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# Photoinduced Anisotropy in Spin-Coated Films of Chiral Smectic Copolymethacrylates Containing Azobenzene Side Groups

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Two copolymethacrylates containing the same phenyl benzoate side group but different azobenzene side groups were compared concerning their orientational behavior upon irradiation with linearly polarized (LP) light. Usually, the irradiation of azobenzene-containing copolymers with LP light at 488 nm results in the photoorientation of the azobenzene side group followed by the cooperative orientation of nonphotochromic side groups. The copolymethacrylates under investigation form stable optically isotropic IsoSm* phases at RT characterized by formation of a hidden layered liquid crystalline structure which is connected with the establishing of a helical superstructure. In this paper the competition between the establishment of the optically isotropic IsoSm* phase and the induction of anisotropy by LP light forcing a phase transition to a smectic structure will be discussed. The influence of the irradiation conditions, the thermal pre-history of the films, and the development of the order by annealing at 30 °C will be reported.

## I. Introduction

The defined preparation of anisotropic polymer films is a goal of great importance for various applications of functionalized polymers. The use of linearly polarized light offers a new approach to induce anisotropic properties in films of photochromic polymers. Different mechanisms have been found for the generation of anisotropy, of which the photoorientation process of azobenzene groups is one of the best studied. The process occurs via angular-dependent excitation of azobenzene moieties, a number of E/Z photoisomerization cycles, and rotational diffusion within the steady state of the photoreaction. In that way, the photochromic groups become oriented perpendicular to the electric field vector of the incident light in the glassy state of the polymers.[1−7]

Among the photochromic polymers, liquid crystalline (LC) side chain copolymers are of special interest distinguished by the cooperative orientation of the azobenzene groups and the nonphotochromic mesogenic side groups and the thermotropic ordering along the photoinduced order. This leads to increased values of optical anisotropy, and therefore in higher values of dichroism and birefringence, and results in a higher stability of the photoinduced order.[8−13] On the other hand, LC polymers appear generally (in bulk and in rather thick films, 2 $\mu$m or more) as turbid, scattering films with polydomain textures. Special efforts should be made therefore to convert them into transparent mono-domain films by external fields or mechanical stress. However, such mono-domain films possess an initial order which has be overcome by the photoorientation process.

In this connection, an unusual mesophase is of special interest that was reported for several chiral side chain homo- and copolymers.[14−16] The so-called "isotropic smectic" mesophase, IsoSm*, of those materials combines transparency and the lack of optical anisotropy with a hidden layered liquid crystalline structure and a helical superstructure. The structure suggested for the IsoSm* phase[17] should be similar to that of the twist grain boundary ($TGB_A$−) phase of chiral smectics[18,19] but has an extremely short pitch of the helical twist considerably less than the visible wavelength range (p ∼ 200−250 nm). In this way, the texture appears visually as amorphous, transparent, and optically isotropic, but nevertheless the polymers contain a short range order with distances in the range of 10−250 nm.

In this paper we report the induction of optical anisotropy in spin-coated films of two photochromic copolymers by irradiation with linearly polarized light. Both polymers form a IsoSm* phase but they are characterized by different kinetics of the formation of the mesophase. The paper is focused on the behavior of thin spin-coated films while the photoinduced dichroism generated in thicker films will be reported in a further publication.

## II. Experimental Section

The chemical structures of the studied copolymers are shown below. The polymers contain the same chiral mesogenic comonomer side group but different azobenzene comonomer units which are distinguished by the substitution in the para position. KW30 contains a *p*-methoxy group, while KM20 is substituted with a *p*-trifluromethoxy group. Note, that the number in the copolymer name indicates the content of the corresponding azobenzene comonomer units in mol %. So, KW30 contains 30% of the photochromic groups and KM20 only 20% (Figure 1). Furthermore, in the case of KM30 a decamethylene spacer and the azobenzene group are connected by a carboxyl group while the hexamethylene spacer of KM20 is connected via an ether group. The synthesis of both polymers has been reported elsewhere already.[20,21] So, the azobenzene group of KW30 is slightly push−pull substituted while the azobenzene of KM20 has an $-O-CF_3$ group in which the electronegativity of the fluorine atoms compensates for the

