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Photoorientation of a Liquid Crystalline Polyester with Azobenzene Side Groups. 1. Effects of Irradiation with Linearly Polarized Blue Light[†]

I. Zebger,[*,‡,§] **M. Rutloh,**[‖] **U. Hoffmann,**[‡] **J. Stumpe,**[*,‖] **H. W. Siesler,**[‡] **and S. Hvilsted**[⊥]

Department of Physical Chemistry, University of Essen, D-45117 Essen, Germany, Fraunhofer-Institute of Applied Polymer Research, Geiselbergstrasse 69 D-14476 Golm, Germany, and Department of Chemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

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The photoorientation process in a polyester with 4-cyano-4′-alkoxyazobenzene side group and long methylene spacers in the side and the main-chain was studied as a function of irradiation with linearly polarized light of 488 nm under systematic variation of the power density and temperature. This model polymer is characterized by liquid crystallinity (g 24 S_X 26 S_A 34 n 47 i) and a strong aggregation tendency. The photoorientation is cooperative, i.e., the orientation of the photochromic side group induces the alignment of the ester unit (which is a part of the main-chain) and both methylene segments in the side- and main-chain. The very high values of the normalized linear dichroism up to 0.8 and the birefringence (above 0.3) are due to the interaction of photoorientation and thermotropic self-organization. The induction of anisotropy shows a pronounced dependence on the power density and the working temperature. This is related to the thermal properties of the LC polymer and the resulting ordering behavior. Surprisingly, the photoorientation process is not restricted by J-aggregation of the azobenzene groups even at low power densities. The highest anisotropy at 27 °C (slightly above T_g) is achieved by a low power density (1 mW/cm^2 and dose of 0.5 mW/cm^{2}s). Higher power densities result in a decrease of the maximum dichroism and, finally, the initially induced small anisotropy is erased during continuing light exposure. At a constant high power density of about 700 mW/cm^2, the saturation value of the dichroism first increases with the irradiation temperature, then passes through a maximum of about 0.8 at 18 °C and finally the film is transferred to the isotropic state at 27 °C. Both effects indicate a significant thermal effect of the laser beam on the polymer film. Taking into account the thermal properties of the investigated polymer it is demonstrated that the photoinduced anisotropy depends strongly on the irradiation conditions.

I. Introduction

The light-induced modification of photochromic polymers containing azobenzene groups is very promising for optical data storage, optical processing and the photoalignment of liquid crystals.[1−7] In addition to the photochromism as a result of the *E*/*Z*-photoisomerization of azobenzenes, the optical properties can be changed by the irradiation with linearly polarized light. This offers a new approach to orient molecules in liquid crystalline guest−host systems,[8] in polymeric matrixes[9] or side-[10−16] and main-chain[17] polymers. Depending on the photochromic moiety, the matrix and the irradiation conditions, different photochemical and photophysical orientation processes can take place. Thus, the generation and modification of optical anisotropy can be caused by angular-dependent photoselection or the so-called Weigert effect,[18,19] the photoorientation within the steady state,[19,20] the optical Freedericksz transition,[21] and the dye-amplified Janossy effect in liquid crystals.[22] Based on our studies (re)orientation processes in polymer films containing azobenzene moieties can be characterized as photochemically induced (re)orientation process of azobenzene groups within the steady state of the *E*/*Z*-photoisomerization.[20,23] It takes place via the repetition of angular-dependent excitation, a number of *E*/*Z*-photoisomerization cycles, and rotational diffusion in the glassy state.[12] In this way the photochromic side groups become oriented perpendicular to the electric field vector of the incident blue light. The process is cooperative in the glassy state of amorphous copolymers,[24] in optically isotropic and aligned films of liquid crystalline polymers[12−14,20,23] as well as in LB multilayers.[25] Alternatively, an orientation process resulting in an orientation parallel to the electric field vector of red incident light has been observed after an initial exposure to nonpolarized or high-intensity polarized UV−vis light.[26,27] This phenomenon, induced in the same polymer as described here, will be discussed in more detail in a forthcoming paper. It will be compared to the effects induced by blue light irradiation.

The combination of the ordering impact of polarized blue light and the self-organization of liquid crystalline polymers (LCP's) is of exceptional interest. In aligned films of LCP's a competition takes place between the thermotropic selforganization and the photoorientation process.[28,29] In this way the photoreorientation may be suppressed by the supramolecular order of the film.[29] But in isotropic films of LC polymers the photoorientation process is not restricted. Moreover as shown very recently, annealing of photooriented LCP films can result in a significant amplification of the photoinduced degree of order.[28−30] Thus, the orientational order photoinduced in the

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[*] To whom correspondence should be addressed.

[‡] Department of Physical Chemistry, University of Essen.

[§] Present address: Department of Physical Chemistry, University of Aarhus, Dk-8000 Aarhus, Denmark.

[‖] Fraunhofer-Institute of Applied Polymer Research.

[⊥] Department of Chemical Engineering.

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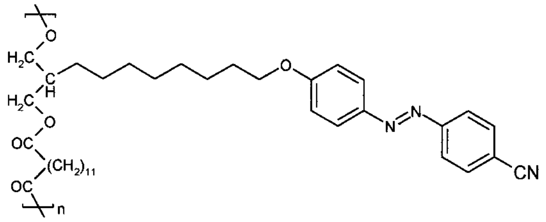

Figure 1. Repeating unit of the investigated polyester.

glassy state acts as an initializing force for the thermotropic self-organization of the LCP's.

The purpose of the present communication is to show the influence of liquid crystallinity and aggregation of the polymer as well as of the irradiation conditions (power density and operation temperature) on the photoinduced anisotropy in the light of the thermal properties of the investigated LC polymer. The results of these studies will be the basis for a comparison with the orientation process induced by red light (as mentioned above) in the same polymer with respect to the orientational distribution and its thermal stability.

II. Experimental Section

The polyester was synthesized by transesterification of 2-[8-(4-(4-cyanophenylazo)-phenoxy)-octyl]-1,3-propanediol and diphenyltridecanedioate in the melt under vacuum at elevated temperature (Figure 1). More details about the general synthesis route are described elsewhere.[31] The particular sample employed in the investigations had a number-average molecular mass, M_n, of 10 400 and a corresponding weight-average molecular mass, M_w, of 29 000 as determined by size exclusion chromatography (SEC) with polystyrene standards calibration.

