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Light-Induced Orientation of Liquid Crystalline Terpolymers Containing Azobenzene and Dye Moieties

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ABSTRACT: Films of liquid crystalline copoly(methacrylate)s with photochromic azobenzene and benzanilide side groups and related terpolymers with additional dye side groups were oriented by the irradiation with linearly polarized visible or, alternatively, UV light. The orientational behaviors of the terpolymers with benzoxazole, stilbene, and anthracene moieties were compared. The irradiation conditions for the photoorientation process were optimized concerning wavelength and dose with respect to the absorption of the dyes and their limited photostability. Caused by the cooperativity of the photoorientation process, the light-induced ordering of the azobenzene group is connected with the alignment of the nonphotochromic co-mesogenic and the dye side groups even below the glass transition temperature. The light-induced orientational order generated in the glassy state was significantly amplified by the subsequent annealing of the irradiated films at temperatures within the mesophase of the co- and terpolymers. Amplification factors up to 30 were found in this series of polymers. The photoinduction process and the subsequent amplification by thermotropic self-organization were investigated in dependence of the polymer composition, the irradiation dose, and the wavelength of the incident light. The required dose or the irradiation time was significantly reduced by the optimization of light-induced and thermal processing, respectively. In this way, dichroic polymer films containing different types of dyes were created.

I. Introduction

The defined preparation of anisotropic films of functionalized polymers is a goal of great importance for various technical applications. All conventional techniques to prepare anisotropic polymer film, such as the LB technique, mechanical stretching, or the alignment of liquid crystalline (LC) polymers on rubbed polyimide surfaces, are time-consuming and discontinuous procedures. The photoalignment technique on photoanisotropic surfaces overcomes some disadvantages of the traditional rubbing technique[1,2] and offers the opportunity of a patternwise alignment in subpixels. But the alignment of LC polymers by surface effects is strongly limited by the high viscosity of the polymers and the film thickness and is influenced by the free surface. The linearly polarized (LP) irradiation of films of photochromic LC polymers containing azobenzene groups offers a new approach to orient films of such polymers. In contrast to all other methods, the light-induced orientation process has the advantage of local variation of the orientational order due to pixelwise irradiation.

The photoorientation process takes place via angular-dependent excitation, a number of E/Z photoisomerization cycles, and rotational diffusion within the steady state of the photoreaction. In this way the photochromic side group becomes oriented perpendicular to the electric field vector of the incident light establishing an oblate order in the films. In the case of amorphous and LC copolymers the process causes a cooperative orientation of nonphotochromic side groups toward the same direction and to a comparable anisotropy as well.[3−9]

Moreover, we have shown recently that the photoinduced order generated in the glassy state of LC polymers can be significantly amplified by annealing in the temperature range of the mesophase. The orientational order, photogenerated in the glassy state, acts as directing force for the thermotropic self-organization process, resulting in a macroscopic alignment of the LC polymers.[10−16] The method combines the easy preparation of spin-coated films with the generation of optical properties characteristic for LCs. So, films with very high values of dichroism or birefringence have been created by the combination of the photoorientation process and the subsequent thermotropic self-organization of the LC polymer, respectively. However, in many cases the in-plane order gets lost, and the annealing procedure leads to a homeotropic orientation.

In the present contribution, the light-induced preparation of dichroic films with specific optical properties introduced by dye moieties will be discussed. The cooperativity of the photoorientation of azobenzene moieties in the bulk and the amplification of the photoinduced order by thermotropic self-organization should be optimized to align multifunctional liquid crystalline terpolymers containing photochromic, mesogenic, and dye side groups. The resulting optical properties of the polymer films in absorption will be discussed with respect to the composition of the polymer and the processing conditions.

The processing conditions were initially investigated with the reference copolymer that does not contain any dye unit.[16−18] The results show that a large dichroism can be achieved using a two steps process: (i) irradiation with linearly polarized (LP) light and (ii) annealing at

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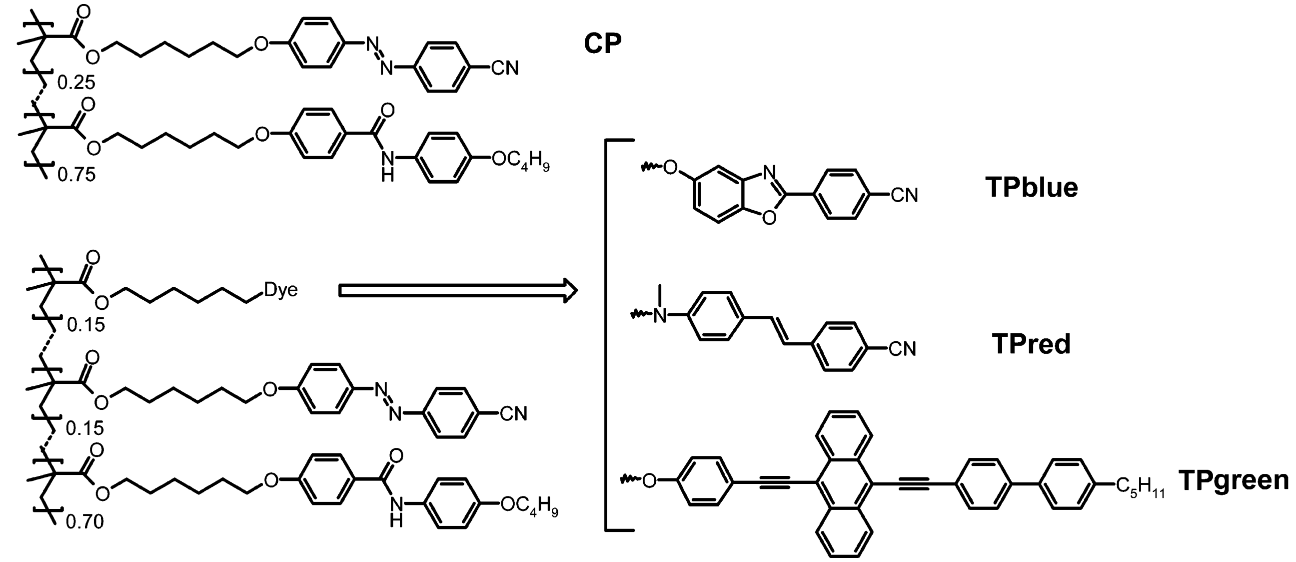


Figure 1. Structure of the investigated terpolymers and the reference copolymer CP.

temperatures within the mesophase. Moreover, the results have shown that the photoorientation works upon irradiating with LP UV light at 365 nm as well as LP green light at 488 nm. The photogenerated order was very efficiently amplified by thermotropic self-organization in the liquid crystalline phase up to dichroism values of 0.77. It was established that this order is almost independent of the energy dose. Therefore, the same anisotropy values were reached as well with high and low irradiation doses. The independence of the orientational behavior from the used irradiation wavelength and dose are important items for this study, when undesired side photoreactions of the incorporated dyes have to be avoided.