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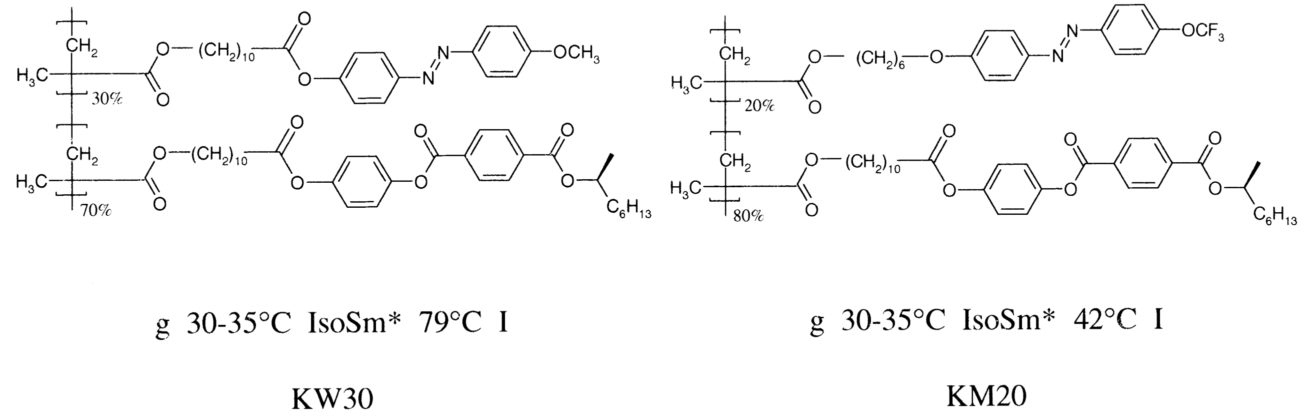


**Figure 1.** Formula of the investigated polymers.

drawing effect of the oxygen atom. This results in oppositely oriented dipole moments in both groups.

Upon cooling from the isotropic state, both polymers form the chiral smectic mesophase, IsoSm*, which is frozen in the glassy state of polymers on further cooling ($T_g \sim 30-35$ °C). The establishment of the mesophase differs drastically in both polymers. Thus, polymer KW30 forms the IsoSm* phase instantly at 72 °C; in this case the phase transition is thermodynamically controlled. In contrast, the same process is kinetically controlled in the case of KM20, and the complete formation of the IsoSm* phase takes up to 24 h, as illustrated by Figure 2a. Moreover, both transition temperature and transition enthalpy depend strongly on the annealing temperature (as shown in Figure 2b). It is well-known that the establishment of mesophases in the case of copolymers with differently long spacers requires more time. More details concerning the kinetically controlled phase transitions of KM20 are given in ref 21.

Thin polymer films were prepared by spin-coating on substrates made from quartz glass (SQ1) at 2000 rpm at 30 s using 0.085 wt % THF solutions of the polymers. The prepared films appeared transparent and nonbirefringent. The film thickness was between 320 and 450 nm. A film of 790 nm[22] was also investigated. The film thickness was measured by an alpha-stepper 200 profilometer (Tencor Instruments).

The anisotropy in the films was induced by the linearly polarized beam of an $Ar^+$ laser (Coherent, Innova 90-4) irradiating at $\lambda = 488$ nm with a power density of 100 mW $cm^{-2}$. A pretreatment of the films was carried out in order to sensitize the films by exposure to nonpolarized UV light ($\lambda = 365$ nm, 24 mW $cm^{-2}$ for 0.5 h).

The difference of the phase shift ($\Delta s$) was measured online using the beam of a He Ne laser during the $Ar^+$ laser irradiation.

The resultant birefringence was calculated from the phase retardation and the thickness of the film.

The angular-dependent UV/Vis absorbance spectra were measured by a XDAP Spectrometer (Polytec). The dichroism for the phenyl benzoate mesogenic groups, $D_{mes}$, and for azobenzene groups, $D_{azo}$, were calculated from the angular-dependent absorbance spectra at 250 nm and at 349 nm, corresponding to

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

where $A_\perp$ is the absorbance perpendicular and $A_\parallel$ is the absorbance parallel to the electric field vector of the incident light.