DSC and polarizing microscopy were used to characterize the thermal properties of the polymer. It shows a glass transition at 24 °C, 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 $\Delta H \approx 5$ cal/g), and a clearing point at 47 °C ($\Delta H <$ 1 cal/g). The S_A phase was identified by its typical texture using a Leitz Ortholux-Pol BK polarizing optical microscope (POM). A Perkin-Elmer DSC 4 instrument was used with varying heating and cooling rates (0.2−40 °C/min).[32]

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 investigations. A microscope spectrometer 3 (Carl Zeiss Oberkochen, spectral range 230−1000 nm with a resolution of 0.5 nm and a lateral resolution of 2 μm) was used to characterize the absorbance within the Ar^+-laser spot.

A variable-temperature, computer-controlled irradiation setup has been applied for the on-line polarization FTIR measurements during the 488 nm Ar^+-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 erasure. A Bruker IFS 88 spectrometer was used to record FTIR spectra with a spectral resolution of 4 cm^{-1}. The polarization of the IR beam was achieved by using a wire-grid polarizer with KRS-5 as substrate. The size of the irradiated sample area was about 3 mm^2.

The 488 nm line of a linearly polarized Ar^+-laser (700−1000 mW/cm^2; Laser 2000 model 532) was used for the irradiation experiments. The irradiation with nonpolarized light (365 nm, 0.5−1.4 mW/cm^2 and 488 nm, 2 mW/cm^2) was carried out using an XBO lamp (1000 W, Hanovia 976 C-1, Spectral Energy Corp.) in combination with a monochromator. All irradiation procedures were carried out in normal incidence.

The phase shift which occurs between the film and a set of polarizers using a linear polarized low power He/Ne-laser beam was measured. Taking into account the film thickness, the light induced birefringence was calculated. Thin films of about 0.1μm thickness were prepared by spin-coating using tetrahydrofurane (THF) as solvent (10 mg polymer in 1 mL). Glass substrates were used for the UV−vis measurements. For the FTIR investigations the films were prepared by casting of a chloroform solution (3 mg polymer in 200 μl solvent) onto KBr plates. The film thickness obtained by this preparation procedure was approximately 5 μm.

To have reproducible starting conditions for the film specimens, the samples were subjected to a thermal pretreatment. Thus, they were kept 10 min in 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-bromo-hexyloxy)-phenylazo]-benzonitrile (BHPB) 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 at room temperature to exclude the presence of *Z*-isomers.

The normalized linear dichroism is defined as

$$D = |(A_{||} - A_{\perp})/(A_{||} + A_{\perp})| \tag{1}$$

where $A_{||}$ and $A_{\perp}$ are the absorbance measured parallel and perpendicular to the reference axis *Z*. To eliminate the influence of the sample orientation on the band intensities, the structural absorbance A_0[33,34] can be calculated from the absorbance values in the three orthogonal directions *X*, *Y*, and *Z*:

$$A_0 = (A_X + A_Y + A_Z)/3 \tag{2}$$

For a uniaxial distribution around the *Z*-axis ($A_{||}$), the *X* and *Y* ($A_{\perp}$) directions are equivalent, so that A_0 can be calculated by

$$A_0 = (A_{||} + 2 \times A_{\perp})/3 \tag{3}$$

III. Results and Discussion

III.1. Light-Induced Modification of Azobenzene Moieties. The UV−vis spectrum of the low molecular *E*-isomers of BHPB[35] in solution (see Figure 2a) which is a model for the photochromic side group is characterized by the strong $\pi-\pi^*$ transition at 365 nm and the n-π^* transition at 450 nm. The photoreaction upon UV irradiation causes a decrease of the $\pi-\pi^*$ absorbance of the *E*-isomer at 365 nm and an increase of the n-π^* absorbance of the *Z*-isomer at 450 nm (Figure 2b). The real spectrum of the *Z*-isomer and the amount of both isomers were achieved by HPLC analysis with a photodiode array detection of the irradiated solution with an extent of approximately 100% of the *Z*-isomer. In supercooled films (see Experimental Section) of the polymer, the maximum of the $\pi-\pi^*$ transition is strongly shifted and becomes much broader.

The spectrum of the supercooled film is characterized by a large bathochromic shift of the $\pi-\pi^*$ absorption maximum starting from 410 nm (Figure 2d) in the case of freshly prepared film, which is shifted up to 450 nm (Figure 2g) for films after a storage time of 200 days at room temperature in the dark. Furthermore, a hypsochromic shoulder at 336 nm is observed. The bathochromic shift indicates the formation of J-aggregates and the hypsochromic shift characterizes the formation of

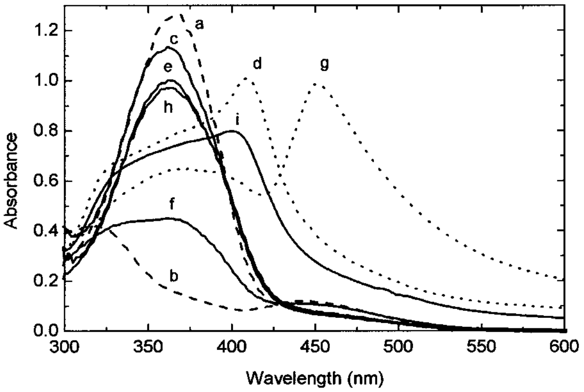

Figure 2. UV−vis spectra of polymer films after different photochemical and thermal treatments and the model compound (BHPB) in solution: (a) spectrum of the initial solution of the pure *E*-isomer of BHPB in THF ($c = 2 \times 10^{-5}$mol/L); (b) spectrum of (a) after 2000 s UV irradiation ($\lambda_{\mathrm{irr}} = 365$ nm, 0.5 mW/cm^2), molar fraction of the *Z*-isomer: >0.99; (c) isotropic melt of the polymer film at 80 °C; (d) rapid quenching of (c) to temperatures below T_g (~24 °C), and then kept at 27 °C; (e) film of (d) after 1800 s irradiation with 488 nm (Ar$^+$-laser, 1 W/cm^2); and (f) film of (d) after 1800 s irradiation with 365 nm using a XBO-lamp at 1.4 mW/cm^2. (g) Following the procedures (c) and (d) but recorded after a storage time of several months. (h) Film of (d) after 1800 s irradiation with an XBO-lamp at 488 nm (2 mW/cm^2). (i) Reaggregated film 24 h after procedure (h) storing the film at 24 °C.

H-aggregates. This behavior can be explained by the $\pi-\pi^*$ stacking of the aromatic side groups (Davidov splitting).