II. Experimental Section

The general route for the synthesis of the monomers and polymers as well as their physical characterization, liquid crystalline behavior, and photophysical properties were described in recent publications.[17,19,20] The polymers were designed to combine a number of properties: liquid crystallinity, specific absorption and emission properties, and photosensitivity, which should allow to orient the system. The polymers consist of 15% azobenzene, 70% benzanilide, and 15% of a dye side group.

Films of the polymers were prepared using THF as solvent (0.15 M calculated for one polymeric repeating unit) by spin-coating on a CT 60 (Karl Suess, acceleration 700 rpm/s at 2000 rpm for 30 s). The films were stored for 1 day at room temperature.

The irradiation of the polymer films was carried out at room temperature with the linearly polarized (LP) light of an Ar^+ laser (Innova 4, Coherent) using the green line at 488 nm (100 mW/cm^2) or, alternatively, the UV light at 365 nm (30−43 mW/cm^2). The time of exposure was varied. After the irradiation procedure, the films were annealed in the liquid crystalline state of the polymers at 60−100 °C up to 3 days. The induced anisotropy was characterized by polarized UV/vis spectroscopy. The measurements were carried out using a diode array spectrometer (Polytec X-dap-04 V2.3) in combination with a Glan-Thomson prism. The dichroism D in the films was calculated from the absorbance measured perpendicular ($A_{\parallel}$) and parallel ($A_{\perp}$) to the electric field vector of incident laser light. A subscript was used to indicate the wavelength at which D was determined.

$$D = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} - A_{\parallel}} \qquad (1)$$

The film thickness was measured using a Dektak^{3}ST profilometer from Veeco.

On the irradiation experiments, the absorbed energy (E_{abs}) (formula 2) could be estimated from the power density of the incident light (P), the irradiation time (t), and the transmission at the irradiation wavelength, calculated from the change of the average absorbance (A_{av}) of the initial and irradiated film.

$$E_{abs} = tP(1 - 10^{-A_{av}}) \qquad (2)$$

III. Results and Discussion

1. Properties of the Materials. The investigated materials were liquid crystalline poly(methacrylate)s obtained by free radical polymerization.[20] Their chemical structures are represented in Figure 1.

All terpolymers are based on a mesomorphic benzanilide unit and a photochromic 4-hexoxy-4′-cyanoazobenzene unit, like the reference copolymer CP. In addition, a third unit with specific optical properties in relation to its absorbance has been chemically incorporated. TPblue has a 2-phenylbenzoxazole-based dye, TPgreen a 9,10-bis(phenylethynyl)anthracene-based dye, and TPred a stilbene-based one. The different chromophores were selected with respect to their photostability, mesomorphic, and different emission properties. In relation to this latter aspect, the benzoxazole dye emits in the blue spectral region, the anthracene in the green, and the stilbene in the red. However, previous work has revealed that the emission of these particular dyes in the terpolymer films is quenched to almost 100% due to the presence of the azobenzene unit.[20] Nevertheless, the names of the terpolymers were given by their emission properties in solution.

The investigated polymers are glassy materials at room temperature and show mesomorphic properties in the range between the isotropic state (179−97 °C) and T_g (39−59 °C). Transition temperatures and mesophases are collected in Table 1. The reference polymer CP and the terpolymers TPblue and TPred show the formation of a SmA phase. TPblue and TPred show some tendency toward crystallization as it is observed from different DSC scans. On heating of TPblue and TPred, a cold crystallization process is observed above the T_g temperature. TPgreen shows the formation of a N mesophase. This different mesogenic behavior is related

Table 1. Thermal Properties of the Investigated Polymers[a]

polymer	T_g	T_i	ΔH_i	mesophase [b]
CP	59	179	3.7	SmA
TPblue	39	135	2.4	SmA
TPred	38	136	1.3	SmA
TPgreen	58	97	0.2	N

[a] Transition temperatures determined by DSC. T_g is the glass transition temperature, T_i is the isotropization temperature, and ΔH_i is the related enthalpy. Temperatures are given in °C and in kJ mol^{-1} of repeating unit using the calculated or the feed composition of the polymer. [b] Determined by the formation of specific textures on the microscope under crossed polarizers.

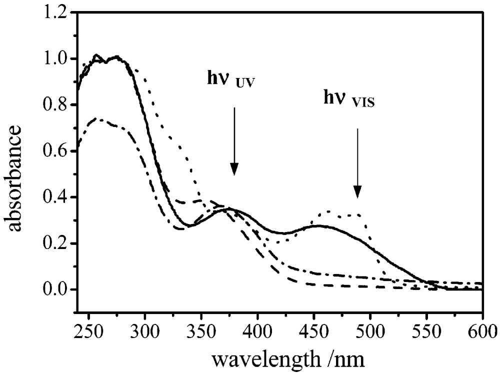


Figure 2. Absorbance spectra of films of the terpolymers TPblue (– –), TPred (—), and TPgreen (· · ·) and of the reference copolymer CP (- · -).

Table 2. Absorbance of the Dye-Containing Terpolymers[a,b]

polymer	absorbance λ_{max}
TPblue	283, 350
TPred	286, 375, 445
TPgreen	273, 367, 453, 475

[a] The absorbance was measured in THF. Data are given in nm. [b] The maximum of the absorbance at the $\pi\pi^*$ transition of the azobenzene unit is at 365 nm, and that of the benzanilide is at 280 nm.

to the structural difference of the anthracene-based dye. All the polymers form films of a good optical quality.

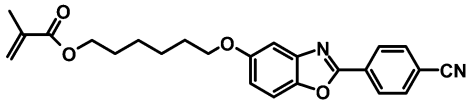
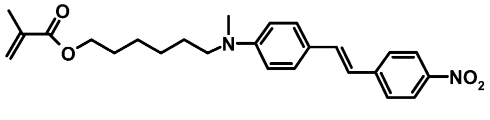
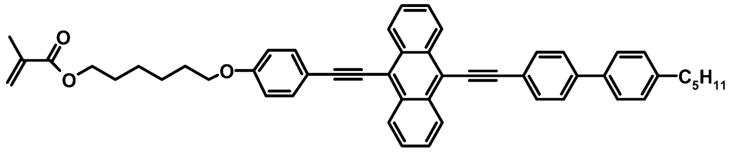
The azobenzene group incorporates photochromic properties into the materials and offers the opportunity for photoorientation processes upon LP irradiation. In this way, the generation of anisotropy takes place in the steady state of E/Z photoisomerization cycles.

