Photoorientation of a Liquid-Crystalline Polyester with Azobenzene Side Groups: Effects of Irradiation with Linearly Polarized Red Light after Photochemical Pretreatment[†]

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ABSTRACT: In contrast to the conventional photoorientation process with blue light, an orientation of 4-cyano-4′-alkoxyazobenzene side groups parallel to the electric field vector of the incident light is generated upon irradiating films of a liquid-crystalline side-chain polymer with linearly polarized red light. The polyester is characterized by smectic and nematic phases $g24S_X26S_A34N46i$ and a strong tendency to form J-aggregates. The process requires a photochemical pretreatment by irradiation with UV light or an exposure to visible light of high power density to produce a certain concentration of the Z-isomer, which destroys any initial orientational order and J-aggregates. The orientation process is cooperative, whereas the light-induced orientation of the photochromic moiety causes an ordering of the alkylene spacers and even of the main-chain segments into the same direction. The most probable mechanism of this two-step process is the angular-selective transformation of the bulky Z-isomers to the rodlike E-isomeric formed by the red light. The aligned E-azobenzene side groups become strongly J-aggregated. Very high values of dichroism of about 0.8 and birefringence of about 0.3 were generated as a result of this combination of the photoinduced orientation process and the thermotropic self-organization, which take place simultaneously under the irradiation conditions. The process results in a uniaxial prolate order of the film, whereas conventional photoorientation leads to a biaxial oblate order. These two different three-dimensional orders have been characterized by FTIR polarization spectroscopy and exhibit also varying intermediate thermal stabilities.

Introduction

In a previous publication,[1] we have shown that the 4-cyano-4′-alkoxyazobenzene groups of the same liquid-crystalline side-chain (LCSC) polymer undergo the conventional photoorientation process upon irradiation with linearly polarized light of 488 nm. This photoorientation takes place by a number of photoselection steps within the steady state of the photoisomerization. The orientation process results in an orientational distribution of the azobenzene side group and all other polymer segments in a plane perpendicular to the electric field vector of the incident light. The investigated polymer belongs to a homologous series of LCSC polyesters with varying aliphatic main- and side-chain length.[2,3]

In addition to this mechanism, a further orientation process was found which results in the orientation of the azobenzene moieties parallel to the electric field vector. This novel, so-called ”biphotonic” holographic storage process was described recently.[4−7] The procedure involves two irradiation steps at two different wavelengths which can be separated in time as much as several minutes. This indicates that the phenomenon is not a classic nonlinear two-photon process generating a higher excited state.[8] Initially, the irradiation with the 488 nm line of the argon ion laser results in a conventional photoorientation, but upon continued exposure exceeding a certain threshold value of power density, an optical clearing process is observed and the film becomes isotropic.[2,4] Subsequent irradiation with linearly polarized light of a HeNe laser (633 nm) results in the induction of optical anisotropy as visualized by a holographic grating.[4] A pure thermal effect can be excluded because of two reasons: On one hand, a wavelength dependence has been observed: the utilization of the 633 nm and the 670 nm lines of a HeNe laser or a diode laser, respectively, lead to the induction of birefringence, while the 780 nm line of a diode laser does not show any effect even at an intensity that was 10 times higher.[4] On the other hand, by using polarization FTIR spectroscopy, Kulinna et al.[2] showed that in contrast to the conventional photoorientation process the HeNe laser aligns the azobenzene moieties parallel to the polarization direction of the incident light. However, no optical anisotropy could be induced using only red light irradiation without any photochemical pretreatment.[5] The same orientation effect was observed for several other polyesters of this homologous series with shorter and longer alkylene segments in the main chain. These structural modifications also result in a variation of the thermal properties, such as glass transition temperature or phase transition enthalpies and temperatures. For the homologues with a longer main-chain excitation wavelengths of 407 and/or 365 nm have been used for the photochemical pretreatment.[9]

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In this case, Ramanujam et al. demonstrated by means of UV−vis and FTIR spectroscopy that a Z-to-E photoisomerization takes place during the subsequent irradiation with red light.

More recently, detailed holographic investigations of some representatives from this polyester series and the same 4-cyano-4′-alkoxy-substituted azobenzene moiety side chain, attached to a poly(methyl methacrylate) backbone, were carried out by Sanchez et al.[5−7] In these approaches incoherent blue light was applied for the first irradiation step and a subsequent photochemical erasure of the gratings stored with a HeNe laser in the second step, although a certain "partial recovery" was observed while keeping the film in the dark. This "memory effect" can be enhanced by an exposure to red light. A remarkable increase of the diffraction efficiency was found in comparison to former investigations.[4] The simultaneous application of blue and red light leads even to the induction of a surface relief.[5,7]

Holographic gratings in azobenzene-containing polymer films caused by the irradiation with red light or as a result of the "biphotonic" orientational procedure are also reported in some other papers.[10−13] In these studies the time gap between the two irradiation steps was on the order of seconds to minutes. Fei et al.[10] have suggested that a triplet−triplet transition from a long-lived triplet state of the Z-isomer should be involved in the mechanism examining poly(vinyl alcohol) films doped with Methyl Orange {sodium salt of 4-[4-(dimethylamino)phenylazo]benzenesulfonic acid} or Ethyl Orange {potassium salt of 4-[4-(diethylamino)phenylazo]benzenesulfonic acid}. This hypothesis was refuted by Bach et al.[11] by transient absorption and holographic experiments utilizing 4-amino-4′-nitroazobenzene embedded in poly(carbonate) films. They confirm the results of Ramanujam et al. described above implying the Z-to-E phototransformation.

Wu et al. utilized nonpolarized UV light (300−500 nm) from a low-pressure mercury lamp (8 mW/cm^2) for the first excitation step of Methyl Yellow {4-(dimethylamino)azobenzene)} in polystyrene or poly(methyl methacrylate) and Ethyl Orange {potassium salt of 4-[4-(diethylamino)phenylazo]benzenesulfonic acid} in poly(vinyl alcohol) as well.[12,13] Unfortunately, in these studies no information about the induced orientational direction with reference to the E-vector is given. For this reason it cannot be distinguished which type of orientational process takes place. In the case of amino-substituted azobenzenes, characterized by bathochromically shifted $\pi-\pi^*$ transitions, our own experiments show that the conventional photoorientation establishing the orientation perpendicular to the E-vector takes place in the case of strong donor−acceptor substituted azobenzenes, such as 4-(dimethylamino)-4′-nitroazobenzene upon HeNe irradiation.[14] Thus, the orientational behavior can be explained by the classical photoorientation process.[15]

Transient absorption spectroscopy reveals an absorption of the Z-isomer as transient species in the red wavelength range[11,13] caused by irradiation with UV or blue light. Furthermore, holograms were induced exclusively by red light exposure, which confirms that a photoreaction takes place at this wavelength. Moreover, in other studies it was demonstrated that photochemical pretreatment with UV light establishing a steady state with a higher proportion of Z-isomers results in an amplification of the conventional photoorientation process. As shown recently,[16,17] such a photochemical decoupling is of great importance in aggregated and ordered systems.