## III. Results and Discussion

**3.1. Absorbance Spectra of the Films.** The UV absorbance spectra of the copolymer films and chloroform solutions are compared in Figure 3. Each spectrum is composed by the overlapping of the transitions of the different 4,4'-disubstituted azobenzene groups and of the 4,4'-disubstituted phenyl benzoate group. The absorption band at 350 nm relates to the $\pi-\pi^*$ transition of both azobenzene moieties and the weak absorption band about 450 nm corresponds to the n-$\pi^*$ transition band of the azobenzene groups. The maxima of absorbance of the phenyl benzoate unit are at 270 and 230 nm, which overlap with the $\phi-\phi^*$ absorption of the azobenzene moiety. The higher phenyl

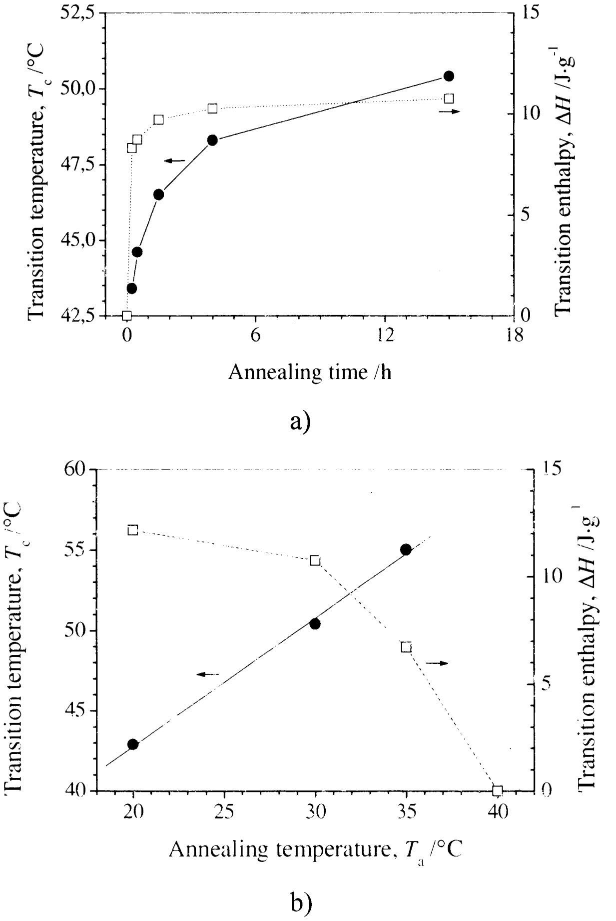


**Figure 2.** Transition temperature, $T_c$, and transition enthalpy, $\Delta H$, of a KM20 sample: (a) annealed at 20 °C, versus the annealing time; (b) annealed for 24 h, versus the annealing temperature, $T_a$. The lines shall guide the eyes only.

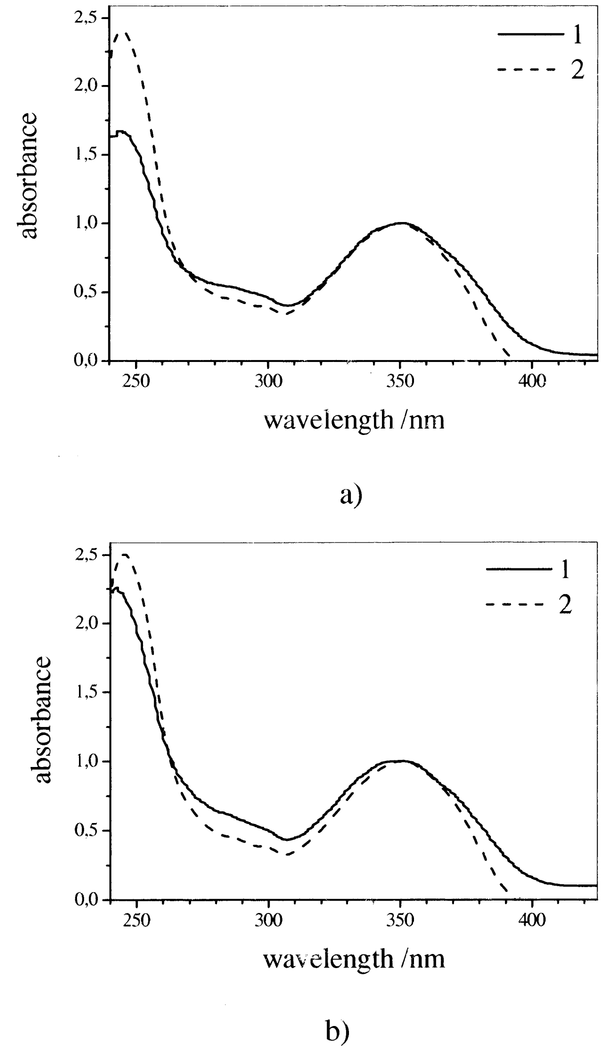


**Figure 3.** UV absorbance spectra of spin-coated films (1) and chloroform solutions (2) of copolymers KW30 (a) and KM20 (b).

benzoate content of KM20 causes the stronger absorbance at 250 nm. In contrast to the $\pi-\pi^*$ transition, the $\phi-\phi^*$ transition of the aromatic cores is not polarized along the long axis. So, the absorbance at 250 nm results from the angle-independent $\phi-\phi^*$ absorption of both aromatic cores and the angle-dependent $\pi-\pi^*$ transition of the ester.