The functionalization of the polymers with the additional chromophoric side group (benzoxazole, stilbene, or anthracene moieties) results in a variation of the corresponding absorption spectra. The UV/vis spectra of the investigated polymer films are shown in Figure 2, and the maxima of the dye absorbance are summarized in Table 2. The spectra of the terpolymer films are characterized by the $\pi\pi^*$ absorbance of the benzanilide group at 280 nm and the $\pi\pi^*$ and $n\pi^*$ absorbance of the azobenzene at 367 and 450 nm, respectively. The $n\pi^*$ transition of the *E*-azobenzene, which is exclusively present in the nonirradiated films, is symmetry forbidden, and as a consequence, the associated band is very weak. In addition, each polymeric film shows bands corresponding to the dye absorbance. The monomeric benzoxazole dye has the maximum absorbance at 336 nm; therefore, for TPblue there is a spectral overlap between the $\pi\pi^*$ transition of the azobenzene and the $\pi\pi^*$ transition of the benzoxazole, resulting in a broad absorbance between 300 and 350 nm. In this way the maximum of the dye absorbance in the polymer TPblue cannot be clearly defined. The stilbene dye of TPred films has the maximum of absorbance at 452 nm, and the anthracene-based dye shows bands at 462 and 487 nm in TPgreen films. Thus, in the case of TPred and TPgreen the spectral overlap occurs between the absorbance of the dyes and the weak $n\pi^*$ transition of the azobenzene unit. The absorbance of all the polymeric films is slightly (up to 10 nm) bathochromically shifted compared to the terpolymers and the monomeric units in THF.

The dichroic properties of the dyes (0.01 mol/kg) were characterized in a nematic mixture of the low molecular liquid crystals K 15 and ZLI 1132 (supplied by Merck, Darmstadt) in a ratio of 1:1. The guest–host mixtures were aligned in 10 μm glass cells containing an aligning layer of rubbed polyimide. The dichroism, *D*, was determined from the maximum of absorbance of the dye.

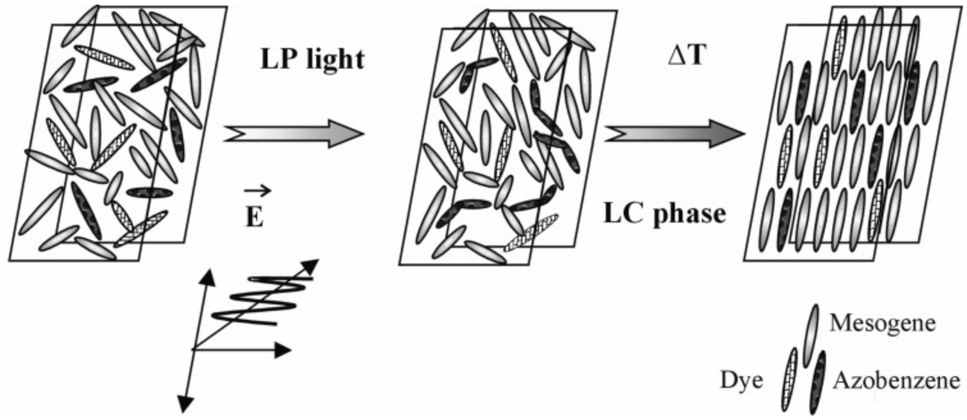
As seen in Table 3, the highest dichroism of about $D_{462} = 0.88$ results for the monomeric anthracene derivative, whereas the stilbene monomer has $D_{452} = 0.73$ and benzoxazole is characterized by the lowest dichroism of about $D_{336} = 0.55$. From the angular-

Table 3. Ratio of Length to Width and the Dichroism of the Monomeric Dyes in LC

	Structure	L / W[a)]	D[b)]
Blue		5.18	0.55
Red		5.61	0.73
Green		4.66	0.88

[a] Aspect ratio of length to width; calculated after optimization of the 3D geometry. [b] Dichroism in glass-cells filled with low molecular liquid crystals K15/ZLI 1132 (Merck) in a ratio 1:1 and 0.3 wt % of the related dye, calculated from the dye absorbancies parallel and perpendicular to the rubbing direction of polyimide.

Scheme 1. Principle of the Orientation of Functional Azobenzene Containing LC Polymers



dependent UV/vis spectra, it was determined that the transition moment of all three dyes is parallel to the long molecular axis of the chromophores.

2. Cooperative Photoorientation of the Dyes and Their Photostability in the Terpolymer Films. The orientation principle is a two-step bulk-photoalignment process, whereas in a first step a small photoinduced order will be introduced upon LP irradiation by the photoorientation of the azobenzene side groups in the glassy state and in a second step the light-induced order will be amplified by annealing in the liquid crystalline phase. In the case of the copolymer CP both ordering principles, the light- and thermo-assisted orientation works cooperatively for both side groups. In this way, we suppose, that the orientation of the incorporated rodlike dyes in the terpolymers takes place cooperatively in the same way (Scheme 1).

If the same photoalignment procedure used for the reference copolymer CP wants to be applied to the dye containing polymers, the absorbance and the photostability of the dyes have to be taken into account.

In the case of TPgreen and TPred, the week $n\pi^*$ transition of the azobenzene moiety is overlapped by the $\pi\pi^*$ transition of the anthracene or the stilbene chromophore. Therefore, the dye absorption might cause an internal filter effect, and for this reason, the LP irradiation with the green light of the Ar^+ laser of 488 nm for the photoorientation process is not applicable but the blue light of 365 nm can be used.

In contrast, the benzoxazole-containing polymer does not absorb in the visible range. In this case the spectral overlapping takes place between the $\pi\pi^*$ transitions of the photochromic azobenzene group ($\lambda_{\max} = 365$ nm) and the benzoxazole moiety ($\lambda_{\max} = 336$ nm). However, at 365 nm, the extinction coefficient of the azobenzene (23 300 cm^{-1} M^{-1}) is larger than that of the benzoxazole (5500 cm^{-1} M^{-1}). Thus, photoorientation could be a priori carried out using UV light (365 nm) or alternatively the green line of the Ar^+ laser (488 nm).

The second problem, in relation to the applicability of the light-induced orientation, is the probability of undesired side photoreactions of the dyes. Because of the limited photostability of the dyes, low irradiation doses introducing only a small anisotropy and giving the lowest photodegradation of the dye should be preferred. The photostability of the dyes can be evaluated by changes on the maximum absorbance of the corresponding dye before and after irradiation.

First of all, different irradiation and annealing conditions were tested with the reference copolymer CP without dye,[13,16,18] which indicate an independence of the anisotropy after the two-step bulk photoalignment using different irradiation wavelengths and doses.

Applying the experiences with the related copolymer CP to the bulk orientation of the dye-containing terpolymers lead to optimized irradiation conditions which result in a maximum anisotropy, as described in Table 4.

Orientation of the Benzoxazole-Containing Terpolymer TPblue. As it was stated above, the light-induced orientation of TPblue was approached with both LP UV light (365 nm) and LP vis light (488 nm).