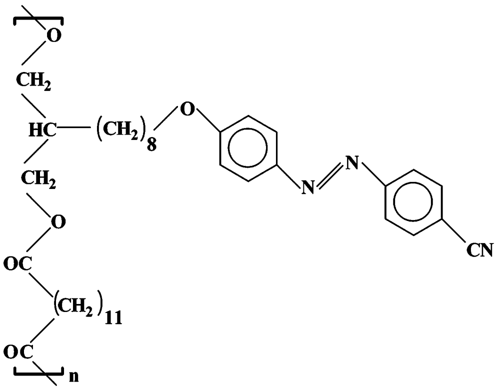

Figure 1. Repeating unit of the investigated polyester.

A very recent review on the different orientation processes of azobenzene moieties attached to amorphous and liquid crystalline polymers is given by Natansohn and Rochon.[18]

In summary, the mechanism of this two-steady-state photoorientation with red light is not understood in detail so far. To shed more light onto this effect, we will compare in this paper both photoorientation processes resulting alternatively in an orientation perpendicular or parallel to the E-vector of the incident light within the same film concerning their induction conditions. Under this aspect the initial state of the films concerning aggregation and orientational order as well as the irradiation conditions with respect to polarization, power density and wavelength have been modified.

Experimental Section

The polyester was synthesized by means of transesterification of 2-[8-(4-((4-cyanophenylazo)phenoxy)octyl]-1,3-propanediol and diphenyl tridecanedioate in the melt under vacuum at elevated temperature. More details about the general synthesis route are described elsewhere.[3] The particular sample employed in the investigations had a number-average molar mass, M_n, of 14 000 and a corresponding weight-average molar mass, M_w, of 29 000 as determined by size exclusion chromatography (SEC) with polystyrene standards calibration. The structure of the investigated polymer is shown in Figure 1.

Differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) were used to characterize the thermal properties of the polymer. It shows a glass transition at 24 °C and transitions between the following mesophases: S_X to S_A at 26 °C (a weak and broad transition), S_A to N at 34 °C (enthalpy $\Delta H \approx 20$ J/g), and a clearing point at 47 °C ($\Delta H < 4$ J/g). The S_A phase was identified by its typical texture using a Leitz Ortholux-Pol BK polarizing optical microscope. A Perkin-Elmer DSC 4 instrument was used with heating and cooling rates between 0.2 and 40 °C/min.[19]

The UV−vis measurements were carried out with a diode-array spectrometer (Polytec X-dap-04 V2.3). A computer-driven stepper with a Glan-Thompson prism was used for the polarization measurements. A microscope spectrometer 3 (Carl Zeiss Oberkochen, spectral range 230−1000 nm with a wavelength resolution of 0.5 nm and a lateral resolution of 2 μm) was used to locally characterize the absorbance within the HeNe laser spot.

A variable-temperature, computer-controlled irradiation setup has been applied for the on-line polarization FTIR measurements during the 488 nm argon ion laser irradiation. This setup was used to follow the photoinduced anisotropy during and after the irradiation as a function of time and temperature, as well as its thermal stability during erasing cycles. A Bruker IFS 88 spectrometer with a spectral resolution of 4 cm^{-1} was used for the FTIR measurements. The polarization of the IR beam was achieved by using a wire-grid polarizer with KRS-5 (TlJ/TlBr 50/50) as substrate. The size of the irradiated sample area was about 3 mm^2.

The 488 nm line of an argon ion laser (700−1000 mW/cm^2; Laser 2000 model 532) and the 633 nm line of a HeNe laser (150−230 mW/cm^2; Spectraphysics model 127) were used for the irradiation experiments. The exposure to nonpolarized radiation (365 nm, 1.4 mW/cm^2; 488 nm, 2 mW/cm^2; 633 nm, 1.5 mW/cm^2) was carried out using an XBO lamp (1000 W, Hanovia 976 C-1, Spectral Energy Corp.) in combination with a monochromator, and additionally a Glan-Thompson prism was used for the polarization of the excitation light. The irradiation was carried out in normal incidence.

Thin films of about 0.1 μm thickness were prepared onto glass substrates by spin-coating using tetrahydrofuran (THF) as solvent (10 mg of polymer in 1 mL). For the FTIR investigations the films were prepared by casting from a chloroform solution (3 mg of polymer in 200 μL of solvent) onto KBr plates. The film thickness obtained by this preparation procedure was approximately 5 μm.

Thermal pretreatment: To have reproducible starting conditions for the film specimens, they were kept 10 min at the isotropic state at 80 °C and afterward placed on a water-cooled metal block of about 15 °C for 10 min or, alternatively, cooled with a rate of about 50 °C/min in a Peltier sample holder.

To study the photochemical behavior in solution 4-(4-(6-bromohexyloxy)phenylazo)benzonitrile (BHPB) as a low-molecular-weight model compound was dissolved in THF. The concentration of the azobenzene was 2×10^{-5} mol/L. THF was purified, dried, and distilled over sodium hydroxide. The solution was filled into a 1 cm cuvette, which was kept in the dark for 5 days at room temperature to exclude the presence of Z-isomers.

The Lambert−Beer law was used for the photokinetic study in dilute solution. While A_t is the absorbance measured as a function of time, c_E is the concentration of the E-isomer, and d is the thickness of the cuvette.

$$A_t = \epsilon_E c_E d + \epsilon_Z c_Z d \qquad (1)$$

$$c_0 = c_E + c_Z \qquad (2)$$

$$A_t = \epsilon_E (c_0 - c_Z) d + \epsilon_Z c_Z d \qquad (3)$$

The unknown values of ϵ_Z (molar absorption coefficient of the Z-isomer) and c_Z (concentration of the Z-isomer) were estimated by a nonlinear fit using eq 3, where c_0 (the overall concentration of all azobenzene isomers) is well-known. Because of the fact that we can assume that the initial concentration of the Z-isomers is zero before the irradiation process starts, ϵ_E can be determined.

