4324 *Macromolecules* **2005,** *38,* 4324−4330

The Generation of Three-dimensional Anisotropies in Thin Polymer Films by Angular Selective Photoproduct Formation and Annealing

C. Christoph Jung, Regina Rosenhauer, Michael Rutloh, Christian Kempe, and Joachim Stumpe*

Fraunhofer Institute of Applied Polymer Research, Science Park Golm, Geiselbergstr. 69, D-14476 Potsdam, Germany

Received November 11, 2004; Revised Manuscript Received February 7, 2005

ABSTRACT: Linearly polarized light can induce an order parallel to the polarization direction of light in polymer films containing different photochromic groups. In principle, this offers the possibility to generate prolate in-plane orders in polymer films. Two such photochemical processes are investigated in this paper. One of them is the irradiation of azobenzene-containing polymer films with linearly polarized red light after an unpolarized UV preirradiation step. The other one is the angular selective photocycloaddition of cinnamate-containing polymer films induced by linearly polarized UV light. Because in both cases the order is low after the irradiation, the liquid crystalline polymer films are annealed in their mesophase to modify the photoinduced order by thermotropic self-organization. The resulting three-dimensional indicatrices, as determined by waveguide spectroscopy, are found to be prolate in-plane, biaxial, or homeotropic in dependence on the polymer structures, preparation conditions, and irradiation conditions of the films.

Introduction

Polymer films with anisotropic physical properties (such as optical or electric properties) have important applications in optical data storage, as optical components, as optical films for displays, and as aligning layers for liquid crystals. Therefore, methods are needed to induce these anisotropies in a defined way and sometimes pixelwise. Light-induced orientation processes possess both properties.

Reviews on the conventional light-induced orientation in polymers have been published by several authors.[1−4]

The conventional photoorientation, as realized for azobenzene-containing polymers by irradiation with polarized blue or green light, leads to an orientation of the molecules perpendicular to the polarization vector of the actinic light. The resulting three-dimensional (3D) indicatrix is therefore oblate (negatively uniaxial), with two long axes and one short axis. The short (optical) axis is parallel to the polarization vector of the irradiation light.

A light-induced orientation and subsequent annealing of azobenzene chromophores in liquid crystalline polymers by irradiation with unpolarized UV−vis light and subsequent irradiation with linearly polarized red light was described by us.[5,6] The orientation induced by this two-step process is parallel to the electric field vector of the red light and has already been described previously.[7] It was demonstrated[5,8] that longer irradiation times for some polymers may lead to an orientation perpendicular to the polarization vector of the red light.

The parallel mechanisms as described above should in principle lead to a prolate (positively uniaxial) indicatrix with two short axes and one long (optical) axis parallel to the polarization vector of the linearly polarized irradiation light. In Figure 1, the development of the indicatrices is shown schematically. Films with prolate orders find important applications as so-called +a-plate compensators in liquid crystal displays[9] and for photoalignment. The two-step irradiation process of azobenzene-containing polymers, as discussed below, has the additional advantage that red light is readily available from He−Ne lasers.

For cinnamate-containing polymers, irradiation with polarized light of suitable wavelength leads, in addition to photoisomerization, to an angular selective photocycloaddition.[10] The resulting photoaddition products are formed preferentially parallel to the polarization vector of the actinic light. The usage of such materials for photoalignment of low molecular liquid crystals has been described.[11,12] Photoproduct distributions of cinnamate polymers were analyzed in a previous publication.[13] This work, however, is hampered by the fact that all reduction of the in-plane absorbance at isosbestic points during irradiation is attributed to dimerization and the possibility of out-of-plane orientation is overlooked.

A weak anisotropy is found in the irradiated films, where the maximum of absorbance is perpendicular to the electric field vector of the actinic light. This should be caused by the remaining cinnamate ester groups, which cannot be excited, and possibly by concomitant photoorientation.

But upon heating in the liquid crystalline phase in the case of thin films of cinnamate-containing liquid crystalline copolymers,[14,15] an alignment occurs parallel to the electric field vector of the actinic light. This should be caused by the highly anisometric photocycloaddition products, which are formed preferably parallel to the electric field vector. In a recently published reference,[15] terpolymers containing fluorescent side chains, mesogenic side chains, and cinnamate-containing side chains were oriented cooperatively by the use of polarized light. The fluorescence of the aligned fluorescent side chains was not quenched by the photochromic cinnamate residues.

The three-dimensional anisotropies resulting from photochemical processes, which generate orders parallel

---

* Author to whom correspondence should be addressed. E-mail: joachim.stumpe@iap.fhg.de.