Upon irradiation with UV light, it was observed that the average absorbance at 336 nm first decreases and later increases. At this wavelength both the azobenzene and the dye unit absorb. Moreover, UV irradiation of the azobenzene results in a larger Z/E ratio. In this way the change of the absorbance is caused by the photodegradation of the dye but also due to formation of the *Z* azobenzene isomer he ($\lambda_{\max} = 225$ and 450 nm). The photodegradation and the reversible formation of the Z isomer leads to a change of the absorbance at this wavelength reverse, so that we can observe a decrease and a subsequent increase of the absorbance at 336 nm in dependence on the irradiation dose (Figure 3 (2)). Nevertheless, as found by UV irradiation of the monomeric benzoxazole in PMMA under comparable conditions, the stability of the dye is quite high (Figure 3 (1)). In this way the observed change of absorbance in TPblue at 336 nm should be mainly caused by the E/Z isomerization of the azobenzene unit.

Figure 4 shows that the irradiation with LP UV light results in a preferred orientation of the azobenzene and the dye side group perpendicular to the electric field vector. The initial photoinduced dichroism of about $D_{367} = 0.17$ can be significantly amplified by annealing at 90 °C in the mesophase up to a value of $D_{367} = 0.42$. Because of the spectral overlapping, it cannot be distinguished between the $\pi\pi^*$ transitions of the photochromic group and the dye moiety. Nevertheless, calculating the dichroism from the maximum of the absorbance as found for the monomers, the dichroisms at 336 and 367 nm are identical after the combined photochemical and thermal processing steps demonstrating the cooperativity of the orientation.

The irradiation of the terpolymer TPblue with LP UV light (365 nm, 43 mW/cm^2) for 60, 300, and 900 s results in all cases in the induction of anisotropy which is efficiently amplified by annealing at 90 °C. The related anisotropies for the different irradiation times and

Table 4. Dichroism of the Terpolymers upon LP UV Irradiation and Annealing[a]

	irradiation conditions[b]		decrease of dye absorbance upon irradiation/%[c]	*D* after irradiation[d]		*D* after annealing[d]		amplification factor[e]
polymer	λ/nm	time/s		D_{azo}	D_{dye}	D_{azo}	D_{dye}	
CP	365	900	without dye	0.29		0.76		2.6
	488	3	without dye	0.04		0.77		20.6
TPblue	365	60	*f*	0.08	0.06	0.33	0.33	5.5
	365	300	*f*	0.17	0.14	0.42	0.40	2.9
	365	900	*f*	0.21	0.16	0.38	0.38	2.4
	488	300	0	0.11	0.09	0.67	0.68	7.5
TPred	365	60	1.7	0.13	0.06	0.44	0.47	7.8
	365	300	13.6	0.23	0.18	0.57	0.59	3.3
	365	900	29.0	0.21	0.19	0.44	0.51	2.7
TPgreen	365	60	3.6	0.09	0.02	0.55	0.67	33.5
	365	300	19.1	0.13	0.09	0.36	0.49	6.5
	365	1020	45.0	0.12	0.11	0.06	0.12	1.1

[a] The films were annealed up to 3 days at 20 °C above T_g. [b] The irradiation was carried out with LP vis light at 488 nm 100 mW/cm^2 or with LP UV light at 365 nm 43 mW/cm^2. [c] The decrease of absorbance was calculated from the absorbance of the virgin and irradiated film at the maximum of the dye absorbance: TPred at 452 nm and TPgreen at 462 nm. The values are estimated taking into account the influence of the changing of the absorbance by the E/Z isomerization of azobenzene.[25,26] [d] The dichroism after LP irradiation and annealing at 90 °C for 15 h were calculated from the absorbance parallel and perpendicular to the electric field vector of incident light. [e] The amplification factor was calculated from the increased dichroism after annealing compared to the dichroism of the irradiated films at the maximum of absorbance of the dye. [f] Not detectable because of the spectral overlapping with the azobenzene absorbance.

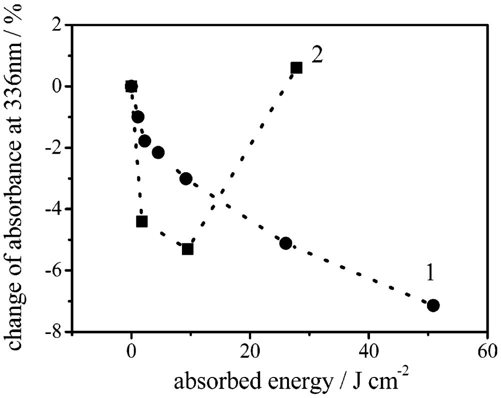


Figure 3. Change of the absorbance at 336 nm of the monomeric benzoxazole in PMMA caused by photodegradation (1) and of benzoxazole and azobenzene in TPblue (2) upon irradiation at 365 nm.

absorbed energies after subsequent annealing are presented in Figure 5. It could be shown that the dichroism after the two-step bulk-photoalignment process is almost independent of the irradiation doses.

Changes in absorbance were observed during the annealing step of the processing films. After annealing, the achieved anisotropy was small compared to the generated anisotropy of the copolymer CP of about $D = 0.77$.[17,20] It was observed that the absorbance perpendicular to the electric field vector remains almost constant whereas the absorbance parallel decreases strongly, resulting in an anisotropy perpendicular to the *E* field vector. In addition, the in-plane average absorbance[21] decreases in this way, indicating the establishment of a significant out-of-plane orientation by annealing. Upon annealing in the LC phase an out-of-plane orientation could be caused by formed nonmesomeric photoproducts, such as *Z*-azobenzene isomeric units or photodegradation products of the benzoxazole. In the case of azobenzene containing aligning layers this effect is well-known as the "command surface effect".[1] To exclude the effect caused by nonmesomeric photoproducts, TPblue films were irradiated with LP vis light (488 nm, 100 mW/cm^2 for 300 s). In this way a dichroism of about $D_{336} = 0.09$ was established, which is slightly lower compared to that due to UV irradiation. Annealing at 85 °C for 1 day results in a dichroism of $D_{336} = 0.64$. Further annealing of the film for 1 day at 100 °C give a dichroism of $D_{336} = 0.68$. This anisotropy is significantly larger compared to that established by UV irradiation. As mentioned above, the possible reason for the limitation of the orientation behavior upon UV irradiation could be the formation of nonmesomeric photoproducts caused by a high amount of Z isomers of the azobenzene or by the photodegradation of the dye. The development of the in-plane average absorbance at 336 nm, which corresponds to the azobenzene and the benzoxazole moiety, and the related dichroism after the irradiation for 300 s are presented in Figure 6. In contrast to the UV-irradiated film, the average absorbance after vis irradiation and annealing remains almost constant, whereas the absorbance perpendicular to the electric field vector increases and the absorbance parallel decreases. Simultaneously, the dichroism increases from 0.09 to 0.68. The high anisotropy and the remaining average absorbance after annealing give rise to the assumption that the film has an in-plane orientation.