The normalized linear dichroism is defined as

$$D = |(A_{\parallel} - A_{\perp})/(A_{\parallel} + A_{\perp})| \qquad (4)$$

where $A_{\parallel}$ and $A_{\perp}$ are the measured absorptions intensities with radiation polarized parallel and perpendicular to the reference axis z, respectively.

To eliminate the influence of the sample orientation on the corresponding band intensities, the structural absorbance A_0[20,21] can be calculated from the absorbance values in the three orthogonal directions x, y, and z:

$$A_0 = (A_x + A_y + A_z)/3 \qquad (5)$$

While the z axis is parallel to the polarization direction of the incident radiation, it propagates along the x axis.

For a uniaxial distribution around the z axis ($A_{\parallel}$), the x and y ($A_{\perp}$) directions are equivalent, so that A_0 can be calculated by

$$A_0 = (A_{\parallel} + 2A_{\perp})/3 \qquad (6)$$

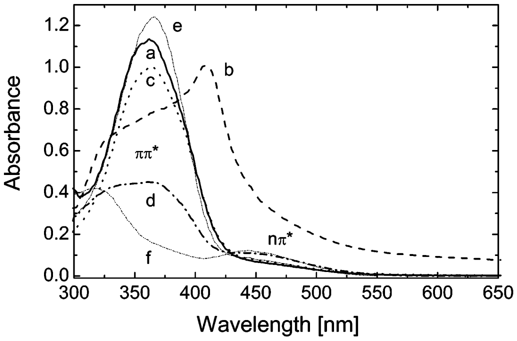

Figure 2. UV−vis spectra of polymer films after different photochemical and thermal treatments and of the model compound 4-(4-(6-bromohexyloxy)phenylazo)benzonitrile (BHPB) in solution: (a) isotropic film at 80 °C; (b) rapid quenching of (a) to temperatures below T_g (~24 °C) and retention at 27 °C; (c) film of (b) after irradiation with 488 nm (5 J/cm^2); and (d) film of (b) after irradiation with 365 nm (6.7 J/cm^2); (e) initial spectrum of BHPB ($c = 2 \times 10^{-5}$ mol/L) in THF; (f) steady-state spectrum of BHPB in THF after UV irradiation with 365 nm (1 J/cm^2). For all irradiation experiments a XBO lamp was used as light source.

For the spectroscopic data recorded only in the film plane we can calculate the mean absorbance A_m, which is equivalent to the spectrum measured with nonpolarized light:

$$A_m = (A_{\parallel} + A_{\perp})/2 \qquad (7)$$

UV−vis spectroscopy was used to characterize the steady state of the photoisomerization process and the orientational order of the photochromic moiety. FTIR spectroscopy was carried out in order to investigate the different mobility and the changes in orientational order of the chromophore, the ester linkage, the methylene units of the main chain, and the alkylene spacer by monitoring the dichroic ratios of characteristic absorption bands.

Results and Discussion

1. UV−Vis Spectroscopic Characterization of the Azobenzene. The UV−vis spectrum of the E-isomer of 4-(4-(6-bromohexyloxy)phenylazo)benzonitrile[22] in solution is characterized by the strong $\pi-\pi^*$ transition at 365 nm and the weak n$-\pi^*$ transition at 450 nm. This spectrum is comparable to those of the polymer in solution and of isotropic polymer films above the clearing temperature (see Figure 2). However, compared to the solution, the spectra of spin-coated or cast films of the same polyester are significantly different. The $\pi-\pi^*$ transition of supercooled films is strongly shifted to longer wavelengths and much broader. Shape and maxima of the spectra strongly depend on the thermal history of the film. Thus, it is characterized by a large bathochromic shift of the maximum of the $\pi-\pi^*$ absorption up to 410 nm in the case of freshly prepared films and up to 450 nm in annealed or aged films. The spectral change indicates that the E-azobenzene side groups undergo strong J-aggregation by $\pi-\pi$ stacking in a head-to-tail arrangement of the molecular dipoles. Furthermore, a hypsochromically shifted band visualized as weak shoulder at 336 nm is observed simultaneously. Such behavior is characteristic for the formation of the arrangement of two moieties in one unit cell, resulting in a Davidov splitting. The aggregation behavior of the polymer was discussed in detail in our previous publication.[1]

For the present study it is important to mention that the generation of a small amount of Z-isomers by E/Z-photoisomerization destroys the azobenzene aggregates,

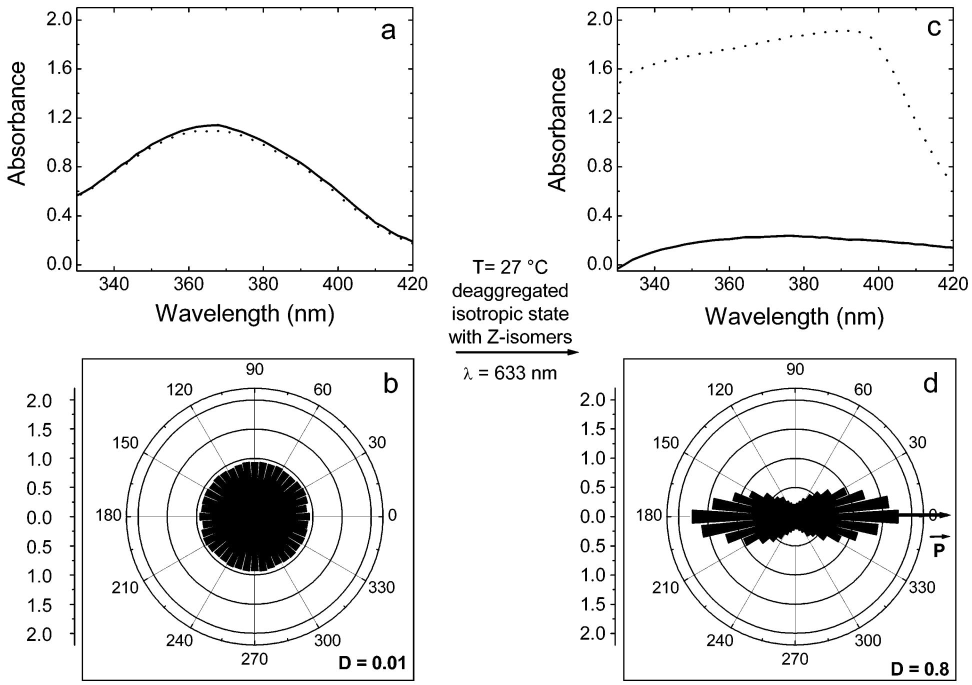

Figure 3. UV−vis polarization spectra parallel (dotted line) and perpendicular (solid line) to the reference axis and resulting polar plots at the maximum of the $\pi-\pi^*$ transition at 365 nm: (a + b) after the argon ion laser irradiation (100 s, 488 nm, 1 W/cm^2, 27 °C); (c + d) after subsequent HeNe laser irradiation (30 min, 633 nm, 230 mW/cm^2, 27 °C).