10.1021/ma0476846 CCC: $30.25

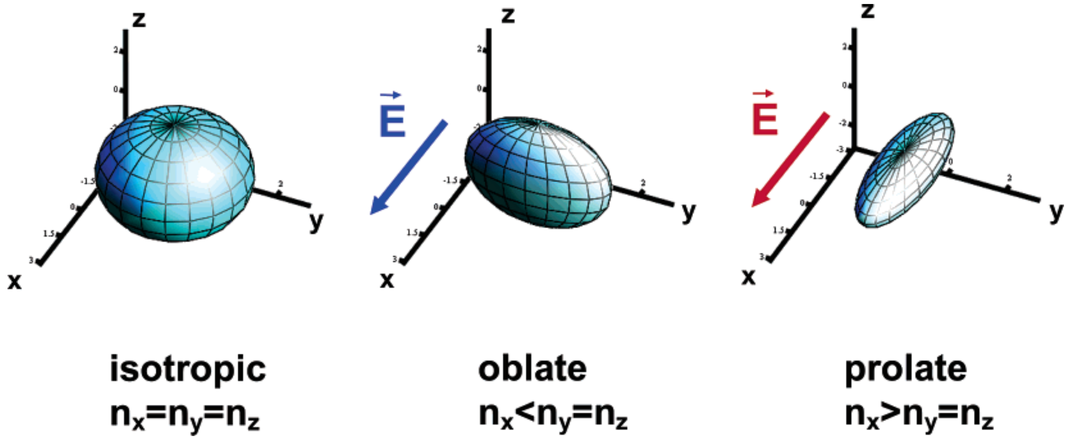


Figure 1. Different idealized indicatrices. Mid: conventional photoorientation. Right: parallel orientation by angular selective photoproduct formation.

Table 1. Chemical Structures of the Polymers

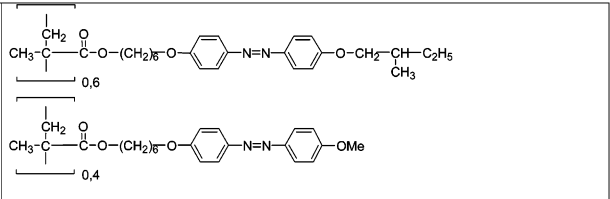
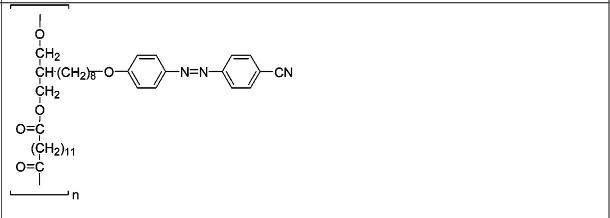
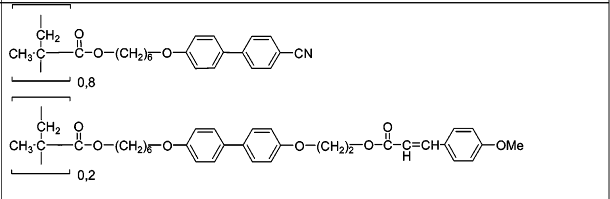
P1	
P2	
P3	

Table 2. Thermal Properties of the Polymers[a]

P1	g 88°C s_f 108°C n 113°C i
P2	g 24°C s_x 26°C s_a 34°C n 47°C i
P3	g 58°C lc 105°C i

[a] Explanation: g, glassy state; s, smectic; n, nematic; i, isotropic; lc, liquid crystalline.

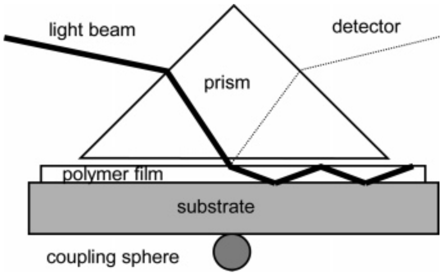


Figure 2. Configuration of the prism coupler for measuring thin polymer films.

to the polarization direction of the actinic light, and which are modified by annealing in the liquid crystalline state of the polymers to give higher anisotropies, will be reported in this paper. The question was whether it is possible to make prolate-ordered films with such processes and whether even other (biaxial) three-dimensional orders can emerge.

Methods and Materials

The chemical structures of the investigated liquid crystalline polymers are depicted in Table 1. P1 and P2 are azobenzene-containing copolymers, which can be oriented using the two-step orientation process. The butoxy-substituent in one of the side chains in P1 reduces aggregation tendencies and also serves to increase its solubility. The long main chain spacer in P2 was introduced to decouple the main chain and side chain and test its effect on the three-dimensional order. P3 is a cinnamate-containing side chain copolymer, which contains a mesogenic 4-cyano-biphenyl side chain. The additional phenyl rings in the cinnamate side chain were introduced to increase the anisometry of this side chain and of the dimeric head-to-tail photoproducts, which should result in a higher aligning force.