As seen from Figure 3a, the shape of the UV spectra of the KM20 film and solution are similar, whereas the absorbance of the KW30 film at 250 nm is reduced by 36% compared with the solution (Figure 3b). This behavior should be caused by the stronger and faster self-ordering tendency forming the IsoSm* phase in films of KW30 at room temperature indicating an increase of the in-plane alignment of the azobenzene side group. The results are in accordance with the difference of the thermal behavior between both polymers as described in Section II.[23]

**3.2. Photoorientation in the Copolymer Films.** The irradiation at $\lambda = 488$ nm with linearly polarized light excites the n-$\pi^*$ transition of the azobenzene chromophores; the subsequent photoisomerization at this wavelength is characterized by a steady state with a small amount of Z-isomers. The excitation is angular dependent, so the repetitive E/Z isomerizations result in the appearance of both birefringence and dichroism in the spin-coated films of KW30 and KM20. We discuss the former polymer first, since the establishment of its mesophase at ambient temperature is not affected by the thermal prehistory of the film and therefore its behavior is less influenced by temperature changes due to light absorption.

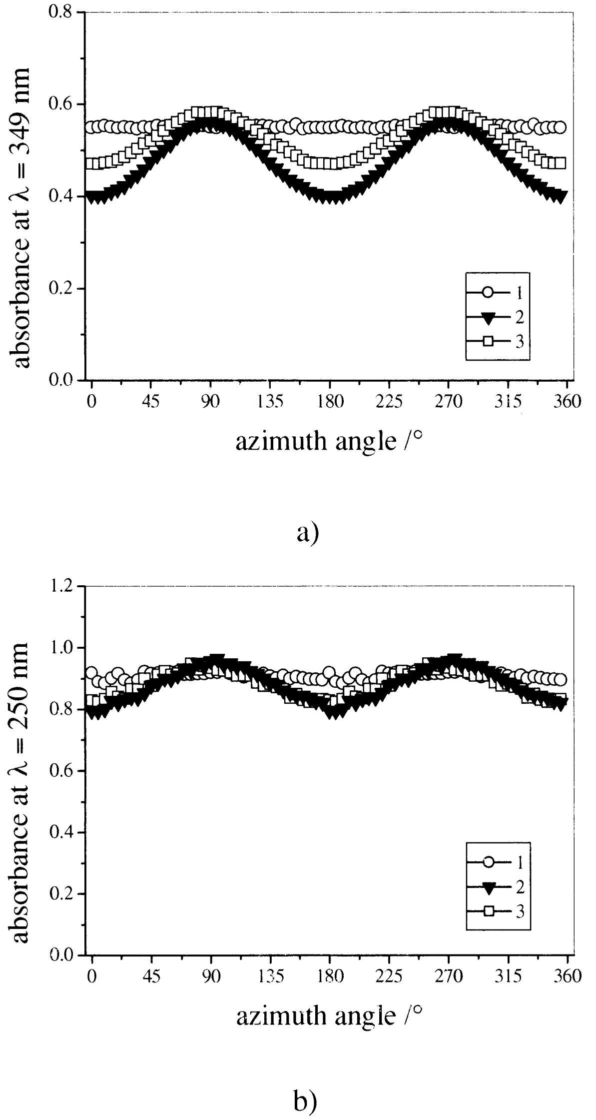


**Figure 4.** Absorbance of KW30 film at 349 nm (a) and at 250 nm (b) versus the film rotation angle: 1, virgin film; 2, irradiated for 5 h at 488 nm; 3, the same, kept after storage for 3 days at room temperature.