The different behavior comparing UV and vis irradiation is in contrast to the behavior of the related copolymer CP. In CP either LP UV or vis light and the subsequent amplification by annealing in the LC phase resulted in a comparable in-plane order.[16] So, the more complex terpolymer TPblue is characterized by a loss of the in-plane absorbance upon the two-step orientation process, which could be explained by a stronger out-of-plane orientation tendency. The vis-irradiated TPblue films do not show formation of nonmesomeric photoproducts; in this way an in-plane orientation is preferred.

It is remarkable that annealing of the film at different temperatures (59, 85, or 100 °C) for 1 day does not result in significant changes of absorbance and anisotropy. This demonstrates that the annealing temperature within the mesophase range does not have a significant importance to the orientational behavior.

Orientation of the Stilbene-Containing Terpolymer TPred. As was aforementioned, only LP UV light is practicable for the photoorientation of TPred. Upon LP UV irradiation the stilbene-containing terpolymer TPred behaves similar to TPblue, but the dye stability detected by the changes of the absorbance at 452 nm is

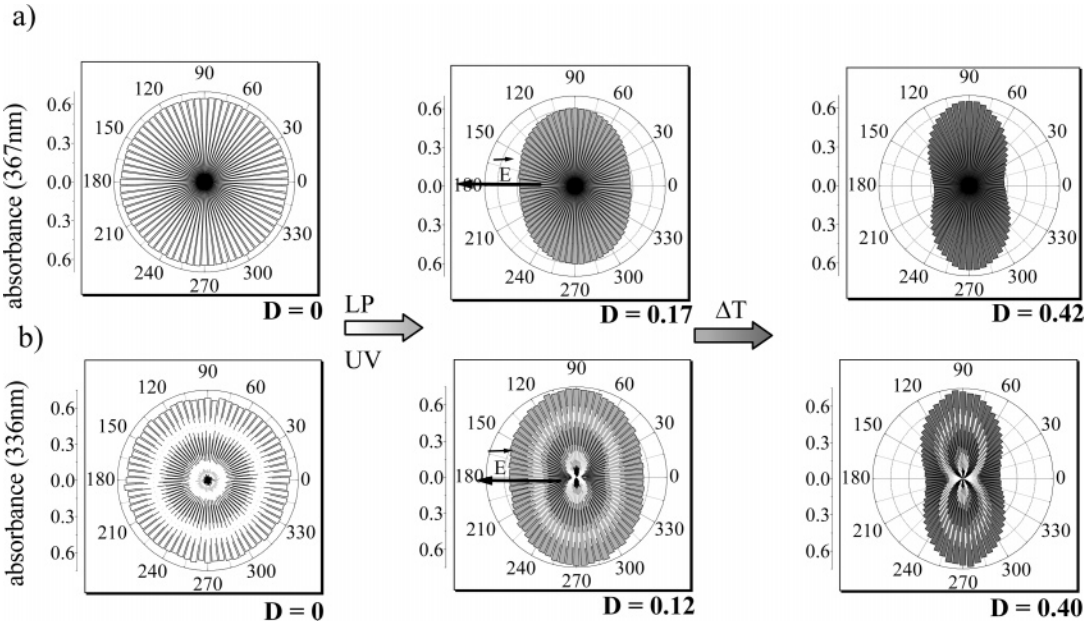


Figure 4. Angular dependent absorbance in a virgin TPblue film (left), induction of anisotropy by irradiation at 365 nm for 300 s (middle), and amplification of the anisotropy by annealing at 90 °C for 15 h (right): (a) azobenzene side group at 367 nm; (b) benzoxazole side group at 336 nm.

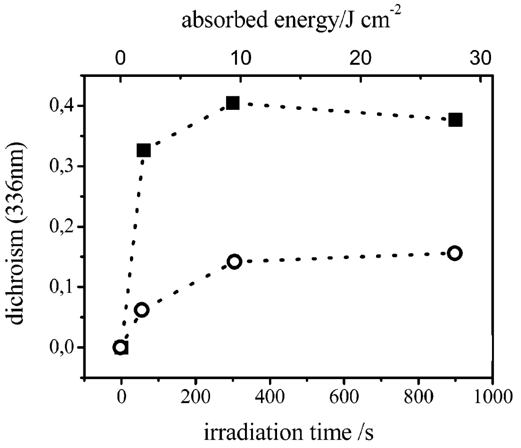


Figure 5. Dichroism at 336 nm in TPblue in dependence from the irradiation time and from the absorbed energy after LP irradiation with 365 nm (○) and after annealing (■) the films for 15 h at 90 °C.

lower compared to the dye of TPblue. Remarkable is that the dye does not have a significant absorbance at the irradiation wavelength of 365 nm, so the degradation of the dye could take place only via an indirect excitation through the azobenzene moiety.

Upon UV irradiation the *Z* isomer of azobenzene is formed, resulting in an increase of the nπ^* absorbance and higher absorbancies in the range of the dye absorbance. The change of absorbance at 452 nm due the E/Z isomerization of azobenzene was estimated from experiments with the related terpolymer TPblue, which have the same azobenzene content but do not have any absorbance of the dye at this wavelength. An increase of absorbance for 0.025 in the steady state of photoisomerization of azobenzene was found. The loss of the in-plane average absorbance due to the degradation of the dye at 452 nm was 13.6% after 300 s (absorbed energy 9.1 J/cm^2) and 29% after 900 s (absorbed energy 31.4 J/cm^2). The values are exactly the same as found for the degradation by irradiation of the monomeric dye in PMMA (Figure 7), indicating that the degradation

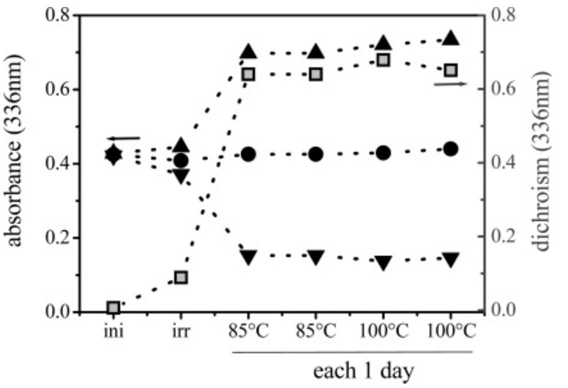


Figure 6. Development of the in-plane average absorbance[21] (●), absorbance perpendicular (▲) and parallel (▼) to the *E*-field vector and the resultant dichroism (■) at 336 nm after LP irradiation for 300 s with 488 nm (irr) after annealing the TPblue film each for 1 day at 85 and 100 °C.