1. Materials. Table 1 give chemical structures of the polymers, and Table 2 gives thermal properties of the polymers.

2. Methods. 2.1. Spin-coating. The polymers were dissolved in tetrahydrofuran (THF) in different concentrations. Solutions below 50 mg/mL were filtered with 200-μm filters (Nalgene) before spin-coating. Glass plates (Corning, n_{HeNe} = 1.5025) were used as substrates, immersed in concentrated sulfuric acid (for at least 2 h), and then rinsed with deionized water. The spin-coating system RC 5/8 (Karl Suss Technique S. A., Saint Jeoire, Frankreich) was used to prepare films in a range from 680 nm to 3.5 μm.

2.2. Prism-coupling. The instrumental setup has been described elsewhere in detail.[16] This measuring technique comprises the coupling of a monochromatic coherent light beam into the investigated film using a highly refracting prism in total reflection (Figure 2). The two in-plane refractive indices and the film thickness are obtained from two measurements with s-light in two different orientations by nonlinear least-squares fitting to published equations.[17] From corresponding measurements using p-light, the refractive index normal to the film plane is obtained. A tilt is detected if the two p-measurements differ significantly.

The polymer film on a substrate is pressed with the help of a metal sphere to the base of a prism (LaSF N9, Schott, n_{HeNe} = 1.84489, 90°), whereby the air gap between prism and polymer film becomes so thin that the evanescent field of the measuring light couples into the waveguide modes of the film. Light source was a frequency stabilized He−Ne laser (Coherent, Model 200, 1 mW, 632.8 nm). The accuracy (repeatability) thereby reached for the measurement of the refractive indices is better than 0.001.

2.3. Transmission Ellipsometry at Variable Angle of Incidence. A homemade null ellipsometer using the same He−Ne laser (Coherent, Model 200) at a wavelength of 632.8

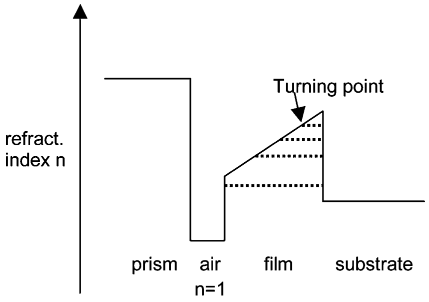


Figure 3. Refractive index profile along the z direction for a gradient, which increases monotonically from the air gap to the substrate side (solid line). The main areas of the modes are shown (dotted lines).

nm (1 mW) was used, which is described in detail in a previous publication.[16]

Results

In the following sections, theoretical simulations concerning the measurement technique, theoretical considerations concerning the creation of photoinduced orders parallel to the electric field vector of actinic light in azobenzene-containing polymer films, and experimental results concerning the photoinduction, and modification by self-organization of three-dimensional orders in azobenzene and cinnamate-containing polymer films will be described.

3.1. Simulation of Prism-coupling Experiments for Inhomogeneous Layers. The prism-coupling method not only allows measuring the average refractive indices in the three dimensions of space, it also allows making statements about anisotropy gradients along the film normal. Simulations of films exhibiting anisotropy gradients were performed to provide insight into the prism-coupling measurements obtained from such films.

The Berreman method is very precise and allows calculation of arbitrary gradients. Here, the refractive index variation in the z direction (normal to the film plane) is represented by many homogeneous layers. The formulation of Schubert[18] was used, and the calculation of the exponential matrix Δ was performed using the diagonal matrix,[19] which was calculated using the software package SSLII.[20]

For the special case when s- and p-polarization are eigenpolarizations, the 4×4 matrix was calculated analytically using the theorem of Cayley–Hamilton[18] and changed into 2×2 matrixes to ensure quicker calculation for s- and p-polarization, separately. A low absorbance of the polymer layer must be assumed to generate minima in the reflectivity curve. In a nonabsorbing and nonscattering medium, the modes are coupled in and coupled out. It should be noted that the imaginary part of the refractive index has to be taken as positive in the applied equations.

The simulations with the help of the Berreman method revealed that increasing gradients cannot be determined very well because of the small intensity of the modes with higher mode index. This is immediately apparent by Figure 3.

The modes in the polymer film exist in a range of higher refractive index. The turning point of the modes with high mode index n_m lies far apart from the prism. Therefore, these modes can only weakly be excited by the evanescent field at the prism base, which decreases exponentially with the distance from the prism.

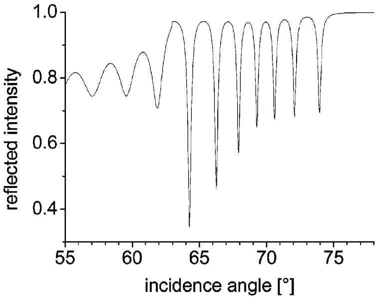


Figure 4. Simulated reflected intensity for a prism-coupling experiment of a inhomogeneous polymer film vs the external incidence angle. The refractive index of the polymer film decreases linearly from $n_0 = 1.62$ to $n_1 = 1.55$. The substrate index is $n_s = 1.5045$. The thickness of the polymer film is $d = 5$ μm. (Prism index $n_p = 1.84489$).