The spectrum of the isotropic phase of the polymer (Figure 2c) is almost identical with the spectrum of the E azobenzene chromophore in solution (see Figure 2a). Upon irradiating the aggregated film with the polarized light of the Ar$^+$-laser (488 nm, 1 W/cm^2), the *E*/*Z*-isomerization takes place and the film is transferred to the isotropic state due to the photoreaction and the heating effect of the high power density of the light. The result is a spectrum quite similar to that obtained from the solution (Figure 2e). A comparable effect can be achieved by using the nonpolarized blue light of an XBO-lamp at 488 nm (2 mW/cm^2), as displayed in Figure 2h. The UV irradiation at 365 nm with the same XBO source (1.4 mW/cm^2) results in a further decrease of absorbance at 365 nm and an increase at 450 nm. This behavior is characteristic for a dynamic equilibrium with a high proportion of the *Z*-isomer (see Figure 2f).

This change is caused by the photoisomerization of the rodlike *E*-isomers to the bulky *Z*-isomer resulting in the disappearance of the aggregation. However, these light-induced morphological and resulting spectral changes are reversible and a few hours (varying with the storage temperature) after the end of the light exposure a reaggregations takes place as shown in Figure 2i. In contrast to the behavior in solution, the change of absorbance of the films is much more complex, because the molecular photoreaction is accompanied by photoinduced changes of molecular aggregation, supramolecular order, and the macroscopic orientation.

The formation of aggregates and LC domains causes light scattering within the film. This results in a significant baseline shift in the UV−vis spectra and in the FTIR spectra, as well.

Moreover, the annealing of the initially isotropic spin-coated films above T_g enhances the development of the aggregates and causes an alignment of the LC polymer in domains. However, defects on the surface of the quartz and KBr substrates cause no reproducible values of the macroscopic optical anisotropy of the films.

A dynamic equilibrium between both isomers is established which is estimated by the relation of the absorption coefficients at the excitation wavelength. The thermal isomerization of the *Z*-isomer to the thermodynamically stable *E*-isomers shows that the process is completely reversible. The rate constant of the *Z*/*E*-isomerization in solution was found to be $k = 0.148$ min^{-1} at 25 °C.

UV and visible irradiation results in significant spectral changes of the films before the wavelength dependent steady states of the photoisomerization are established. As shown recently for LB multilayers of azobenzene containing polymers the aggregates become destroyed by the generation of a small amount of *Z*-isomer shifting the absorbance maximum to a value, which is characteristic for the monomeric azobenzene moiety.[36]

In summary, a strong aggregation of the donor/acceptor substituted azobenzene moieties by $\pi-\pi$-stacking is observed which results in the dominating formation of J-aggregates. This suggests a head-to-tail arrangement of the azobenzene moieties in a herringbone structure of the side groups in cast and spin-coated films. In contrast to other systems, this arrangement in aggregates in the case of this polyester with long alkylene chains is very sensitive against light but the aggregation is reversible as the isomerization itself. As shown recently, this phenomenon is especially strong in the case of LC homopolymers changing order and molecular dynamics.[37] With respect to the goal of the paper it is important to investigate how this aggregation influences the orientation process upon irradiation with linearly polarized light.

The assignment of the most significant absorption bands in the FTIR spectra of the LC polyester film is given in Table 1. Furthermore the peak positions after thermal quenching in the aggregated state and the relative peak shifts after subsequent irradiation with the 488 nm wavelength of an Ar$^+$-laser at 27 °C as well as after thermal transformation to the isotropic state at 80 °C are compared. The determination of the peak maxima is based on a cubic interpolation according to an algorithm developed by Akima.[38]

The characteristic IR frequencies of the different polyester segments are changed by the aggregation and the photoinduced deaggregation process. By focusing on baseline-corrected absorption bands which are sensitive to the degree of order in the system, it can be shown that Ar$^+$-laser irradiation causes a destruction of the aggregates and a transfer to the isotropic state of the film. This results in changes of the wavenumbers which are displayed in the table. In analogy to the thermal induction of the isotropic phase at 80 °C, a significant shift to higher wavenumbers of the CH$_2$-stretching bands of the methylene-units of spacer and main chain [$\nu_{\mathrm{as}}(\mathrm{CH_2})$ and $\nu_{\mathrm{s}}(\mathrm{CH_2})$] is indicating an increase in the conformational disorder.[39] This effect is less pronounced in the case of the carbonyl band [$\nu(\mathrm{C{=}O})$] leading to the assumption that the ester linkage is less involved in the aggregate structure. Contrary, a shift to lower wavenumbers is observed for the $\nu(\mathrm{C{\equiv}N})$ and $\nu(\mathrm{CH})_{\mathrm{oop,ar}}$ absorptions as a consequence of the disordering process.[39] Furthermore a significant spectral change in the range of the aromatic out-of-plane vibration $\gamma(\mathrm{CH})_{\mathrm{oop,\ ar}}$ at 852 cm^{-1} (see Figure 3b) clearly indicates the presence of a certain amount of *Z*-isomer after the photochemical transfer to the isotropic phase.[27]

The two last-mentioned absorptions with orthogonal transition moments are displayed for the different states of order in Figure 3. They allow us to exclude a preferential homeotropic alignment of the aggregated film; otherwise, a decrease of intensity for

TABLE 1: Frequencies of the Different Structural Units of the Polymer in the Aggregated State of a Supercooled Film and Relative Peak Shifts after Thermal Isotropization at 80 °C and after Photochemical "Clearing" upon Irradiation with an Ar^+-Laser (488 nm, 700 mW/cm^2, at 27 °C), Respectively

		relative frequency shift $\Delta\nu$ (cm^{-1})		
band assignment[a]	frequency (cm^{-1}) aggregated state	after photoinduced erasure	after thermal isotropization	structural origin
$\nu_{as}(CH_2)$	2924.0	+2.5	+3	main-chain + spacer
$\nu_s(CH_2)$	2852.0	+1.5	+2.5	main-chain + spacer
$\nu(C\equiv N)$	2228.0	−0.5	−1.0	chromophore
ν (C=O)	1734.5	+0.5	+1.5	ester linkage
ν (C=C)$_{ar}$	1601.0	−2.0	−2.5	chromophore
	1582.0	−0.3	−0.5	chromophore
ν (C=C)$_{ar}$	1501.5	−0.2	−0.5	chromophore
ν_{as}(C−O−Ar)	1257.0	−2.5	−3.5	chromophore + spacer
ν_s (C−O−Ar)	1019.0	−3.5	−5.0	chromophore + spacer
$\gamma(CH)_{oop,\,ar}$	852.0	−2.5	−3.5	chromophore

[a] as= antisymmetric, s= symmetric, ar = aromatic, oop= out-of-plane.