indicated by the change of the spectrum to that of a nonaggregated film. Thus, UV and vis irradiation result in a hypsochromic shift of the spectrum before the steady states of the photoisomerization are established. However, these aggregates are rebuilt with the reformation of the E-isomeric form by thermal Z-to-E isomerization. A similar behavior is described for the case of LB multilayers formed by azobenzene-containing polymers.[23]

Wavelength Dependence of the E/Z Photoisomerization in Solution. The wavelength dependence of the molecular photoreaction and of the photoorientation processes seems to be one of the keys for the explanation of the new orientation mechanism. Figure 2e,f shows the establishment of the steady state of the E/Z-photoisomerization for 4-(4-(6-bromohexyloxy)phenylazo)benzonitrile upon UV irradiation (365 nm, 0.5 mW cm^{-2}) in THF. The photoreaction is characterized by the simultaneous decrease of the $\pi-\pi^*$ absorbance of the E-isomer at 365 nm and an increasing absorbance at about 320 nm as an indication for the formation of the Z-isomeric form. A parallel increase of the absorbance in the range of the $n-\pi^*$ transition is observed caused by the larger absorbance of the Z-isomer at 450 nm. The steady state was calculated using eq 3. The “real” spectra of the Z-isomer and the ratio of the absorbances were achieved by HPLC analysis with photodiode array detection of an irradiated solution.

The thermal isomerization of the Z-isomer to the thermodynamically stable E-isomer shows that the process is completely reversible. The rate constant of the thermal Z-to-E isomerization in THF solution was found to be $k = 0.148$ min^{-1} at 25 °C.

The ratio of both isomers in the steady state in solution is measured in dependence of the relevant excitation wavelengths of this study (the molar ratios of the Z-isomer are given in parentheses): 365 nm (0.98), 457 nm (0.258), 488 nm (0.265), and 633 nm (0). For the study it is important to mention that the absorbance at 633 nm for both the polymer in solution and as film is very low (practically negligible). No change of absorbance indicating the E-to-Z or Z-to-E photoisomerization was detected in an E-isomer or, alternatively, in a Z-isomer-rich solution irradiated with a HeNe laser (633 nm, 600 mW cm^{-2}).

2. Photoorientation Parallel to the Electric Field Vector of Red Light. The irradiation of a film of this polymer with linearly polarized red light (633 nm) results in an orientation of the azobenzene moieties parallel to the electric field vector. However, this process takes place only after a photochemical pretreatment of the polymer film if the sample is irradiated before the second irradiation step with nonpolarized UV light or related to the low glass temperature of the polymer at 24 °C, with linearly polarized blue or green light of high power density.

But no anisotropy can be induced if the film is irradiated exclusively with linearly polarized red light without such a pretreatment. During the photochemical pretreatment of the film the thermodynamically stable E-azobenzene moieties undergo the photoisomerization and different amounts of the Z-isomer are generated. Because of the formation of Z-isomers, the J-aggregates are destroyed. Moreover, any orientational order in the film is erased at higher concentrations of the Z-isomer. Therefore, necessary requirements for the “red” orientation process seem to be the generation of a certain amount of Z- isomers, the isotropization of the film, and a deaggregation of the azobenzene moieties. For instance, this has been achieved by an argon ion laser irradiation with high power density (1 W/cm^2, 488 nm, polarized light, 100 s). As a consequence of the irradiation, the peak maximum of the $\pi-\pi^*$ transition is shifted to shorter wavelengths up to 360 nm (Figure 3a), and simultaneously an increase of the absorbance at 450 nm is observed (similar to Figure 2c). The subsequent irradiation with a linearly polarized HeNe laser (633 nm, 230 mW/cm^2, 30 min, at 27 °C) creates a new steady

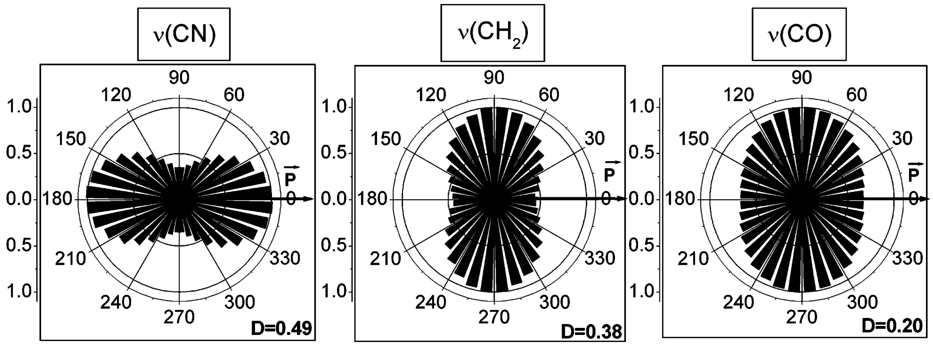

Figure 4. Angular distribution of the normalized, integrated absorption of characteristic FTIR absorption bands of different polymer segments after argon ion laser irradiation (100 s, 488 nm; 700 mW/cm^2, 27 °C) and subsequent HeNe laser irradiation (30 min, 633 nm, 150 mW/cm^2, 27 °C). The data derived from the $\nu(CH_2)$ absorption band data represent an overall value for the side and main chains. The polarization directions of the argon ion and HeNe laser were parallel.

state, which is dominated by E-isomers. This is indicated by the decrease of the absorbance in the range of the n−π* transition. The angular-dependent Z-to-E photoisomerization is related to the orientation of the E-azobenzene moieties parallel to the electric field vector of the incident light, as shown in Figure 3c,d. In the case of this LC polymer the generated dichroism of the π−π* transition of the azobenzene moiety of about 0.8 is extremely high. Irradiating the same polymer exclusively with 488 nm at comparable power densities and below T_g (18 °C), a comparable dichroism was photoinduced by the conventional photoorientation process, but it results in an orientation perpendicular to the electric field vector[1] (see also section 3).