An example for a simulation of a prism-coupling experiment is shown in Figure 4. Here, the refractive index of the film decreases from the air interface to the substrate interface.

Reflection losses at the prism entrance and exit windows were neglected. The distances between the minima of the reflected intensity for angles above the total reflection between prism and substrate at 63° first become smaller and then increase again with increasing incidence angle. This characteristic pattern is caused by the gradient. A polymer film that is homogeneous along the z direction produces minima, whose distances decrease monotonically with increasing incidence angle.

3.2. Theoretical Considerations about a Possible Mechanism of the Two-step Irradiation Process of Azobenzene-containing Polymers. The direction of the transition moment in relation to the azobenzene isomers is of importance for the mechanism of the orientation process, which is induced by nonpolarized UV–vis irradiation and subsequent linearly polarized red light irradiation. Exposure to nonpolarized UV light establishes a steady state with a high amount of Z isomers in the case of donor–donor and weakly donor–acceptor substituted azobenzenes. The subsequent irradiation with linearly polarized red light generates a weak orientational preference parallel to the electric field vector.[5] A possible explanation for this effect relies on the assumption that the angle between the transition moment of the Z isomer and the transition of the E isomer is smaller than the magic angle (54.7°) for a fixed N=N direction of the azo group (whose direction on average should not change during isomerization). The explanation is based on the high ratio of Z isomers produced by the UV light. These Z isomers do undergo Z–E isomerization induced by linearly polarized red light preferentially if they are oriented parallel to the polarization direction. The rotational diffusion of the more globular Z isomer should be enlarged compared to that of the rodlike E isomer. This even increases the proportion of the Z isomers, which will at some point lay more or less parallel to the polarization direction of the red light. Thereby more E isomers will have been produced by isomerization (photoisomerization and thermal isomerization) from Z isomers that were lying parallel to the polarization direction of the actinic light than from Z isomers that were lying perpendicular to the polarization direction because these can only react via thermal isomerization. Therefore, the resulting anisotropy of the E isomers is also parallel to this direction if the angle between the transition moments

Table 3. Three-dimensional Indicatrix of a Film of Copolymer P1[a]

treatment	n_x	n_y	n_z	d/μm	Δn_{zx}	Δn_{yx}	$\sum n_i/3$	
freshly prepared	1.620	n. d.	1.618	n. d.	−0.002	n. d.	1.619	isotropic
irradiated	1.632	1.623	1.627	n. d.	−0.005	−0.009	1.627	biaxial $x > z > y$
annealed	1.672	1.531	1.629	0.68	−0.043	−0.098	1.611	biaxial $x \gg z \gg y$

[a] Irradiation conditions can be found in the text. Annealing at 100 °C (12 K above T_g).

of the *E* isomers and the transition moments of the *Z* isomers is smaller than the magic angle.

Quantum chemical calculations for a 4-cyano-4′-alkoxy-azobenzene[16] give an angle of 67° between the transition moments of the *E* isomer and the *Z* isomer if the N−N bond does not change its orientation during isomerization. This would be about 12° too high for parallel alignment. In contrast to this, the angles in crystals of unsubstituted azobenzene[21] would nearly support the explanation given above. Possibly, the average N−N bond direction changes during isomerization because of matrix effects. The orientation of the isomerization product might be given by the anisotropic shape of the matrix (the shape of the hole in the immediate molecular environment of the azobenzene residue if the azobenzene residue is thought to be removed), which is caused by the slightly anisotropic shape of the *Z* isomer. On the other hand, the quantum chemical calculations might deviate from the real values by about 12°, which would not make the assumption of matrix effects necessary.

3.3. Experimental Results for the Orientation Processes Using Angular Selective Photoproduct Formation in Azobenzene and Cinnamate-containing Polymers. Two strategies using azobenzene and cinnamic ester containing liquid crystalline side chain polymers were investigated to generate films with prolate order. In two cases, a two step procedure is applied where, in the first step, the films were irradiated (for azobenzene divided into two steps) in the glassy state at room temperature, and in a second step, the photoinduced anisotropy became modified by the thermotropic self-organization attributable to annealing above the glass transition. A special case is P2 because the glass transition is close to the room temperature. Therefore, the irradiation steps are immediately connected with the annealing step.