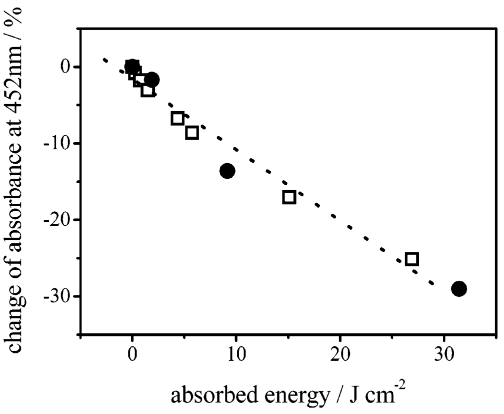


Figure 7. Change of the absorbance of the monomeric stilbene in PMMA (□) and of the stilbene unit in TPred (●) upon irradiation at 365 nm.[25]

of the monomeric dye in PMMA and the covalently bonded dye in TPred behaves similarly. It is well-known that the stilbene moiety can undergo E/Z photoisomerization and [2 + 2] photocycloaddition, and furthermore

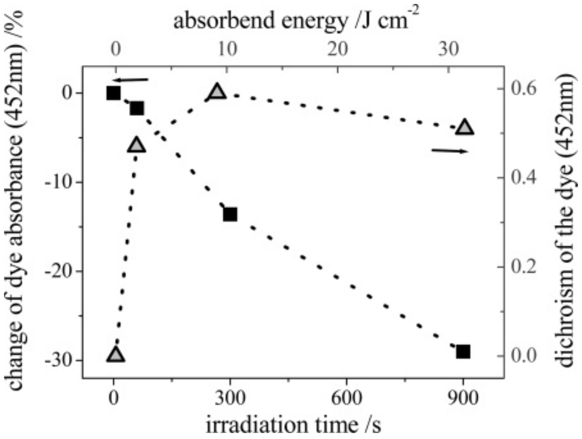


Figure 8. Change of the absorbance[25] in TPred (■) at 452 nm upon LP irradiation at 365 nm and the related dichroism (▲) after annealing the film for 15 h at 90 °C in dependence from the irradiation time and from the absorbed energy.

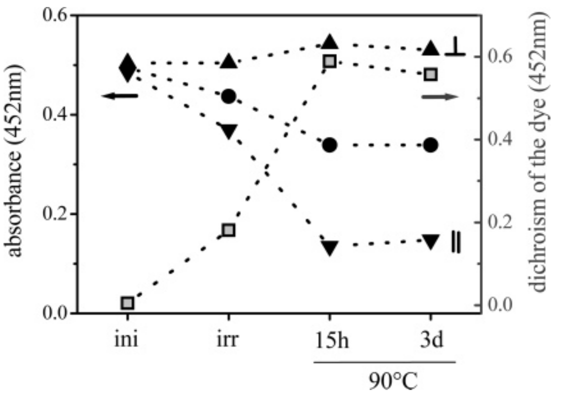


Figure 9. Development of the in-plane average absorbance[21] (●), absorbance perpendicular (▲) and parallel (▼) to the E-field vector, and the induced dichroism (■) after irradiation for 300 s with LP UV light and subsequent annealing of a TPred film, detected at the absorbance of the stilbene.

the Z isomer can react by cyclization forming dihydrophenanthrene. The significance of these different photoreactions of the stilbene moiety on the orientation process was not studied in detail. However, the donor–acceptor substitution should decrease the effect of these side reactions.[22,23]

The highest anisotropy was achieved by LP UV irradiation for 300 s and subsequent annealing above T_g for 15 h. After this two-step procedure the dichroism of the stilbene side group amounts to $D_{452} = 0.59$ and that of the azobenzene group $D_{367} = 0.57$. This indicates that the photoreactions of the stilbene moiety do not disturb significantly the ordering process. This is also demonstrated by the fact that the variation of the irradiation time between 60 and 900 s results only in a relatively small change of the dichroism between $D_{452} = 0.59$ to $D_{452} = 0.47$ (Figure 8).

As seen from Table 4, the dichroisms of the dye and the azobenzene side group after irradiation and annealing are in all oriented TPred films in the same order of magnitude. In dependence on the irradiation time, the absorbed energy varies between 1.9 and 31.4 J/cm².

The evolution of the in-plane absorbance[21] of stilbene at 452 nm and the induced dichroism of the side group upon UV irradiation and subsequent annealing are presented in Figure 9. Similar to the UV-irradiated TPblue films, the in-plane average absorbance of the dye is decreased by irradiation and annealing while the dichroism increases significantly due to annealing in the smectic phase of the polymer. The annealing procedure causes a slight increase of the absorbance perpendicular to the electric field vector whereas the value parallel to E strongly decreases. The strong decrease of absorbance could be related as aforementioned to a partially out-of-plane orientation of the side groups due to interfacial effects on the thermotropic self-organization process.

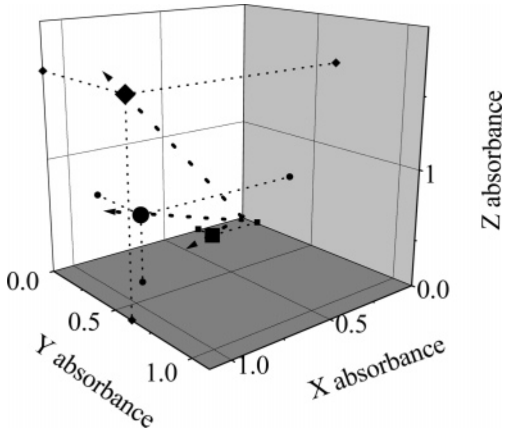


Figure 10. Vectors of the x, y, and z absorbancies of the $\pi\pi^*$ transition of azobenzene after irradiation and annealing of TPred films of different thickness with $d = 146$ nm (■), $d = 450$ nm (●), and $d = 771$ nm (◆).

The influence of the film thickness on the ordering process was studied as well. Three spin-coated films with different thickness characterized by their different absorbance at 367 nm, A_{367}, of about 0.19, 0.64, and 1.15 were irradiated for 300 s at 365 nm and annealed for 15 h at 90 °C. The initial absorbancies of the stilbene side group, A_{452}, were in the same order, starting from 0.16 to 0.49 and 0.84. The thickness of the films varies from 146 to 450 and 771 nm. The absorbed energy in the film was found between 6.9 and 12.4 J/cm². The detected in-plane order parameter of the dye decreases in the thickest film. In this film only a dichroism $D_{367} = 0.28$ was found, whereas the dichroism of the thinner films show significantly higher values so at $D_{367} = 0.50 \pm 0.07$[25] ($d = 146$ nm) and 0.57 ($d = 450$ nm).