As mentioned before, the absorbance of both isomers at the excitation wavelength of 633 nm is very small. In some publications it was discussed that the absorbance of the Z-isomer at this wavelength is higher compared to that of the E-isomer.[13] The direction of the π−π* and the n−π* transition moment coincides with the long axis of the E-isomer. The decrease of absorbance in the range of the n−π* transition indicates the occurrence of Z-to-E isomerization. Simultaneously, the maximum of the π−π* absorption band is shifted to 411 nm. This indicates the formation of head-to-tail or so-called J-aggregates of E-isomeric azobenzene side groups. With respect to the strong sensitivity of the aggregates regarding the presence of Z-isomers their existence in the oriented film can be excluded as already discussed above. Thus, the aggregation demonstrates that Z-to-E photoisomerization was induced by the irradiation with red light (Figure 3c). In principle, UV−vis spectroscopy is the most suitable method to characterize such π−π interactions, but it has to be mentioned that the separation of the simultaneously occurring processes is difficult because the aggregation results in films which strongly scatter light.

Mechanisms such as the dye-amplified optical Freedericksz transition or Janossy effect[24,25] can be excluded, with respect to the relatively low power density used in our experiments.

The irradiation below the glass transition temperature at 18 °C results in the same process as described above at a working temperature of about 27 °C. But the extent of the photoinduced dichroism was found to be much smaller ($D = 0.3$) compared to the induction at 27 °C. Similar effects with respect to the temperature dependence of the induced anisotropy using red light have been found by Sanchez et al.[7]

While UV−vis polarization spectroscopy characterizes the orientational distribution of the azobenzene moieties, FTIR polarization spectroscopy is able to describe the orientational behavior of all polymer segments in the film. Thus, in agreement with the UV−vis spectroscopic results, the FTIR polar plots (Figure 4) demonstrate the parallel orientation of the azobenzene moiety and the other polymer segments to the polarization direction of the HeNe laser light (150 mW/cm^2, 27 °C). Therefore, the maximum of the integrated absorbance of the $\nu(C{\equiv}N)$ vibration band of the photoactive moiety coincides with the those of the π−π* transition (see Figure 3d), both exhibiting transition moments along the mesogenic long axis. In contrast, the maximum of the $\nu(CH_2)$ absorption band of the spacer and the main chain and the $\nu(C{=}O)$ absorption band of the ester group, which have transition moments normal to the local segmental axis, are directed perpendicular. This indicates that all polymer segments are oriented parallel to the electric field vector of the incident radiation. The orientation process is strongly cooperative, whereas the light-induced orientation of the photochromic groups causes the alignment of the nonphotochromic polymer segments to a common ordered state.

The differences between UV−vis and FTIR investigations could be due to the different experimental conditions. First, there are different diameters of the irradiated spot, which are required for these methods. Second, the film thickness is not equivalent; in the case of the FTIR investigations the films are 20 times thicker compared to the samples for the UV−vis study. For instance, different irradiation intensities are necessary to achieve similar photoinduced erasure effects at the same external temperature because the amount of photochromic azobenzene moieties involved in the photochemical process strongly influences the degree of photoinduced heat and the reorientation process.[26]

Variation of the Photochemical Pretreatment. The question under investigation is which is the most suitable way for the photochemical pretreatment and which are the crucial photoinduced properties of the film in this mechanism. With this aim different steady states of the E/Z photoisomerization were established in the film by variation of the excitation wavelength, power density, and exposure time. In this way various concentrations of Z-isomers are formed, and the morphology of the polymer films is changed to a different extent. The E/Z ratio was estimated using the absorbance of the π−π* transition of the E-isomer at 365 nm. The absorbance found in the isotropic state above the clearing point at 80 °C is assigned to the E-state of the film because the amount of the thermodynamically unstable Z-isomer can be neglected at this temperature. The

Table 1. Irradiation Conditions of the Photochemical Pretreatment and the Resulting Dichroism Due to Irradiation with Polarized HeNe Laser Light:

	pretreatment				HeNe irradiation
case[a]	wavelength (nm)	power density	exposure time (min)	E/(E + Z) ratio	dichroism
A	488	2 mW/cm^2	6	0.95	0.09 ± 0.018
B	488	2 mW/cm^2	42	0.86	0.1 ± 0.02
C	365	1.4 mW/cm^2	80	0.45	0.55 ± 0.12
D	488	1 W/cm^2	1.7	0.9	0.8 ± 0.1

[a] A: Short irradiation causing only deaggregation. B: Causing deaggregation and establishing the steady state with a small amount of Z-isomers. C: Causing deaggregation and establishing a steady state with a high amount of Z-isomers. D: Causing deaggregation and phase transition to the isotropic melt, whereas the amount of Z-isomers is approximately the same compared to case B. While linear polarized light was used for case D, for the other types of pretreatment the irradiation was carried out with unpolarized light.

photoinduced dichroism was investigated in dependence of the exposure conditions of the pretreatment, but the subsequent linearly polarized HeNe laser light exposure was carried out under identical conditions (see further details in Table 1).

Two or more repetitions of each experiment were carried out, and the scattering of the results is expressed by the error values in Table 1. The steady states are almost perfectly reproducible. Procedures a and b irradiating with 488 nm cause almost a deaggregation but result only in small values for the dichroism of about 0.1. Much higher dichroism values of about 0.5 are generated due to an initial UV irradiation with 365 nm (c)—a pretreatment carried out with small power density, too, but generating a much higher concentration of the Z-isomer. However, the highest dichroism of about 0.8 was found after irradiating with linearly polarized light of an argon ion laser of high power density (d) as pretreatment. This procedure results in a comparable amount of Z-isomers as in (a) and (b) and also causes the deaggregation of the azobenzenes. But in contrast to procedures a and b, a phase transition to the isotropic state is induced. As reported recently,[1] the low power density of the argon ion laser irradiation (488 nm) results in the conventional photoorientation of this polymer, while high power densities cause an isotropization of the sample by erasing the initially induced anisotropy. The experiments suggest that there is no direct relation between the amount of the Z-isomers induced by the pretreatment and the magnitude of the optical anisotropy generated by the HeNe laser irradiation. On the other hand, a comparable exposure of a nonaggregated film obtained by rapid cooling from the isotropic melt to 27 °C during light HeNe laser exposure and without any photochemical pretreatment does not result in any anisotropy. It is not clear so far whether this is caused by the absence of Z-isomers or because of morphological reasons such as the formation of J-aggregates or any orientational order of subdomains within the film. Thus, the most important prerequisite seems to be the formation of a certain amount of Z-isomers or, maybe even, of isolated E-isomers in an isotropic, nonaggregated polymer matrix. A second important point seems to be the liquid-crystalline environment of the photochromic moiety, causing an amplification of the photoinduced orientational order by the thermotropic self-organization in the LC state. A classical two-photon character of the process should be excluded because of the time gap between the initial step of the pretreatment and the subsequent laser irradiation, which can be extended up to several minutes.[2,8] Furthermore, the power density of the used laser beam is also relatively low.