In the case of azobenzene-containing polymers, the in-plane order after irradiation is parallel to the electric field vector of the actinic light and after annealing, too. In the case of cinnamate-containing polymers, the long wavelength absorbance in the UV−vis region would be expected to be perpendicular, and the long molecular axis of the head-to-tail photoproducts should be parallel to $\vec{E}$. The order of the photoproducts should govern the annealing behavior. Correspondingly, the photoproducts in the case of the red light process for azobenzene-containing polymers are the reisomerized *E* isomers, which generate the aligning force.

All numerical results are compiled in an overview (Table 6) at the end of the results section.

3.3.1. Results for the Two Steady-state Irradiation Process of Azobenzene-containing Polymers. As reported, the photoorientation with linearly polarized red light after UV preirradiation results in an indicatrix with the long axis parallel to the electric field vector.[5,6] In the following experiments are described amplifying the induced anisotropy by annealing of films, thick enough to be characterized concerning the generated spatial order by waveguide spectroscopy.

Table 4. Three-dimensional Indicatrix of a Film of Azobenzene-containing Polymer P2[a]

treatment	n_x	n_y	n_z	d/μm	Δn_{zx}	Δn_{yx}	$\sum n_i/3$	
irradiated	1.665	1.588	1.514	1.4	−0.171	−0.077	1.589	biaxial $x \gg y \gg z$

[a] Prepared, irradiated (and annealed) as stated in the text.

Copolymer P1. From the smectic (s_F), azobenzene-containing copolymer P1, a relatively thin (680 nm) film was prepared. The freshly prepared film had a small oblate uniaxial orientation, where the refractive indices in the plane of the film n_x and n_y were slightly higher than the out-of-plane refractive index n_z with a birefringence $\Delta n_{zx} = -0.002$. The average refractive index was 1.619.

The UV irradiation (365 nm, 11 mW/cm^2) was performed four times for 3 min from both sides of the film. This procedure was adopted to ensure a complete irradiation of the whole film. It results in the case of such homopolymers in an isotropization of the film. The subsequent HeNe irradiation (632.8 nm, 500 mW/cm^2) resulted in a small preferential orientation parallel to the polarization direction (*x* direction) as already shown.[5] The measurements show that n_z was enlarged, too, so the result was a biaxial film. Maybe this was caused by an orientation induced by the unpolarized UV light at normal incidence, which leads to enrichment of molecules in the *z* direction. All results are summarized in Table 3.

The birefringence in the film plane was amplified by annealing by a factor of 10 and reached a high value near −0.1. The *z* component of the orientation did increase only slightly.

Polymer P2. The polyester P2 has two long aliphatic spacer groups in the side chain and the main chain. This results in a low T_g close to room temperature and a very specific ordering tendency. In addition to a nematic and a s_A phase, a high-ordered smectic phase is exhibited. The specific intermolecular interaction causing a microphase segregation results in a very pronounced formation of *J* aggregates of 4-alkoxy-4′-cyanoazobenzene. Also, the polymer has a higher tendency to align parallel to the glass substrate.[16] A 1.4-μm-thick film has been prepared and investigated by waveguide spectroscopy. The film showed some scattering before the irradiation. After UV irradiation for some seconds (333.6−363.8 nm, 20 W/cm^2), while heating with a hot air blower, the opaqueness vanished, and the polymer was irradiated for 1 h at 200 mW/cm^2 using linearly polarized red light (632.8 nm). The resulting birefringence in the plane of the film was determined with a Retarmet (Zeiss) as $\Delta n_{yx} = -0.077$. The refractive indices $n_y = 1.588$ and $n_z = 1.514$ were determined using the prism coupler. Therefore, $n_x = 1.665$ and an average refractive index of 1.589 resulted (Table 4).

The long time irradiation with red light did not lead to a change of the sign of the orientation for this polymer as observed for other polymers.[5] In contrast to these experiments, the simultaneous self-organization led after short irradiation periods to the amplified orientation parallel to the electric field vector. This orientation was found to be stable even at prolonged irradiation because of the liquid crystalline properties. In this case, both steps, induction of anisotropy and annealing, occur simultaneously because of the low T_g of the polymer.

It should be stated that the films did exhibit smaller determined birefringences than normally observed for thinner oriented films of this polymer.[22] This might be due to anisotropy gradients in the thicker films.

3.3.2. Results for the Angular Selective Photocycloaddition in a Cinnamate-containing Copolymer. In contrast to azobenzene-containing polymers, cinnamate-containing polymers are transparent for visible light. This makes them interesting for application as retarders in displays. It is known that liquid crystalline copolymers with cinnamate units orient (at least in thin films[14]) after an irradiation with polarized UV light and subsequent annealing in the liquid crystalline phase parallel to the polarization direction of the irradiation light. In principle, this would open a way to realize prolate in-plane indicatrices. Therefore, the three-dimensional refractive indices of thicker films of the cinnamate-containing copolymer P3 and their macroscopic alterations after irradiation and annealing were investigated.

