cases almost oblate orders, as for the amorphous polymer. The direction perpendicular to the film plane is in all cases slightly less preferred in comparison to the direction perpendicular to the polarization of the laser light and in the film plane.

Annealing of these films in the liquid crystalline state gave completely different results from the erasure, that was observed in the case of the amorphous polymer P1. The film made from the polymer P2 remained oblate, but showed almost a two-fold increase in the birefringence values. This was expressed in a strong decrease of the refractive index in the x direction and increases in the other two directions. The thickness for this film seemed to decrease, too. Results for P2 are listed in Table 2.

TABLE 2: 3D refractive indices and thickness of a film made from P2 measured by waveguide spectroscopy. Irradiation see Experimental. Annealing for 5 min at 79 °C.

	n_x	n_y	n_z	d (μm)	
Fresh	1.650	1.649	1.655	1.8	Isotropic
Irradiated	1.610	1.679	1.673	1.8	Oblate
Annealed	1.565	1.683	1.682	1.7	Oblate

The waveguide modes for y and z direction for the annealed film of P2 were very difficult to excite, because of a high absorbance due to anisotropic scattering. Therefore, the result was checked by the Ehringhaus method, which gave an in-plane birefringence of 0.12, which is in accordance with the values from waveguide spectroscopy.

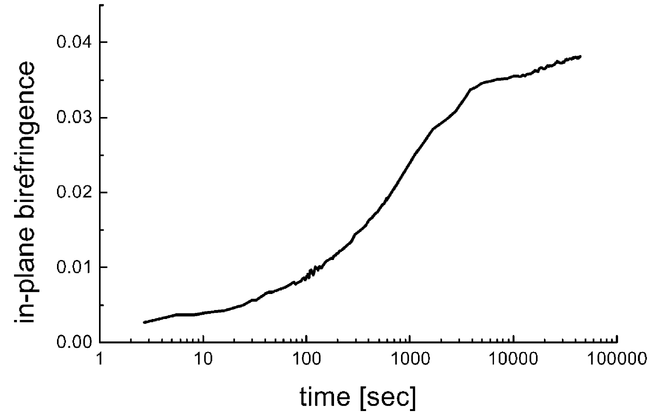

FIGURE 3. Development of the in-plane birefringence of the 4.1 μm thick film of polymer P3 during the irradiation with linearly polarized light of a wavelength of 488 nm and a power density of 50 mW/cm².

Polymer P3 showed the results listed in Table 3. This polymer showed a homeotropic orientation after annealing. The exact values are in this case to be taken with caution because of a gradient in the film.

TABLE 3: 3D refractive indices and thickness of a film made from P3 measured by waveguide spectroscopy. Irradiation see Experimental. Annealing for 23 h at 85 °C.

	n_x	n_y	n_z	d (μm)	
Fresh	1.584	1.584	1.584	4.1	Isotropic
Irradiated	1.571	1.608	1.603	(3.3)	Oblate
Annealed	1.573	1.578	1.604	(2.4)	Homeotropic

In order to investigate the origin of the gradient in this film a 50 nm thin layer of polyimide was spin-coated onto the substrate and rubbed in the y direction prior to the deposition of a 5.0 μm thick film of P3. This film was isotropic directly after spin-coating and became also homeotropic after annealing at 85 °C for 17 d. Therefore it was concluded, that the orientation at the air interface is the reason for the homeotropic order in annealed films of this polymer.

CONCLUSIONS

The results show that the conventional photoorientation gives almost oblate orders in films prepared from amorphous or liquid crystalline polymers. Annealing of the film above T_g results in erasure of the order for the amorphous polymer P1. The liquid crystalline polymer films exhibit different behaviour, when annealed in their liquid crystalline phase. Polymer P2 shows an amplification of the photoinduced oblate order, whereas the film made from P3 can be characterized by a mainly homeotropic order. In the case of films made from the polymer P3 the air interface seems to be responsible for the homeotropic order exhibited by the annealed film, as shown by an experiment with an orienting layer made from polyimide.

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