3. Comparison of the Two Light-Induced Orientation Processes. Depending on the irradiation conditions, especially the excitation wavelength, an orientation of the azobenzene side groups can be induced either perpendicular or parallel to the electric field vector of the incident light in the same film of the polymer: (a) Blue, green, or UV light, (e.g., the line of an argon ion laser at 488 nm) results in the conventional photoorientation process,[1] generating an orientation perpendicular to the electric field vector of the incident light as displayed in Figure 5a. (b) Irradiation with linearly polarized red light of a HeNe laser (633 nm) causes an orientation of the azobenzene moieties parallel to the electric field vector after a photochemical pretreatment of the film (Figure 5b).

High values of the linear dichroism D of about 0.8 and birefringence values of about 0.36 are found as a result of both orientation processes. Thus, very large values of the optical anisotropy are photogenerated by both mechanisms in the case of this smectic polyester. Hence, one of the goals of this study is to provide an explanation for the very large values of the optical anisotropy in contrast to amorphous polymers.

The opposite effect of the two light-induced orientation processes can be easily proved by FTIR polarization spectra after the corresponding irradiation. The dichroic difference spectra, derived from the spectra measured parallel and perpendicular to the polarization direction of the incident light, are shown in Figure 6 and clearly demonstrate the difference of the induced orientations.

Investigation of the Three-Dimensional Order. It has to be mentioned that in both cases optical anisotropy was induced under experimental conditions where the propagation direction of incident light corresponds to the film normal. Birefringence, UV−vis, and FTIR dichroism were measured by detecting the projection of the orientational distribution onto the film plane (azimuthal anisotropy, in-plane component of the anisotropy or anisotropy in the $y-z$ plane). But so far, we did not discuss the anisotropy in the third dimension, which means in the normal or in the direction of the x axis, respectively. Han et al. have intensively studied this problem for amorphous and liquid-crystalline photoaddressable polymers after irradiation with polarized and nonpolarized UV and blue light using IR and UV−vis spectroscopy (taken at various angles of incident) and conoscopic investigations.[27,28,32] They have found a biaxial orientation with a pronounced out-of-plane component of the azobenzene moieties using linearly polarized light and a preferential orientation along the propagation direction after irradiation with unpolarized light. However, there is presently no information about the three-dimensonal orientational distribution for the process induced with red light. The characterization of the three-dimensionality of the photoinduced order should be one of the key problems for the understanding of both mechanisms, the thermal stability of the photoinduced anisotropy and the reversibility of the processes. Furthermore, the control of the three-dimensional order of the photoinduced anisotropy is of great importance for the application in the field of optical data storage and the photoalignment of liquid crystals.[27−32]

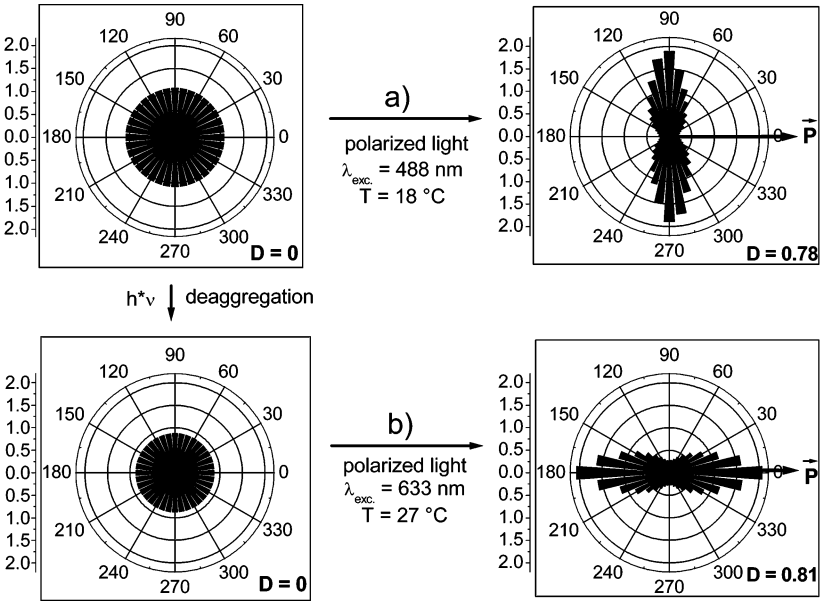

Figure 5. Two different orientation mechanisms based on irradiation with linearly polarized light of different wavelengths and after various photochemical pretreatment.

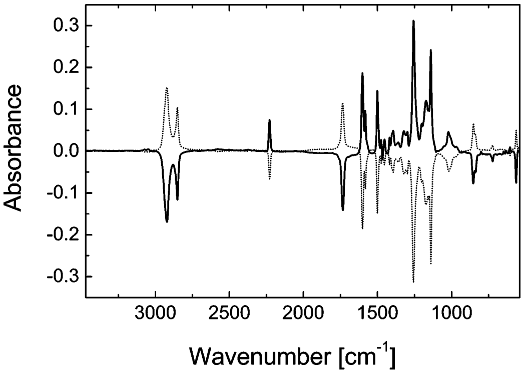

Figure 6. Dichroic difference spectra for the orientation with red light (full line) and for the orientation with blue light (dotted line).

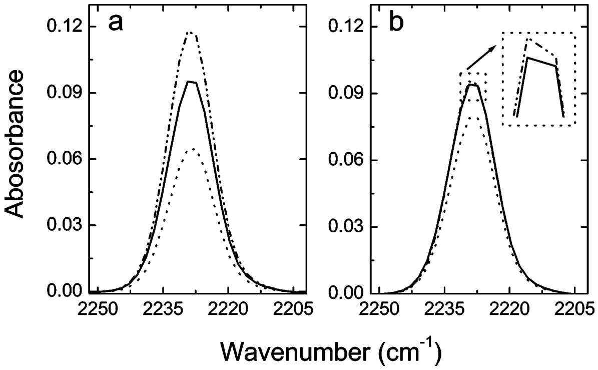

Figure 7. Mean absorbances (a) and structural absorbances (b) of the ν(C≡N) absorption band calculated from the polarization spectra recorded at 25 °C: (—) after quenching from the isotropic state; (• • •) after argon ion laser irradiation at 18 °C only; (-• •-) after argon ion and subsequent HeNe laser irradiation at 27 °C.