*Photoorientation of KW30 Films.* The angular-dependent absorbance of a KW30 film at 349 and 250 nm is presented in Figure 4. The first wavelength corresponds to the photochromic azobenzene moiety (a) and the second one to the mesogenic phenyl benzoate group (b). As seen from Figure 4, the virgin film does not show any angular dependence of absorbance. That means that here exists no macroscopic order at all. However, the irradiation with linearly polarized light for 5 h causes an orientation of the azobenzene groups resulting in a dichroism of about $D_{\mathrm{azo}} = 0.17$. If the anisotropy of the mesogenic side group is calculated in the same way, a value of about $D_{\mathrm{mes}} = 0.1$ is found. It demonstrates qualitatively the cooperativity of the orientation process. With respect to the spectral overlapping of the different transitions, the dichroism of this moiety cannot be estimated in a quantitative way and compared with that of the azobenzene group, because the absorbance contains an angle-independent component. The dichroism values of all the experiments are summarized in Table 1.

After storage for 3 days the $D_{\mathrm{azo}}$ value is reduced by 41% (Table 1), and it is changed to $D_{\mathrm{azo}} = 0.036$ after 4 months. The low stability of the photoinduced order can be related to

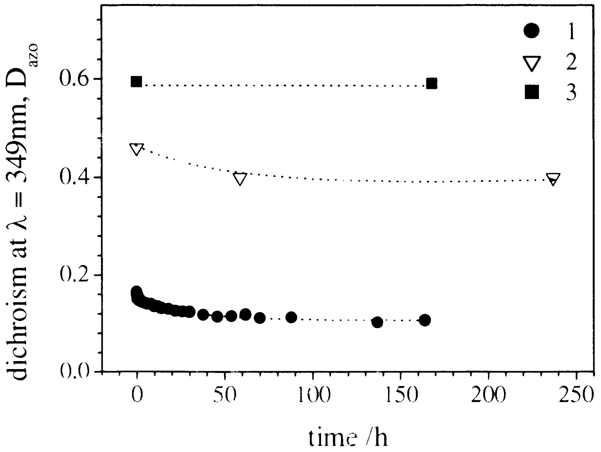


**Figure 5.** Dichroism of photoinduced order of the photochromic groups, $D_{azo}$, induced in KW30 film of different history and its evolution with time at 30 °C: 1, virgin film; 2, film with UV pretreatment; 3, thermally assisted photoorientation. The lines shall guide the eyes only.

**TABLE 1: Values of Photo-induced Birefringence, $\Delta n_{ind}$, and Corresponding Dichroism Values of the Photochromic Group, $D_{azo}$, of the Polymer Films with Different History upon Irradiation with Ar$^+$ Laser (488 nm, 100 mW cm$^{-2}$, 5 h)**

| | KW30 | | | KM20 | | |
|---|---|---|---|---|---|---|
| | irradiated for 5 h | | kept 3 days at 30 °C | irradiated for 5 h | | kept 3 days at 30 °C |
| | $\Delta n_{ind}$ | $D_{azo}$ | $D_{azo}$ | $\Delta n_{ind}$ | $D_{azo}$ | $D_{azo}$ |
| virgin film | [a] | 0.17 | 0.1 | [a] | 0.27 | 0.40 |
| UV-sensibilized | [a] | 0.46 | 0.40 | 0.045 | 0.25 | 0.30 |
| irradiation during the cooling | 0.094 | 0.59 | 0.59 | 0.046 | 0.24 | 0.29 |
| freshly molten film | [a] | [a] | [a] | [a] | 0.26 | 0.30 |

[a] Not detected.

the elasticity of the main chain which accommodates to the highly twisted TGB-like structure. Being frozen in the glassy state, the conformation of the main chain would resist the photoorientation trying to turn the pendant groups back to their initial (undisturbed) positions.

It has been shown earlier that the intermediate UV irradiation of ordered films, in which the polymers undergo any aggregation or other self-organization process, can increase considerably the efficiency of the photoorientation process upon subsequent exposure with linearly polarized visible light.[24,25] This type of activation is caused by the destruction of the ordered domains caused by E/Z isomerization of the azobenzene. A photoinduced order can obtained, if a linearly polarized Vis irradiation is carried out before the self-organization starts again. In good agreement with that, the experiments of the KW30 films show that the UV pretreatment immediately followed by a linearly polarized irradiation at 488 nm results in much higher photoinduced anisotropy ($D_{azo} = 0.46$) as compared to the virgin film (Figure 5). The degree of order achieved is almost 5 times higher. The higher absolute value of anisotropy results in higher stability of the anisotropy, too: the loss is only 13% in 10 days.