Figure 10 visualizes the vectors of the x, y, and z absorbancies of the azobenzene at 367 nm characterizing the 3D order of the oriented films. The x absorbance (A_x) corresponds to the direction perpendicular and the y absorbance (A_y) parallel to the E field vector of the incident actinic light. The z absorbance (A_z) was calculated by the assumption of an isotropic distribution of the chromophores in x, y, and z direction in the initial spin-coated film, A_{iso}. It can be concluded that the thickness of the films plays an important role establishing the spatial order of the films after the photoorientation process and thermal alignment.

$$A_z = 3A_{\text{iso}} - A_x - A_y \tag{3}$$

The angle γ between the substrate plane and the vector of the x, y, and z absorbance can be calculated using the relation of the vector of absorbance and the transition moment by the assumption of a uniform orientation of all molecules in the initial film:

$$\sin\gamma = \sqrt{\frac{A_z}{A_x + A_y + A_z}} \tag{4}$$

Table 5. Absorbancies of TPred Films of Different Thickness and the Angle between the Vector of Absorbancies and the Substrate Plane

d/nm[a]	A_{iso}[b]	A_x[c]	A_y[c]	A_z[d]	γ[e]
146	0,191	0,293	0,113	0,17493	33,3
450	0,621	0,862	0,343	0,65924	36,5
771	1123	1098	0,615	1,61735	44,2

[a] Film thickness in nm. [b] Absorbance of the isotropic film. The isotropic extinction was corrected by the loss of dye absorbance upon irradiation. [c] Measured perpendicular (A_x) and parallel (A_y) to the *E*-field vector of incident light after the two-step orientation procedure. [d] Calculated by the assumption of an isotropic contribution of the initial films by formula 3. [e] Calculated by formula 4.

The results are summarized in Table 5. The result clearly demonstrates that thicker films result in a larger out-of-plane component with a higher value of z absorbance and a higher angle between the substrate plane and the absorbance vector compared to thinner films. A gradient of the spatial distribution within the oriented film caused by the attenuation of the incident light upon the photoorientation process or a different behavior of the polymer−air interface compared to the bulk is suggested. The detailed explanation of this phenomenon requires further investigations.

Orientation of Anthracene-Containing Terpolymer TPgreen. As was stated, the photoorientation experiments of TPgreen were carried out using LP UV light. The competition between the photodegradation of the dye and the induction of anisotropy by the azobenzene side group was investigated with respect to the irradiation conditions. Upon UV irradiation the related anthracene moiety of the nematic terpolymer TPgreen shows a strong photodegradation of its π-system. Probably, the origin of this process is the photooxidation of the anthracene moiety in the 9,10-positions. But the [4 + 4] photocycloaddition reaction connecting two anthracene moieties via the 9,10-positions or the photocycloaddition reactions of the triple bonds could take place as well. For instance, the exposure for a period of 1020 s (absorbed energy 36.1 J/cm^2) causes a decrease of the average absorption of the chromophore at 462 nm of about 49%. These values are given, as in TPred, after considering the change of absorbance due to E/Z isomerization of azobenzene. An increase of the absorbance at 462 nm for 0.011 in the steady state of photoisomerization of azobenzene was estimated from experiments with the related terpolymer TPblue. To attain a maximal dichroism by the two-step photoalignment procedure, the optimization of the irradiation conditions was required to get the indispensable photoinduced anisotropy with the lowest photodegradation of the dye. Figure 11 shows that the orientation is more efficient using a low irradiation dose, whereas the anisotropy after the complete two-step orientation procedure decreases strongly at long irradiation times. Obviously, we deduce that the photodegradation products disturb the alignment process in the LC phase. Upon irradiation of the film for 60 s (absorbed energy 2 J/cm^2) and subsequent annealing, the highest dichroism was found (D_{462} = 0.67) because the photodegradation of the dye is low. Figure 12 shows the evolution of the absorbance and the induced anisotropy of the anthracene chromophore for this case.

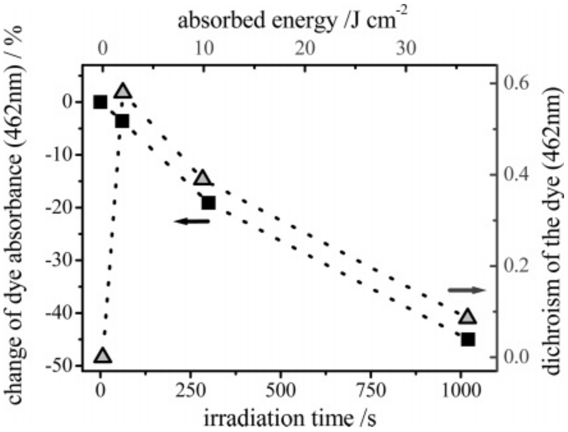


Figure 11. Change of the absorbance[26] in TPgreen (■) at 462 nm upon LP irradiation at 365 nm and the related dichroism (▲) after annealing the film for 15 h at 90 °C in dependence from the irradiation time and from the absorbed energy.

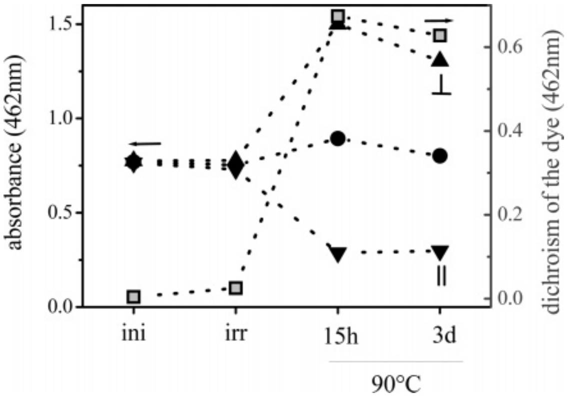


Figure 12. Development of the in-plane average absorbance[21] (●), absorbance perpendicular (▲) and parallel (▼) to the *E*-field vector, and the induced dichroism (■) after irradiation for 60 s with LP UV light and subsequent annealing of a TPgreen film, detected at the absorbance of the anthracene (462 nm).

When comparing the irradiated and the annealed films, the absorbance perpendicular to the electric field vector of light increases and the parallel to it decreases, resulting in a high value of anisotropy; however, the in-plane average absorbance[21] at 462 nm remains almost constant. This proves that variations are due to photoorientation and is not caused by the angular-dependent photodegradation. The high order parameter and the remaining in-plane average absorbance lead to the assumption that a significant in-plane alignment of the system took place. This result demonstrates once more that the photostability plays an important role to achieve a high dichroism in the plane of the film. Obviously, the films undergo stronger out-of-plane alignment or the anisotropy gets lost when nonmesomeric photoproducts disturb the thermal development of the order.