Two different ways of preparation were used. The first series of four films with thicknesses between 1.2 μm and 3.5 μm were prepared from a THF solution (c = 40 mg/mL) of P3 by casting, waiting, and spinning. These films showed average refractive indices between 1.593 and 1.604, where the thinnest film had the highest refractive index (this could by caused by the densest packing). These average refractive indices seemed to correlate with the preferential orientations. The denser films showed a stronger z component of their orientation. The birefringences varied from 0.001 to 0.041. For all spin-coated films of this series, the z component was the highest component of their indicatrix.

Polarized irradiation of three films using a wavelength of 325 nm and a power density of 10 mW/cm^2 was performed. The polarization direction defines the x direction. The resulting birefringences in the plane of the films were dependent on film thickness and irradiation time. The value of $\Delta n_{yx} = -0.010$ was reached for a film of thickness 1.2 μm, which had been irradiated for a duration of 3 min 45 s. For the other films, values of -0.001 (2.8 μm, 10 min 11 s) and -0.002 (3.5 μm, 6 min) resulted. The high value of the thinnest film might indicate some self-ordering tendency during the irradiation, whereas the other two films did only show small changes. A reduction of the averaged refractive index, because of the conversion of the double bonds of the cinnamate residues into the single bonds of the cyclobutane adducts by the photocycloaddition, could not be detected by comparing the average refractive indices after irradiation of 1.607 with the value before irradiation of 1.604, 1.599 (compared to 1.599), and 1.595 (compared to 1.595), respectively. This is probably due to the small conversion efficiency. The respective refractive index in z direction was higher than the highest refractive index in the film plane for all three films. This is reflected in the values for Δn_{zx} of 0.035, 0.009, and 0.008.

Annealing of the 1.2-μm film from the cinnamate-containing copolymer P3 at 100 °C for one day resulted in a loss of the birefringence in the film plane and a preferential orientation perpendicular to the film plane with an out-of-plane birefringence of $\Delta n_{zx} = 0.155$ was realized. This may be due to the anisotropy before annealing or due to interfacial interactions of the liquid crystalline copolymer. The interfacial interaction leads to a reduction of the surface energy by conformational changes leading to anisotropy of the interfaces, which might be transferred to the volume of the film on annealing in the liquid crystalline state. In this case, the angular selective formation of photocycloaddition products was not sufficient to govern the orientation of the film.

Preparation of two more films (with thicknesses of 770 nm and 1.7 μm) was performed using a higher concentrated THF solution (c = 131 mg/mL) of the same copolymer P3. The preparation of the thinner film was accomplished with a rotation speed of 1000 rpm (acceleration 300 rpm/s, duration 30 s) of the thicker film in two steps with rotation speeds of 300 rpm (100 rpm/s, 30 s) and 2000 rpm (700 rpm/s, 30 s). The averaged refractive indices of the films were almost equal (1.602 and 1.602) and similar to those of the first series. However, the thinner film, prepared by fast one-step spinning, showed a preferential orientation in the film plane with $\Delta n_{zx} = -0.007$, whereas the film that had been prepared by slow spinning in the beginning showed a positive out-of-plane birefringence of $\Delta n_{zx} =$ 0.009, similar to the films prepared by casting and spinning. This is a strong hint toward a preparation dependency of the initial order in films freshly prepared from this polymer.

The irradiation with polarized light of the different wavelength of 365 nm at a power density of 14 mW/cm^2 resulted in birefringences in the film plane of $\Delta n_{yx} = -0.006$ (thinner film, 23 min duration of irradiation) and $\Delta n_{yx} = 0.002$ (thicker film, 30 min). The averaged refractive indices were 1.607 and 1.603 and therefore somewhat higher compared to the initial state. This behavior was similar to the differently prepared first series. As in the first series, the self-ordering tendency during the (shorter) irradiation might be stronger in the thinner film. In the second series, no filter effect has to be taken into account because of a very low absorption of the polymer at the irradiation wavelength of 365 nm. Therefore, the actinic light is not attenuated along the z direction in the film, in contrast to the first series with an irradiation wavelength of 325 nm. The thicker film had a higher preference for the z direction ($\Delta n_{zx} = 0.011$ compared to $\Delta n_{zx} = -0.003$).

Annealing of the two films for a duration of 3$^1/_2$ days at 100 °C resulted for the thinner film in an almost in-plane prolate order. Here the birefringence in the film plane had a value of $\Delta n_{yx} = -0.157$ and was comparable with the value of the homeotropic aligned film of the first series. The refractive indices for all states of this film are presented in Table 5.

Annealing of the thicker film led to refractive indices in the film plane of $n_x = 1.628$ and $n_y = 1.553$ and a refractive index perpendicular to the film plane of $n_z =$ 1.646. The closer inspection of the prism-coupling results of this film yielded further information concerning the question of homogeneity in the z direction and the question, whether the air interface shows a homeotropic orientation as described for other polymers[23] or whether the glass interface is responsible for a homeotropic orientation.