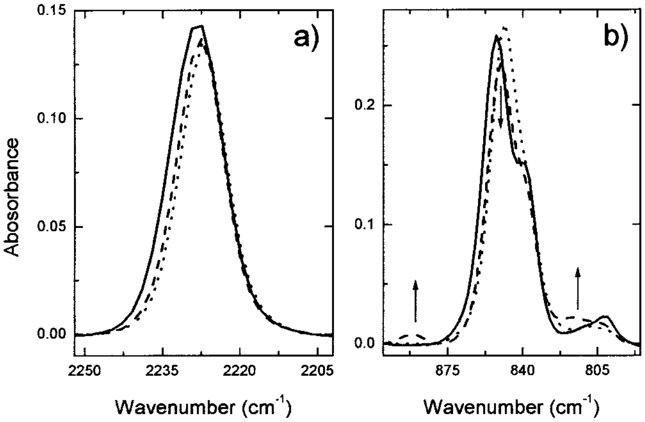

Figure 3. Changes of selected baseline corrected absorption bands, characteristic for the degree of order of the polymer at different temperatures and irradiation states [(—) quenched and aggregated at 27 °C; (− −) after "Ar^+-laser erasure" at 27 °C; (· ·) 80 °C, isotropic state].

bands with a transition moment parallel to the local segmental axis (e.g., $\nu(C\equiv N)$, Figure 3a) and an increase of those with a perpendicular transition moment ($\gamma(CH)_{oop,\,ar}$, Figure 3b) would be observed by a comparison of the aggregated state with the molten isotropic state of the polymer film.

III.2. Photoorientation Generated by Ar^+-Laser Irradiation. The irradiation with linearly polarized blue light (488 nm) induces an optical anisotropy in supercooled spin-coated films, which are macroscopically isotropic and strongly aggregated initially (Figure 4). The light exposure results in a preferred orientation of the azobenzene groups perpendicular to the electric field vector of the linearly polarized light. The change of UV−vis absorbance indicates approximately a steady state with 5% of the *Z*-isomer. Surprisingly, an extremely high dichroism up to 0.8 is photogenerated in the films using 488 nm and a power density of 1 W/cm^2 at an operating temperature of 18 °C. This is remarkable higher compared to other polymers with the same photochromic group.[37,40,41]

The chromophore orientation perpendicular to the electric field vector can also be induced by other wavelengths in the range of the $\pi-\pi$ and n-π transition, e.g., 365, 436, and 514 nm. This means that this orientation mechanism takes place at all wavelengths, where a steady state of the photoisomerization is established.

It has to be considered that the thermal properties of the polymer are changed by excitation and photoisomerization. Both the *Z*-isomer concentration and the thermal effect caused by the high power density of 1 W/cm^2 can overcome any restrictions due to molecular aggregation and orientational order. The shift of the absorbance maximum from 405 to 365 nm indicates that the chromophores become deaggregated during the orientation process due to the *E*/*Z*-isomerization. However, a reaggregation is observed after the thermal *Z*/*E*-isomerization and structural relaxation of the polymer matrix as a function of time.

On one hand, the *Z*-isomers cause a depression of the temperatures of the glass transition, that of the mesophase transitions and the transfer to the isotropic phase; on the other hand, the temperature within the film is increased from about 10 to 20 °C by internal conversion.[42] This is of special importance in the case of this polymer, because the initial T_g value is close to the operating temperature. The exposure causes a transition from the glassy state to the liquid crystalline state. Thus, the orientation process starts in the glassy state at 18 °C, induces anisotropy but simultaneously the system is transferred temporarily into the liquid crystalline state. The consequence is that the further orientation process takes place in the mobile, long-range ordered liquid crystalline state. Thus, the anisotropy is increased by further photoorientation in combination with the thermotropic self-organization of the LC polymer above T_g as shown for the first time in ref 31. Such an amplification of photogenerated anisotropy induced in the glassy state by subsequent annealing has recently been shown for polymers with higher T_g, which allows us to separate both driving forces via the temperature.[28,40] In this way, a very high optical anisotropy is generated, which is much higher compared to other amorphous and liquid crystalline polymers with higher T_g values containing the same photochromic moiety.

While UV−vis spectroscopy was used to characterize the molecular aggregation, the steady state and the orientation of the *E*-azobenzene chromophores, IR polarization spectroscopy reveals a more detailed picture of the orientational order of all segments of the polymer and their mobility in the film. But it has to be emphasized that a quantitative comparison is only allowed for vibrational absorption bands and electronic transitions which have the same direction of the transition moment relative to the long axis of the azobenzene moiety and its related photoinduced orientational direction, respectively.

The angular dependence of specific vibrational modes characteristic for the different polymeric segments is optically isotropic in the initial state and becomes anisotropic due to the Ar^+-laser irradiation under the same conditions (488 nm, 700 mW/cm^2, 18 °C, see Figure 5). The dichroism of 0.74 found for the $\nu(C\equiv N)$ stretching vibration, which has a transition moment parallel to the long axis of the azobenzene moiety and represents the photochromic group, is in very good agreement