In addition to the general problem of the spectroscopic characterization of the three-dimensional order, the photochemical modification of the azobenzene moieties and the aggregation have to be considered in the system. This is the reason why our investigations were carried out by IR spectroscopy and were not done by UV—vis spectroscopy because, as discussed before, the latter is more influenced by these processes. The problem is alleviated if the absorption of the anisotropic films can be related to the isotropic state of the same film. For this purpose the structural absorbance (eq 6) and the mean absorbance (eq 7) are utilized. The mean absorbance is equivalent to the absorbance measured without polarizer.

The samples in the isotropic aggregated states, such as spin-coated films or films cooled rapidly from the isotropic melt, are compared with the oriented films after photoinduced orientation. While the mean absorbance is a tool to check the orientational distribution in a qualitative manner, the structural absorbance can be used to prove quantitatively the validity of an assumed uniaxial orientational distribution relative to the reference direction before, during and after the irradiation process. If a uniaxial model can be applied, the value of the structural absorbance should be constant, despite some smaller deviations caused by structural changes. The assumption is that before irradiation the freshly prepared film specimen is macroscopically isotropic in all three directions. The validity of this assumption was proved in previous investigations.[1,3]

The spectroscopic data are compared before and after both irradiation processes at a temperature of 25 °C. In Figure 7 shows the structural absorbances and the mean absorbances of the ν(C≡N) absorption band. The conventional photoorientation induced by argon ion laser light was carried out below T_g at 18 °C while the orientation induced by HeNe laser light was performed at 27 °C.

The argon ion laser irradiation results in a significant in-plane dichroism combined with a preferential out-of-plane orientation of all polyester segments which is shown exemplarily by the decreasing A_0 value of the ν(C≡N) stretching vibration (see Figure 7b). The mean absorbance A_m decreases for all absorbances with a transition moment parallel to the segmental axis, e.g., ν(C≡N) absorption band (see Figure 7a), and increases in the case of bands with a perpendicular transition moment such as the $\nu(CH_2)$ or ν(C=O) bands (not shown here) compared to the isotropic initial state. This is in agreement with the population of a non-rotationally symmetric orientational plane perpendicular to the electric field vector of the incident light at 488 nm, as proposed by other studies, which have applied null ellipsometry and waveguide spectroscopy to study the conventional photoorientation process after laser irradiation.[33,34] Or in other words, this means optically that the light-induced order of the film is characterized by two different long axes perpendicular to the E-vector and one short axis parallel to the E-vector (biaxial oblate order).

Therefore, eq 6 and its assumptions are not valid for the observed orientational state. The increase of the out-of-plane orientation compared to the initial isotropic state causes a decrease of the displayed average and structural absorbance values. For this reason, the linear dichroism values, derived directly from the angular-dependent UV−vis and FTIR spectra in the film plane, were used to characterize the photoinduced anisotropy of the films.

In contrast to that, the structural absorbance of all segments is practically the same before and after the HeNe irradiation process. This is demonstrated by the $\nu(C{\equiv}N)$ absorption band representative for all other bands (see Figure 7b). This indicates that eq 6 is valid for the orientation process using red light. In contrast to the conventional photoorientation, the HeNe laser irradiation process results in an increase of the mean absorbance A_m of all bands with a transition moment parallel to the long axis of the azobenzene (see Figure 7a) and a decrease of the A_m values of all absorptions with a transition moment perpendicular to the segmental axis (not shown here). These results are in agreement with a uniaxial orientation of the LC polymer, whose director corresponds to the E vector of the incident HeNe light. Optically, this means that the light-induced order is characterized by one long axis parallel to the E-vector and two equivalent short axes perpendicular to the E-vector (prolate order).

In conclusion, the two-step procedure results in a prolate orientational distribution parallel to the E-vector (preferred orientation in z direction) while the conventional photoorientation process leads to a biaxial oblate orientation of the polymer segments populating a plane between the x and y axes, with a preferential out-of-plane alignment (x direction).[1]

The thermal behavior of the photoinduced anisotropy reveals further information concerning the type of the induced order, transferring differently aligned films via their mesophases to the isotropic melt. This was done by heating the same film in two experiments with a rate of 10 °C/min up to 80 °C, which is far beyond the clearing temperature of 47 °C. The resulting changes of IR dichroism and mean absorbance of characteristic bands are plotted vs the temperature in Figure 8.

The dichroism of the $\nu(C{\equiv}N)$ band and the $\nu(C{=}C)_{ar}$ band (not shown in this figure) are always in very good agreement, while, as discussed above, the absolute values of dichroism of all other evaluated bands are different depending on the direction of their transition moment relative to the local segmental axis. The temperature dependence of the orientational order of all bands is quite similar, demonstrating the cooperativity of the dynamics of all polymer segments. But the thermal behavior of the anisotropy is found to be different for films photooriented by either argon ion or HeNe laser irradiation. In both cases the photoinduced anisotropy decreases in the nematic phase with increasing temperature and is completely erased at the clearing temperature of 47 °C. A significant difference is observed in the smectic phases. The anisotropy remains constant in the case of the film oriented with a HeNe laser (Figure 8b) up to 38 °C, while a stepwise decrease of the dichroism is observed in the conventionally photooriented sample (Figure 8a).

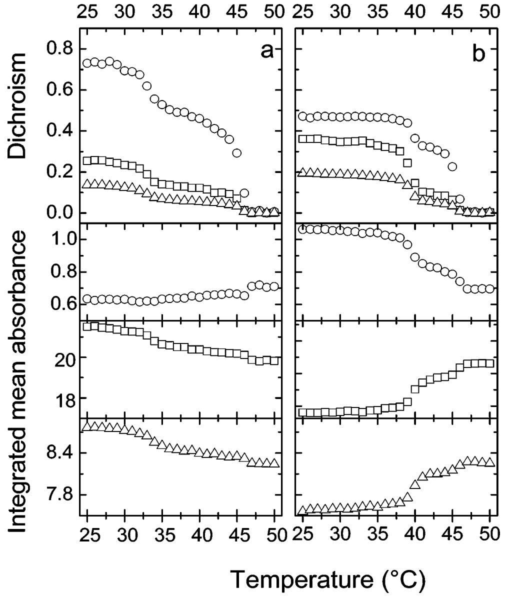

Figure 8. Dichroism and integrated mean absorbance of the different segments of the polymer vs temperature during the erasure process (a) after argon ion laser irradiation at 18 °C and (b) after argon ion laser-induced erasure and subsequent HeNe irradiation at 27 °C; both heating cycles start from a "reference temperature" of 25 °C: (□) $\nu(CH_2)$ absorption band [methylene groups of spacer and main chain]; (○) $\nu(C{\equiv}N)$ absorption band [chromophore]; (△) $\nu(C{=}O)$ absorption band [ester linkage].