The reflectivity curve for s-polarization (Figure 5) perpendicular to the polarization of the actinic light

Table 5. Three-dimensional Indicatrix of a Film of the Cinnamate-containing Copolymer P3[a]

treatment	n_x	n_y	n_z	d/μm	Δn_{zx}	Δn_{yx}	$\Sigma n_i/3$	
freshly prepared	1.604	n. d.	1.597	n. d.	−0.007	n. d.	1.602	isotropic
polarized irradiation	1.610	1.604	1.607	n. d.	−0.003	−0.006	1.607	biaxial $x > z > y$
annealed	1.702	1.545	1.559	0.77	−0.143	−0.157	1.611	∼prolate $x \gg z > y$

[a] Prepared, irradiated and annealed as stated in the text.

Table 6. Overview over All Films at All Treatment Stages

	fresh		irradiated			annealed		
d/μm	$\bar{n} = 1/3\ \Sigma n_i$	Δn_{zx}	$\bar{n}$	Δn_{yx}	Δn_{zx}	$\bar{n}$	Δn_{yx}	Δn_{zx}
P1, azobenzene two-step process								
0.68	1.619	−0.002	1.627	−0.009	−0.005	1.611	−0.098	−0.043
P2, azobenzene two-step process								
1.4	n. d.	n. d.	n. d.	n. d.	n. d.	1.589	−0.077	−0.171
P3, cinnamate, first series, spin-coated after 2−2.5 min evaporation, 325 nm irradiation								
1.2	1.604	0.041	1.607	−0.010	0.035	1.609	0.009	0.155
2.7	1.600	0.008	1.599	−0.001	0.009	n. d.	n. d.	n. d.
3.4	1.593	0.001	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
3.5	1.597	0.005	1.595	−0.002	0.008	n. d.	n. d.	n. d.
P3, cinnamate, second series, spin-coated from a 130 mg/mL solution w/o waiting								
0.77	1.602	−0.007	1.607	−0.006	−0.003	1.611	−0.157	−0.143
1.7	1.602	0.009	1.603	0.002	0.011	1.609	−0.075	0.018

clearly shows that a gradient existed in this film. The distance between the two intensity minima at higher incidence angles is larger than the distance between the intensity minima at smaller incidence angles.

When regarding the depths of the intensity minima for p- and s-polarization, it becomes obvious that the refractive index n_z increases with distance to the air interface, whereas the orientation parallel to the irradiation direction is strongest at the air interface. This is obvious from the fact that the minimum of reflected intensity for p-polarization is much less deep at higher incidence angles than the minima at smaller incidence angles. The minima for s-polarization are more or less of the same depth. Therefore, the glass interface shows a more homeotropic orientation, whereas the molecules at the air interface are oriented mainly in the in-plane direction parallel to the polarization direction of the actinic light.

Because the strong gradient in this comparatively thin film falsifies the actual values of the refractive indices determined from the equations of ref 17, the film was also investigated by transmission ellipsometry at variable angle of incidence. Using the average refractive index and the thickness of the fresh film values of $n_x = 1.600$, $n_y = 1.560$, and $n_z = 1.645$ resulted. The biaxial character of the order and the value of n_z were therefore correctly represented by the evaluation of the prism-coupling experiment, whereas the in-plane birefringence was overestimated because of the gradient.

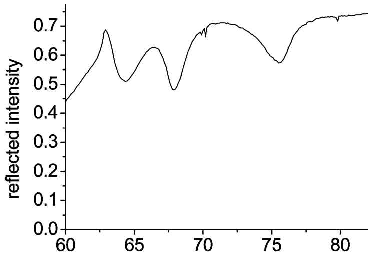


Figure 5. Prism-coupling experiment (s-polarization, see text) of a 1.7-μm-thick film of the copolymer P3. Preparation, irradiation and annealing conditions: see text.

Conclusion

A prolate order in the film plane can be induced in liquid crystalline polymer films containing azobenzene or, alternatively, cinnamic ester groups. The base of the photoinduction of a prolate order is in both cases the angular selective formation of a photoproduct. In the case of azobenzene-containing polymers, *E* isomers are angular selectively formed in a film rich in *Z* isomers generated by UV light. In the case of cinnamate-containing polymers, photocycloaddition products are formed preferentially parallel to the electric field vector of the incident light.

However, the study shows that in addition to the basic effects, the ordering tendency of the polymer and the very small initial order of the films has to be considered. The interaction of the polymer P3 with the glass interface leads to a tendency for out-of-plane orientation, in contrast to the interaction with the air interface as observed for a different polymer.[23] Therefore, the copolymer P3 also shows a different behavior for the investigated films of P2, which interacted with its interfaces in a way that the planar orientation is preferred. It was shown that the out-of-plane tendency of P3 films can be overcome by suitable spin-coating conditions. The formation of an indicatrix that was nearly in-plane prolate was successful for a thinner film, which was prepared using high spinning speeds. For a differently prepared thicker film of the same polymer, a biaxial order resulted.