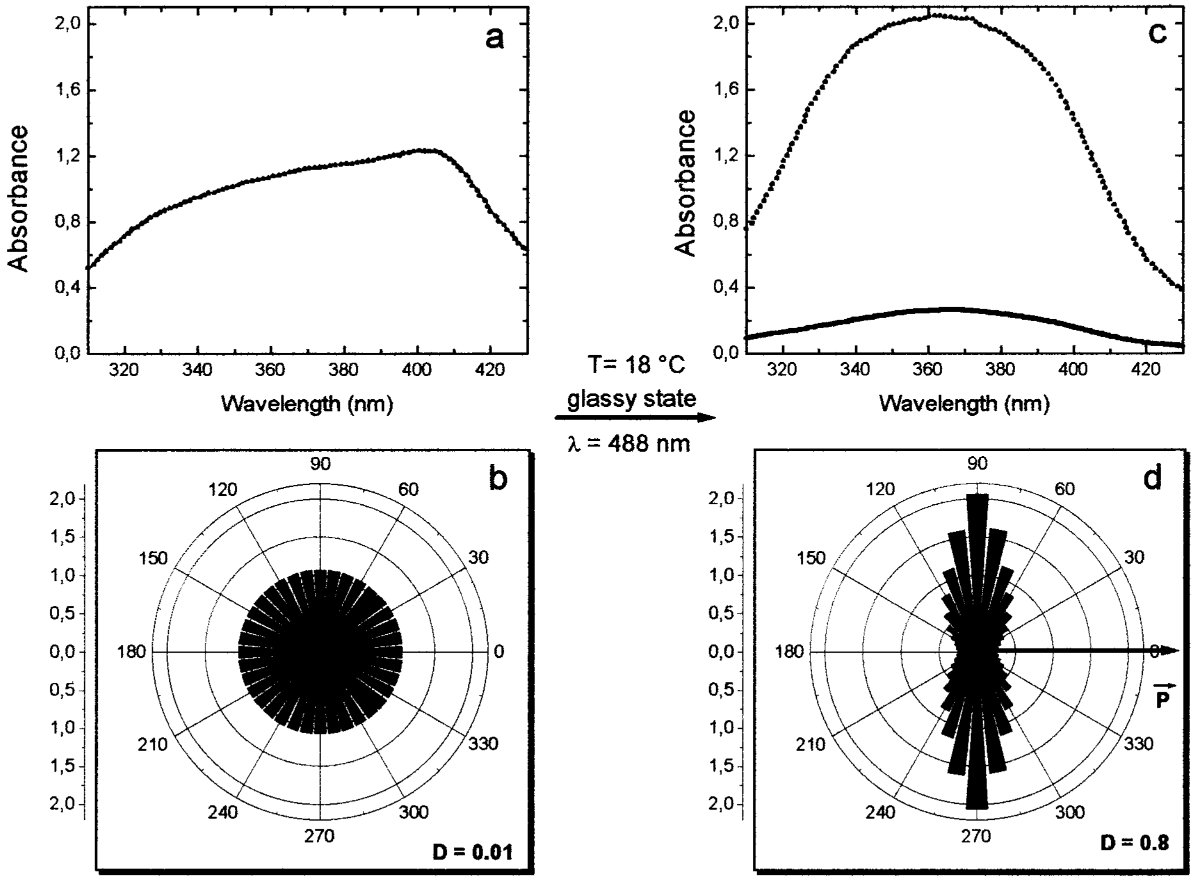

Figure 4. Polarized UV−vis spectra parallel (solid line) and perpendicular (dotted line) to the electric field vector and the resulting polar plots at the maximum of absorbance, (a + b) before and (c + d) after Ar$^+$-laser irradiation (488 nm, 1000 s, 700 mW/cm^2, 18 °C).

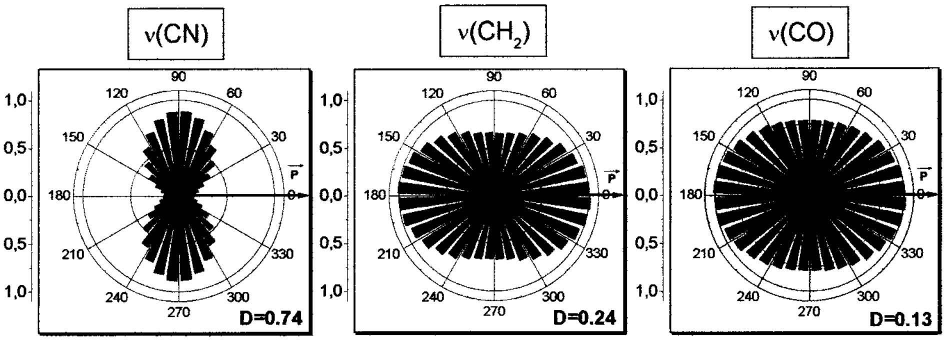

Figure 5. Angular distribution of the normalized and integrated absorption of characteristic FTIR bands of different polymer segments after Ar$^+$-laser irradiation (1000 s, 488 nm, 700 mW/cm^2) at 18 °C. The ν(CH$_2$) vibration data exhibit an overall value for side- and main-chain.

with the direction and value found by the UV−vis data of the $\pi-\pi^*$ transition.

Figure 5 demonstrates that this light-induced orientation of the photochromic moiety causes an orientation of nonphotochromic polymer segments, such as the alkylene chains of the spacer and of the main chain as well as of the ester group of the backbone. Thus, the main conclusion is the fact that the orientation process is cooperative including the whole macromolecule and results in an anisotropic polymer film of high order. This was recently confirmed with specifically deuterated species of this polyesters series by FTIR polarization spectroscopy.[43] The transition moments of the ν_s(CH$_2$) vibrations of the methylene units of the spacer and the main-chain and that of the ν(C=O) vibration of the carbonyl group in the ester moiety are perpendicular to the local segmental axis in comparison to those of the azobenzene moieties. Thus, we have to conclude that both, the spacer and the backbone, are aligned parallel to the mesogenic azobenzene moieties. However, the dichroism of these absorption bands is smaller compared to the cyano stretching vibration or the $\pi-\pi^*$ absorption. This could be caused by a smaller photoinduced order of these segments and by the fact that these transitions are not directed parallel to the long axis of the azobenzene.

III.3. Temperature Dependence of the Photoorientation Process. The influence of the temperature on the photoorientation process was measured on-line by FTIR spectroscopy irradiating with a constant power density of the Ar$^+$-laser (488 nm, 700 mW/cm^2) at temperatures below and above T_g (∼24 °C). As shown in Figure 6, the kinetics of the induction of dichroism of the ν(C≡N) absorption strongly depends on the external temperature. The increase of temperature in a range close to, but below T_g causes a higher mobility of the polymer matrix. Moreover, the photogenerated Z-isomers destroy the aggregates and decrease any initial orientational order and, in

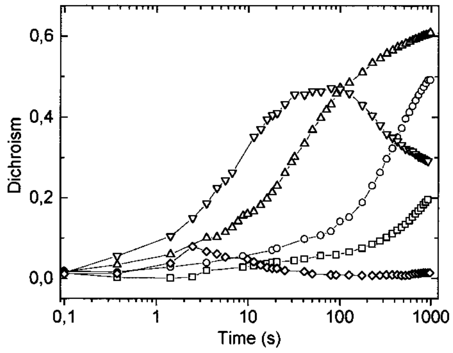

Figure 6. Time dependence of ν(C≡N) dichroism upon Ar$^+$-laser irradiation (488 nm, 700 mW/ cm^2) at different temperatures: (□) 10 °C, (○) 15 °C, (△) 20 °C, (▽) 25 °C, (◇) 27 °C.