Reasons for this behavior could be the following: (i) The discussed general difference in the type of photoinduced orientational order. (ii) The difference in the aggregation of the azobenzenes moieties, which are strongly aggregated in the HeNe laser oriented film, in contrast to those in the argon ion laser oriented film. This changes the stability of the established order. (iii) Variation of the irradiation temperatures and different exposure times for the incident light.

The temperature dependence of the integrated mean absorbance clearly demonstrates the principal difference in the orientational order photoinduced by both processes. While the mean absorbance of the $\nu(C{\equiv}N)$ absorption band increases in films oriented by the conventional photoorientation process with increasing temperature, that of the films oriented by a HeNe laser decreases. In this way the same absorbance value is established in the isotropic melt of the film, but it is reached from opposite directions. Therefore, the isotropization by thermal erasure results in an increase of absorbance values for parallel transition moments in films irradiated at 488 nm and in a decrease in films exposed to red light (633 nm). This demonstrates clearly the existence of two different photoinduced orders. The $\nu(CH_2)$ and $\nu(C{=}O)$ absorption bands exhibit a comparable thermal behavior of the integrated mean absorbance, but the course is inverted.

To give a more detailed picture of the photoinduced three-dimensional orientational order, further studies using waveguide spectroscopy and ellipsometry are in progress.

Conclusions

The direction of the photoinduced orientation and the type of the three-dimensional orientational order can be controlled by the irradiation wavelength of linearly polarized light in the same film of a smectic polyester with 4-cyano-4′-alkoxyazobenzene side groups.

Thus, the exposure with linearly polarized green, blue, or UV light of an argon ion laser (514, 488, or 351 nm) results in the conventional photoorientation process, causing an orientation perpendicular to the electric field vector of the incident light. The process takes place without any pretreatment of the film. Such a conventional orientation process takes place in all cases in which a steady state between E- and Z-isomers is established. It occurs by the repetition of a number of angular-dependent photoselection events and rotational diffusion within the steady state of the photoisomerization. In the studied polymer the azobenzene moieties are not aggregated after the induction process caused by the remaining Z-isomers in these steady states. High power density of light causes an erasure of the initially induced anisotropy and results in an isotropization of the sample. In the case of the LC polymer under investigation a maximum of dichroism of about 0.8 can be achieved by optimizing the operating temperature and the power density.[1]

In contrast to this mechanism, the irradiation with linearly polarized red light of a HeNe laser (633 nm) causes an orientational order parallel to the electric field vector. This process required a photochemical pretreatment of the sample. Three requirements have to be fulfilled by the E/Z photoisomerization: the formation of a certain amount of Z-isomers, a deaggregation, and the complete isotropization of the polymer matrix. This can be achieved for example upon irradiation with nonpolarized UV light (365 nm, 1.4 mW/cm^2, 4800 s) or with polarized visible light of high power density (488 nm, 1 W/cm^2, 100 s). The subsequent irradiation with red light results in the preferred orientation of the azobenzene side groups parallel to the electric field vector. The key step of the new mechanism should be the angular-selective photoisomerization from the Z- to E-isomeric form. In other words, only those Z-isomers with a transition moment parallel to electric field vector of the incident light undergo Z-to-E photoisomerization. In contrast to the first mechanism, there seems to be no steady state between both isomers; with respect to the higher molar extinction coefficient of the Z-form relative to the E-form ($\epsilon_Z \gg \epsilon_E$) at the excitation wavelength, E-isomers are exclusively formed in one step. Because of a much faster rotational diffusion of the more spherical Z-isomers relative to the rodlike E-isomer, a certain statistically aroused enrichment of aligned azobenzene moieties preferentially in the polarization direction of the perturbing external electric field of the HeNe laser is found. This photoselective formation of E-azobenzene isomers results in a cooperative orientation of all polymer segments and an orientational order parallel to the laser polarization direction. The strong J-aggregation after the procedure indicates that all Z-isomers undergo an isomerization to the E-isomeric form. The importance of the temporarily generated Z-isomers for the mechanism is demonstrated by the fact that no orientation is induced upon irradiation with 633 nm light without photochemical pretreatment.

Very high values of optical anisotropy with dichroism values of about $D \approx 0.8$ are photoinduced by both orientation mechanisms in films of this liquid crystalline polyester. This is in contrast to much smaller values in the case of other polymers containing the same photochromic moiety.[35] On one hand, this should be caused by the pronounced cooperativity of both orientation processes whereas the light-induced orientation of the photochromic azobenzene moiety causes an alignment of all other polymer segments such as spacer and polyester backbone. On the other hand, the induction of anisotropy is enhanced by the interplay of the photoorientation processes and thermotropic self-organization in the case of a smectic polymer.[32] This effect becomes very pronounced due to the light-induced heating effect, whereas the photoisomerization causes a decrease of the glass transition T_g and the other phase transition temperatures. The interplay of light-induced ordering effects are especially strong in the case of this particular polymer with respect to the small difference between its T_g and the operating temperature. Thus, the film either is temporarily transferred from the glassy state to the mesophase (orientation with blue light) or takes place in the LC phase (orientation with red light), and the oriented azobenzene chromophores act as an aligning force in the LC polymer in the mesophase. This had been studied for the conventional photoorientation process in polymers with high T_g values, which allow to separate the photoorientation process and the amplification of optical anisotropy upon annealing.[36] In the case of this polymer both ordering processes take place simultaneously with respect to the thermal properties of the polymer.[1]

In addition to the orientational direction, the three-dimensional structure of the order photogenerated by the two processes is also different. While the spectral data confirm a uniaxial prolate order as a result of the HeNe laser irradiation, a biaxial oblate order with a preferential out-of-plane component was found in the case of the conventional photoorientation process in the glassy state, which is in agreement with the order detected by waveguide spectroscopy.[34] The difference in the three-dimensional order seems to influence the stability of the induced order. As shown earlier,[2,3] any anisotropy can be erased by heating the sample above the clearing temperature. Further investigations are in progress to clarify the photoinduced order generated in the films by both mechanisms.

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