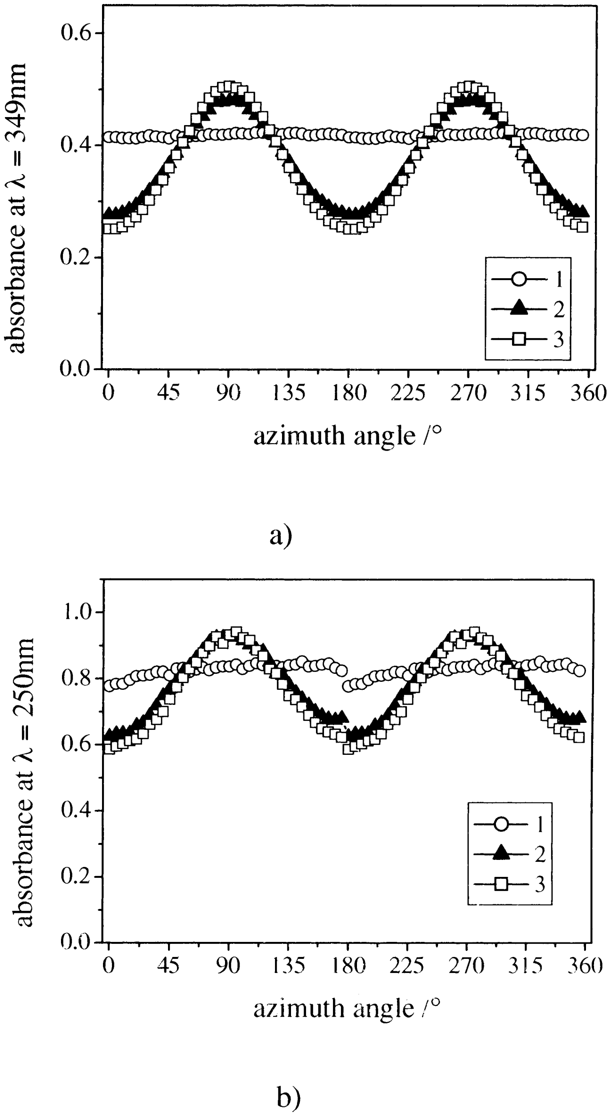
A further interesting case is the photoorientation during the phase transition (curve 3 in Figure 5). The experiment was carried out irradiating a film with linearly polarized light for 6 h in a nonisothermal way, in which the starting temperature was above the phase transition (at 80 °C) cooling to room temperature. The generated dichroism was as high as $D_{azo} = 0.59$. Such a high orientational order can be assigned to a photoinduced order of nematic and smectic polymers. For this reason we suggest that an order is established which is far from the IsoSm* structure. Photoorientation should result in an oblate or biaxial order of the film overcoming the helical or other substructure with its macroscopically isotropic properties. The orientation obtained by this process is surprisingly stable, showing only a small decrease of about 0.6% within 9 months when kept at room temperature. The film shows the cooperative orientation of the phenyl benzoate group as well resulting in a dichroism of $D_{mes} = 0.29$, which remains constant after 9 months of annealing, too.

To summarize this section, the nonactivated KW30 film is characterized by the well-established and stable IsoSm* phase, which restricts the photoorientation process. Moreover, the strong ordering tendency of the polymer to establish the IsoSm* phase results in a fast relaxation of the films photooriented at room temperature having only a comparably small anisotropy. However, the activation of the films by irradiation with UV light as photochemical pretreatment or the thermally assisted photoorientation results in much higher values of anisotropy compared to the LP vis irradiation "of virgin films" linearly polarized Vis irradiation. As a result of both pretreatments, the initial order of the film and the IsoSm* ordering tendency is overcome and a higher mobility is established. In the case of the photochemical pretreatment, this is caused by the formation of a high content of more polar and crooked Z isomers, which modify the intermolecular interaction decreasing the ordering tendency. In the case of the thermal pretreatment, a similar effect is caused by the temperature dependence of the intermolecular interactions. In both cases, the photoorientation from a macroscopically or a microscopically isotropic sample results in much higher dichroism values. Moreover, the total values of anisotropy indicate that starting from the light-induced order a uniaxial order of the system is established which is long-term stable below $T_g$. The orientation created by such a thermo- or UV-assisted photoorientation process can be kept for years. It should be noted that heating above the phase transition of 79 °C erases any orientational order, and the film is capable of a further new photoorientation process.