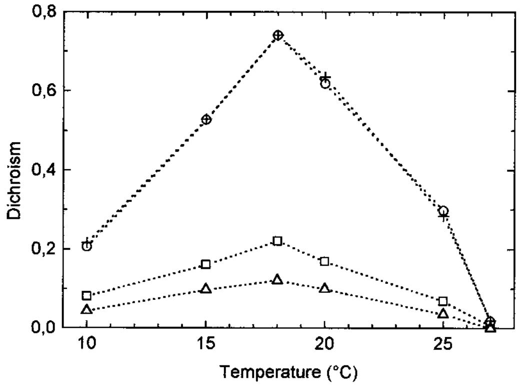

Figure 7. Temperature dependence of the dichroisms of the different segments after 1000 s of Ar$^+$-laser irradiation (488 nm, 700 mW/cm^2): (□)ν (CH$_2$) [methylene groups of side- and main-chain], (○) ν (CN) [chromophore], (+) ν (C=C)$_{ar}$ (1600 cm^{-1}) [chromophore], (△) ν (CO) [ester linkage].

addition, one can expect that this effect reduces T_g and the clearing temperature T_{cl} . Furthermore, we have to consider, that, at higher temperatures, the rate constant of the thermal *Z*/*E*-isomerization is increased.

The development and the final values of the photoinduced dichroism of the photochromic moiety and the other polymeric segments is different at various temperatures (Figures 6 and 7). Obviously, the external temperature and the temperature, which is generated in the sample, especially in the surrounding of the azobenzene moieties, caused by the exposure to a high power density of the Ar$^+$-laser, influences the kinetics of the photoorientation process. Thus, an increase of the dichroism for the ν(C≡N) absorption and the rate of its induction is found from 10 to 20 °C. A maximum at 18 °C exists as shown in Figure 7, but the photoinduced heat causes a decrease of the dichroism at higher temperatures upon continued irradiation. At 27 °C in the LC phase, the initially induced dichroism is completely erased during further irradiation. Optical isotropization and deaggregation are indicated by POM and UV−vis spectroscopy suggesting an increase of the temperature in the film above the clearing point.

Figure 7 provides an overview on the saturation values of the dichroism induced in the different polymer segments after 1000 s of irradiation as a function of temperature. As discussed for the ν(C≡N) band the photoinduced anisotropy of all segments increases in the glassy state with raising temperature to a maximum at 18 °C, but a further increase of temperature decreases the anisotropy and at 27 °C no anisotropy could be detected. This clearly demonstrates the cooperativity of the orientation process involving all segments of the polymer and the occurrence of the light-induced erasure dependence on the external temperature and power density with respect to the thermal properties of the polymer.

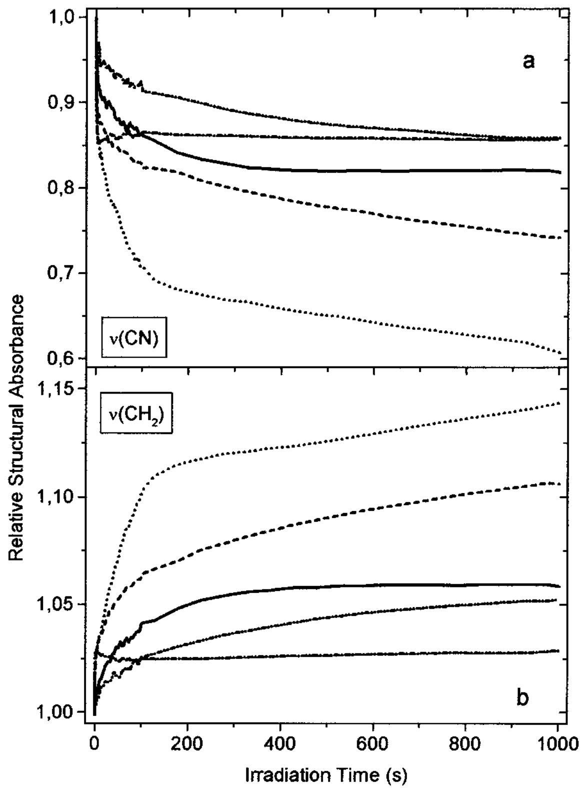

Figure 8. Calculated relative structural absorbance values of two selected absorption bands, characteristic for the different polymer segments, during the laser irradiation of a polymer film at various temperatures: (-••) 10 °C, (—) 15 °C, (- -) 20 °C, (• •) 25 °C, (-•-) 27 °C.

To investigate the three-dimensional orientational order in the sample, the isotropic aggregated states, such as spin-coated films or films cooled rapidly from the isotropic phase, are compared with oriented films. The socalled structural absorbance A_0 (eq 3) can be used to prove 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 structural absorbance should be constant, apart from some smaller deviations caused by structural changes and aggregation. The assumption is, that the freshly prepared and thermally pretreated film specimen is macroscopically isotropic in all three directions before irradiation. This was confirmed by the FTIR spectra of both states displayed in Figure 3 and discussed above. This behavior is different, compared to the investigations of Neher et al. where the polymer films are found to be isotropic in-plane but show a certain out-of-plane orientation after spin-coating.[45]

To emphasize the changes of the orientational distribution in comparison to the initial state, the relative structural absorbance was calculated by dividing the calculated structural absorbance value at the time, *t*, by the value of the nonirradiated sample.

The irradiation with an Ar$^+$-laser causes a decrease of the relative structural absorbance of all bands with a transition moment parallel to the long axis of the azobenzene unit, as, for example, the ν(C≡N) band, (see Figure 8a), while an increase of those absorption bands is observed having a transition moment perpendicular to the structural unit, e.g. for the ν(CH$_2$) absorptions (see Figure 8b). The same behavior is found for the ν(C=O) vibration. The $\pi-\pi^*$ transition of the azobenzene moiety shows the same behavior as the ν(C≡N) band. But the analysis is more complex because of a small amount of *Z*-isomers after the irradiation process and the subsequent aggregation, which take place simultaneously. Generally, the result is in agreement with the behavior of a series of amorphous and liquid crystalline polymers.[44]

Taking into consideration the inclination of the transition moments toward the molecular azobenzene axis and the backbone of the methylene segments both absorptions described in Figure 8 indicate a more distinct out-of-plane orientation of the photochromic side group, the main chain and the spacer of the side chain due to the photoorientation process. The observed deviations from the uniaxial orientational distribution are stronger than the changes in the absorbance spectra caused by the structural modifications of the film by thermal (Figure 3a value of 0.83) or photoinduced (at 27 °C) transfer to the isotropic state after about 30 s (see Figure 8ab). 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 shown by other studies using LC polymethacrylates, too.[45] This indicates that eq 3 and its assumptions are not valid for this orientational state. 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 order). It is indicated by a decrease of the structural absorbance. For this reason we used the linear dichroism values, derived directly from the measured UV−vis and FTIR polarization data in the film plane to characterize the photoinduced anisotropy in the polymer films.