However, the effect of the initial order of the polymer films on the final orientation after annealing can also be used to achieve the final goal to prepare prolate films. So, annealing of a comparatively thin film, prepared with higher spinning speeds from the azobenzene-containing copolymer P1, led to a nearly prolate order after the UV−vis and red light two-step orientation process.

In both cases specific values of retardation can be established by subsequent nonpolarized or polarized irradiation steps.

The induction of in-plane prolate orders has been shown to be possible. It does not only rely on the parallel orders directly induced by light but also on the initial order of the films, the chemical structure of the polymers, and the irradiation conditions.

Acknowledgment. We thank A. Vinuales, M. Pinol, J.-L. Serrano, University of Zaragoza (P3), G. Galli, University of Pisa (P1), and S. Hvilsted, Technical University of Denmark, Lyngby (P2) for the preparation of the polymers. The project was funded by the European Union.

References and Notes

(1) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.
(2) Shibaev, V.; Bobrovsky, A.; Boiko, N. *Prog. Polym. Sci.* **2003**, *28*, 729.
(3) Shibaev, V. P.; Kostromin, S. G.; Ivanov, S. A. In *Polymers as Electrooptical and Photooptical Active Media*; V. Shibaev, Ed.; Springer: Berlin, 1996.
(4) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139.
(5) Kempe, C.; Rutloh, M.; Stumpe, J. *J. Phys.: Condens. Matter* **2003**, *15*, S813.
(6) Zebger, I.; Rutloh, M.; Hoffmann, U.; Stumpe, J., Siesler, H. W.; Hvilsted, S. *J. Phys. Chem. A* **2002**, *106*, 3454−3462.
(7) Kulinna, Ch.; Zebger, I.; Hvilsted, S.; Ramanujam, P. S.; Siesler, H. W. *Macromol. Symp.* **1994**, *83*, 169.
(8) Rutloh, M.; Zebger, I.; Hoffmann, U.; Stumpe, J.; Siesler, H. W. *Polymer Prepr.* **1998**, *39*, 324.
(9) Yeh, P.; Gu, C. *Optics of Liquid Crystal Displays*; John Wiley & Sons: New York, 1999.
(10) Sapich, B. *Einfluss Photochemischer Prozesse auf Dynamik und Ordnung Photochromer Polymere*, Ph.D. Thesis, University of Potsdam, 2001.
(11) Schadt, M.; Schmitt, K.; Kozinkov, V.; Chigrinov, V. *Jpn. J. Appl. Phys.* **1992**, *31*, 2155.
(12) Dyadyusha, A. G.; Marusii, T. Y.; Reznikov, Y. A.; Khizhnyak, A. I.; Reshetnyak, V. Y. *JETP Lett.* **1992**, *56*, 17.
(13) Ichimura, K.; Akita, Y.; Akiyama, H.; Kudo, K.; Hayashi, Y. *Macromolecules* **1997**, *30*, 903.
(14) Kawatsuki, N.; Suehiro, C.; Yamamoto, T. *Macromolecules* **1998**, *31*, 5984.
(15) Rosenhauer, R.; Fischer, T.; Stumpe, J. In *Proceedings of SPIE*; SPIE: Bellingham, WA, 2004; Vol. 5213, p 169.
(16) Jung, C. C. *Lichtinduzierte Generierung und Charakterisierung Optischer Anisotropie*, Ph.D. Thesis, University of Potsdam, 2004.
(17) Yamamoto, S.; Koyamada, Y.; Makimoto, T. *J. Appl. Phys.* **1972**, *43*, 5090.
(18) Schubert, M. *Phys. Rev. B* **1996**, *53*, 4265.
(19) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland, Elsevier: Amsterdam, 1987; p 347.
(20) Tanaka, M.; Ninomiya, I.; Torii, T.; Hasegawa, T.; Hatano, K.; Hatano, Y.; Yoshida, T.; Tone, K.; Kobayasji, T.; Hosono, T. *Scientific Subroutine Library II;* Fujitsu: Tokyo, 1987.
(21) Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*; Academic Press: New York, 1967.
(22) Zebger, I.; Rutloh, M.; Hoffmann, U.; Stumpe, J.; Siesler, H. W.; Hvilsted, S. *Macromolecules* **2003**, *36*, 9373.
(23) Jung, C. C.; Rutloh, M.; Stumpe, J. *Mol. Cryst. Liq. Cryst. Sci. Technol.* **2002**, *375*, 713.

MA0476846