As seen in Figure 13, after the irradiation for 60 s the photoinduced dichroism of the azobenzene side group D_{367} amounts to 0.09. This value is 4 times larger compared to that of the anthracene side group (D_{462} = 0.02). It is obvious that the cooperative photoorientation of the large anthracene moiety in the glassy state is less efficient when compared to other dyes. However, after annealing in the nematic phase for 15 h the order parameter of the anthracene side group increases to D_{462} = 0.67. This value is larger than that of the azobenzene side group (D_{367} = 0.55). The amplification factor for the anthracene moiety is 33.5. However, it is not clear whether a low amount of angular-selective photooxidation products or photocycloadducts of the anthracene moiety contribute to the orientation process in addition

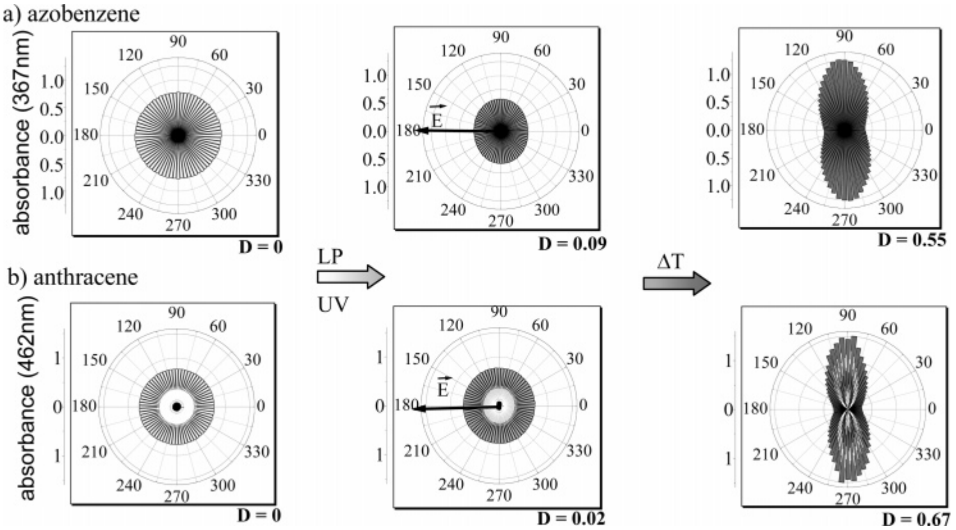


Figure 13. Angular-dependent absorbance in a virgin TPgreen film (left), induction of dichroism by irradiation at 365 nm for 60 s (middle), and amplification of the anisotropy by annealing at 90 °C for 15 h (right): (a) azobenzene side group at 367 nm; (b) anthracene side group at 462 nm.

to the photooriented azobenzene units. The effects are difficult to distinguish because all aligning forces of different opportunities could result in an alignment perpendicular to the *E* field vector.

Moreover, the anthracene moiety can be used to photo-cross-link the film, if the absorbance of this side group in the visible range is not of special interest. So, the [4 + 4] photocycloaddition reaction generated by nonpolarized vis irradiation could be connected with an interesting side effect, which could result in a stabilization of the photoinduced anisotropy.

IV. Conclusion

The study shows that spin-coated films of multifunctionalized LC polymers can be efficiently aligned due to a two-step procedure combining an initial photoorientation process in the glassy state of the film with the thermotropic self-organization by subsequent annealing within the liquid crystalline phase. This procedure results in anisotropic monodomain films of nematic and smectic polymers.

The investigated polymethacrylates contain photochromic azobenzene side groups, nonphotochromic but mesogenic benzanilide groups, and side groups with different dye moieties. So, polymers containing covalently bonded dye groups of the benzoxazole, anthracene, and stilbene type were synthesized, which differ concerning absorbance and emission. In this way different functions were introduced into the polymer. The photochromism of the azobenzene moiety allows the generation of anisotropy. The mesomorphism of the benzanilide side groups leads in combination with the rodlike structure of the other side groups to liquid crystalline properties, allowing the ordering of the polymer films by thermotropic self-organization. While these side groups act as light-driven and thermally stimulated compartments to generate anisotropy in the films, the third group can be the carrier of other functional properties, which becomes anisotropic as well. In the case of the dye-containing polymers dichroic films have been created up to a dichroism of 0.7. In this way, the developed method is suitable to generate highly dichroic films of different types of dyes in which a patternwise alignment in subpixels can be achieved.

The irradiation conditions were varied concerning wavelength and irradiation time or dose with respect to the limited photostability of the dyes and internal filter effects to achieve a high efficiency of the orientation process. The conventional excitation of the azobenzene at 488 nm generating the photoorientation process was only useful in the case of the benzoxazole-containing terpolymer. With respect to the absorption of other dye moieties at this wavelength the irradiation with linearly polarized UV light was applied. In this way a small anisotropy was photoinduced within the terpolymer films, whereas the photodegradation of the dyes can be neglected under the selected excitation conditions using short irradiation times.

The study demonstrates that a very small photoinduced anisotropy in the volume of the films is sufficient to align the polymer films by thermotropic self-organization. In the case of the extended anthracene chromophore containing polymer, a maximum amplification of the photoinduced order of 33.5, an amplification of 7.8 in the case of the stilbene, and 7.5 for the benzoxazole-containing polymer were found. Such a bulk photoalignment caused by a light-induced initializing process and followed by a thermal amplification step is of general interest for the information technology and material science.

The investigated polymer films differ with respect to the absorbance of the different dyes. The molecular dyes emit in spectral range of the blue, green, and red; however, in the films the fluorescence is completely quenched in the presence of the azobenzene groups. This is useful for the creation of dichroic absorptive films, which should not show any emission. A method to create films characterized by anisotropic emission of the same dyes will be presented in a forthcoming publication.

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(21) The in-plane average absorbance (A_{ip-av}) was calculated by the absorbancies parallel ($A_{\|}$) and perpendicular ($A_{\perp}$) to the *E* field vector in the oriented films using $A_{ip-av} = (A_{\|} + A_{\perp})/2$. In this way the loss of the in-plane absorbance upon annealing could be related directly to an increase of the out-of-plane orientation. This estimation is valid only under the assumption of an isotropic distribution of the initial films and the absence of aggregation effects in the film.

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(24) The error of the calculated dichroism is high because of the small absorbance parallel to the *E*-field vector after the two-step orientation process.

(25) The values are estimated, taking into account the influence of the changing of the nπ* absorbance by the E/Z isomerization of azobenzene. An increase of the absorbance at 452 nm for 0.025 in the steady state of photoisomerization of azobenzene was estimated from experiments with the terpolymer TPblue.

(26) The values are estimated taking into account the influence of the changing of the nπ* absorbance by the E/Z isomerization of azobenzene. An increase of the absorbance at 462 nm for 0.011 in the steady state of photoisomerization of azobenzene was estimated from experiments with the terpolymer TPblue.

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