In analogy to the in-plane anisotropy a strong influence of the temperature is also found for the out-of-plane component. The deviation of the relative structural absorbance from the reference value "1" becomes more pronounced with the temperature increasing from 10 to 25 °C and a maximum is observed at 25 °C while the maximum of the in-plane dichroism was found at 18 °C. Obviously, the light-induced order becomes modified by the thermotropic selforganization of the LC polymer with increasing temperature as also found for other systems.[40,44,46] It is erased partially or completely by exceeding the clearing temperature caused by photoinduced heat at the irradiation temperatures of 25 and 27 °C, respectively. Due to this partial erasure after 100 s of irradiation at 25 °C the calculated data has to be interpreted carefully. Thus, it seems, that the additional changes in the structural absorbance A_0 (for all segments) are of the same magnitude as for the photochemical induction of an isotropic phase at 27 °C, as described above.

III.4. Dependence of the Photoorientation Process on the Intensity of the Laser Irradiation. The dependence of the induction process on the thermal and photochemical effects induced by the Ar$^+$-laser light upon variation of the power density at about 27 °C in the LC phase is visualized in Figure 9.

For this experiment, films of a thickness of about 4 μm were used. The induction of anisotropy starts more efficient with increasing power density, as is obvious from the different slopes of the initial linear part of the curves. The steady state of the photoisomerization process is established faster and the photoorientation process becomes more efficiently. Under all conditions an intermediate maximum of the photoinduced dichroism, at comparable doses of about 500 mW/cm^{2}s, is observed on continued irradiation (see Figure 9a).

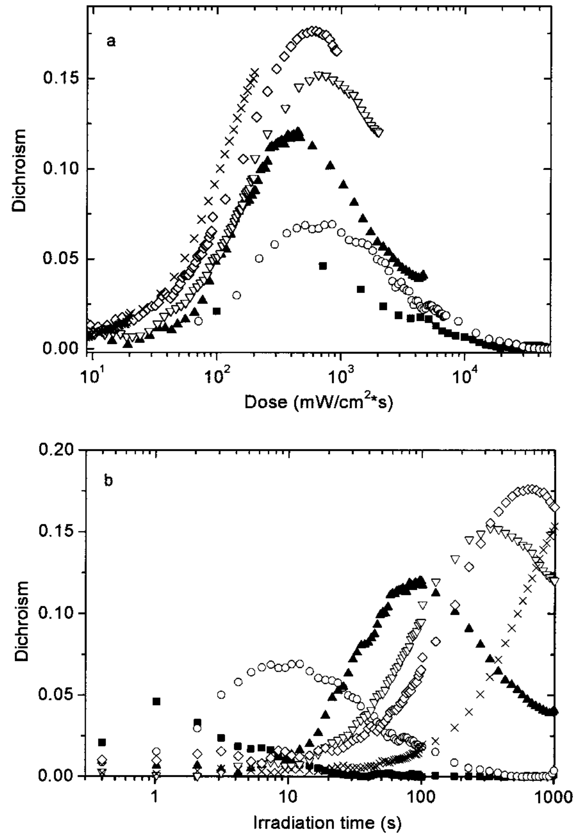

Figure 9. Photoinduced dichroism of the ν(C≡N) band versus dose (a) and irradiation time (b) for different intensities of the Ar$^+$-laser light (488 nm) at 27 °C: (■) 700.0 mW/cm^2, (○) 70.0 mW/cm^2, (▲) 4.6 mW/cm^2, (▽) 2.0 mW/cm^2, (◇) 0.9 mW/cm^2, (X) 0.2 mW/cm^2.

This shows that there is no restriction of the orientation process caused by the initial order, because the maximum is practically independent of the applied dose. This behavior is in contrast to results observed in aligned films of side-chain LCP's and LB multilayers of other liquid crystalline polymers with strong H aggregation and higher T_g values or with pronounced orientational order.[12,28] In these cases the initial order causes an intensity-dependent threshold of photoisomerization and, especially, of the photoorientation. The reason for the specific behavior of the polyester is the fact, that the long alkylene chains form a matrix which can be easily modified by temperature and photoisomerization. In this way even small power density destroys effectively all aggregates. This seems to be the reason why the highest dichroic ratios were found at very low power density of 0.2 and 1 mW/cm^2. Additionally, the induced anisotropy breaks down in shorter periods with increasing power density. This behavior should be caused by the thermal effect of the laser light and the stronger dynamics within the steady state, which induces a transition to the isotropic state at 70−700 mW/cm^2 after about 430 or 30 s, respectively. At low power densities the clearing dose of about 25 W/cm^2 s could not be achieved within the "standard irradiation time" of 1000 s, see Figure 9b. Furthermore, there is a better combination of photoorientation and self-organization resulting in higher dichroism values in the case of this LCP. The long term stability of the induced orientational order at room temperature is excellent due to the recombination of liquid crystallinity and aggregation after the linearly polarized irradiation.

The birefringence is a very important property with respect to practical application in the field of optical data storage and optical components. Therefore, the generation of birefringence was studied at room temperature (24 °C, close to T_g) by irradiating thin polymer films of about 150 nm with the

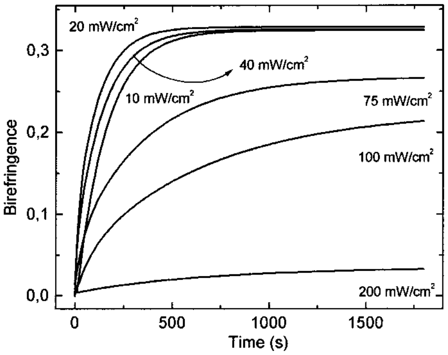

Figure 10. Photoinduced birefringence versus the irradiation time for different intensities of the Ar$^+$-laser light (488 nm) at 24 °C.

488 nm line of an Ar$^+$-laser. The general trend, which was observed for the dichroic ratio by IR investigations is found here as well (Figure 10). A maximum of birefringence is observed in the case of 10 to 40 mW/cm^2. The highest efficiency and the highest values are found for 20 mW/cm^2, but much lower values of birefringence are generated with increasing power density (75, 100, and 200 mW/cm^2). At higher values (700 mW/cm^2) no birefringence can be induced. The differences compared to the IR dichroism (Figure 9ab) should be related to the temperature difference and the lower film thickness of about 150 nm for this study compared to 2−5 μm used for the IR study.[47] Thus, the intermediate maximum or the corresponding partial erasure of anisotropy could not be detect. This seems to be related to the variation in the three-dimensional order in the dependence on the film thickness. This could be caused by surface effects, which may strongly lead in combinations with the thermal effects to a change in the course and the kinetics of the induction of the anisotropy.

IV. Conclusions

The investigations show that the azobenzene moieties of this type of liquid crystalline polyester undergo a strong J aggregation caused by the $\pi-\pi$ stacking of the aromatic cores. In agreement with other studies[46] this seems to be stimulated by the liquid crystallinity of the smectic polymer, which is obviously accompanied by a strong microsegregation tendency between the 4-cyano-4′-alkoxyazobenzene moieties, the extended alkylene spacers of the side and main chains and the polar ester linkage in the case of this polymer. While H-aggregation dominates in the most smectic side-chain polymers as well as in quite similar polyesters,[48,49] the 4-cyano-4′-alkoxyazobenzene units of this polymer are arranged in a head-to-tail fashion of the dipoles forming J-aggregates. The irradiation of the polymer films with a high intensity of linearly polarized light of an Ar$^+$-laser (488 nm) results in the distortion of the aggregates and the orientation of the azobenzene groups caused by selforganization or photoorientation. In contrast to the behavior of aggregates in other polymers the aggregates of the polymer under examination are destroyed even by low light intensities. While usually aggregation is contraproductive for photoisomerization and photoorientation, this is not the case in the investigated polymer, because the aggregated state can be intermediately manipulated by irradiation with light. This seems to be possible in the case of J-aggregation and is caused by the soft alkylene matrix, which can be easily modified by temperature and light when photochromic moieties are embedded.

The analysis of the threedimensional orientational distribution indicates a significant out-of-plane component of the photoinduced orientation resulting in a biaxial order, as shown by other studies, too.[45] This orientation process is cooperative even in the glassy state, i.e., the orientation of the photochromic side group induces the alignment of the ester unit of the main chain, and the alkylene chains of the side and main spacers ordering the whole polymer film. The orientation process takes place with the same efficiency and without any photochemical pretreatment of the aggregated film. It occurs by the repetition of the angular-dependent photoselection and the rotational diffusion within the steady state of the photoisomerization process at 488 nm.

With respect to the thermal and resulting ordering properties of the LC polymer, the induction of anisotropy shows a pronounced dependence on power density and working temperature. In contrast to H-aggregated polymers the photoorientation process of this polyester is not restricted by the J-aggregation even at low power densities, because all aggregates are destroyed by establishing the steady state of the photoisomerization at 488 nm. After this orientation process the azobenzene moieties are not aggregated due to the formed *Z*-isomers, but the J-aggregates are rebuild simultaneously to the *Z*/*E*-isomerization and a subsequent structural relaxation of the polymer matrix occurs. The highest value of anisotropy is achieved at 27 °C at a low power density, while increasing power densities result in a decrease of the maximum dichroism and, finally, the generated initial anisotropy is erased due to continuing irradiation. This can be used for an intermediate transfer to the isotropic state of the LCP films.

The orientation process takes place in the glassy state and in the mesophase, as well, whereas a maximum of anisotropy is induced at a temperature of about 6 °C below the glass transition temperature of the bulk polymer. Thus, at constant power density of 700 mW/cm^2 the saturation value of the dichroism increases first with the irradiation temperature, passes through a maximum up to 0.8 some degrees below the glass transition and finally the film is transferred to the isotropic phase at 27 °C at subsequent exposure with high power densities. Taking into account the thermal properties of the polymer the results indicate a significant thermal effect of the laser beam in the polymer film and demonstrates that the photoinduced anisotropy depends strongly on the irradiation conditions.

The very high values of the observed dichroism of 0.8 and birefringence of about 0.3 are caused by the interplay of photoorientation and the simultaneous thermotropic selforganization of the polymer. The induced values of optical anisotropy generated in the LCP films are much larger than in the case of amorphous polymers. The ordering process becomes very efficient due to light-induced heating effects, which are caused by the decrease of the transition temperatures by the photoisomerization. This is of special importance for the investigated polyester because of the small difference between the initial T_g value and the operating temperature. Thus, the film is temporarily transferred from the glassy state to the mesophase and the oriented azobenzene chromophores act as an aligning force in the LC polymer. This phenomenon has been studied in polymers with high T_g values which allow to separate the photoorientation process and the amplification of optical anisotropy upon annealing while both processes take place simultaneously in the case of the investigated polymer.[40] Thus, the maximum dichroism of about 0.8 was achieved by the optimization of the operating temperature and the power density.

In this system we cannot really discriminate between the influence of aggregation and LC ordering. In this case the $\pi-\pi$ stacking contributes to the intermolecular interactions and the liquid crystallinity of the system; thus, it contributes to the thermotropic selforganization and to the establishment of higher values of dichroism. A restricting condition is the fact that the spatial structure of the aggregates corresponds to the LC order and the light-induced order. In other papers we have shown that an intermediate UV exposure destroys aggregates and the orientational order of the aligned films. This decoupling procedure transferred the film in an intermediate, more mobile state which allows a much more efficient photoorientation process. On the other hand, the reaggregation improves the thermotropic selforganization, thus the aggregation contributes to higher values of optical anisotropy and their high stability.

The results presented in this communication are the basis for further investigations, where an orientation of the same polymer parallel to the electric field vector has been induced in a two-steady-state photoorientation process upon irradiation of a photochemically pretreated film with linearly polarized red light of a He/Ne-laser (633 nm). These results will be discussed in a forthcoming paper.

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Note Added after ASAP Posting

This article was released 3/8/2002 with minor errors in a table, in figure captions, and in the text. The correct version was posted on 3/20/2002.

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