All the effects—the restriction and the drastic enhancement of the photoinduced order with the increasing stability—can be explained by the competition and/or the combination of light-induced orientation and the self-organization of the LC polymer.

*Photoorientation of KM20 Films.* The main difference between the similar copolymers KW30 and KM20 is the time that is required for the formation of the IsoSm* mesophase. The process is very fast for KW30 but takes substantial time (up to 24 h) in the case of KM20. The conclusion of our recent publication[21] was that while the establishment of the IsoSm* order in KW30 films is thermodynamically controlled, in the case of KM20 this should be kinetically governed.

The angular-dependent absorbances of a KM20 film at 349 and 250 nm are presented in Figure 6a and 6b, as discussed, those wavelengths correspond to the maximum of the azobenzene moiety and to that of the phenyl benzoate group together with the $\phi-\phi^*$ transition of the azobenzene, respectively. The corresponding values of the photoinduced dichroism, $D_{azo}$, are summarized in Table 1 along with the photoinduced birefringence, $\Delta n_{ind}$. As seen from Figure 6 and from Table 1, the virgin KM20 film is isotropic and allows the photogeneration of a considerably higher order ($D = 0.27$), as compared with KW30. Such an enhancement should be caused by the fact that restricting forces to the photoorientation process do not exist in the initial KM20 or they are much smaller compared to



a)

b)

**Figure 6.** Angular-dependent absorbance of KM20 films at 349 nm (a) and at 250 nm (b) versus: 1, virgin film; 2, irradiated at 488 nm for 5 h; 3, the same film after storage for 3 days at 23−30 °C.

KW30. This agrees well with the conclusion made above in Section 3.1 on the stronger self-ordering tendency for the latter polymer, which reveals itself also in the instant establishment of the IsoSm* phase instead of a slow, kinetically governed process as for KM20.

As illustrated in Figure 7 (curve 1), the storage of the film at 30 °C after the irradiation procedure results in a remarkable increase of the order of up to $D = 0.4$. This is in the same value of order as obtained for the UV-sensitized film of KW30. Interesting is the fact that the annealing at 30 °C does not develop the macroscopically isotropic IsoSm* structure, but results in the amplification of the photoinduced anisotropy of the film. The effect of such post-orientation of the anisotropy at 30 °C is caused by the self-organization of the polymer. A similar behavior was found for smectic polymers upon annealing in the LC phase.[26−28]

It is worth noticing that the amplification of the photoinduced order by the self-organization depends on the irradiation condition. Thus, the irradiation of the film in intervals smaller than 30 min but in total for 5 h results in a comparable order of about $D_{azo} = 0.29$. However, this order is unstable, and disappears after 4 days at ambient temperature. Moreover, the irradiation for 1 h up to 50% of the saturation value, $D_{azo} = 0.15$, produces an order which cannot be amplified by self-organization: the dichroism grows up to only $D_{azo} = 0.17$ after 3 days. Furthermore, if such a film is irradiated at 30 °C, it does not show any photoorientation effect at all. This temperature is close to $T_g$ and $T_c$. The behavior can be explained by local heating in the surrounding of the azobenzene moieties close to the transition point at 42 °C.

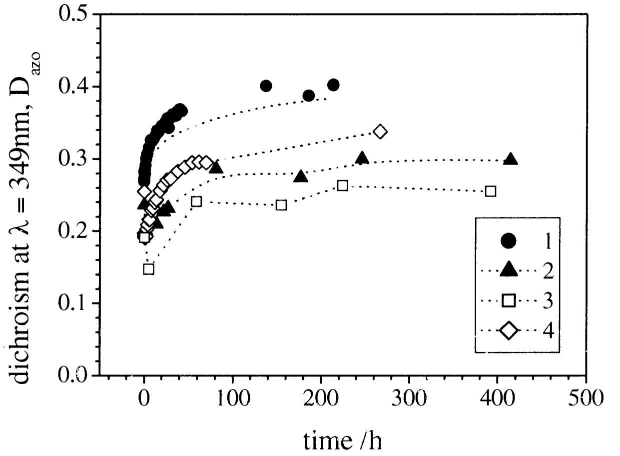


**Figure 7.** Growth of $D_{azo}$ in KM20 films of different history caused by keeping in darkness after irradiation procedure (23−30 °C): 1, virgin film; 2, film after UV pretreatment; 3, film irradiated during the cooling; 4, filmwhich was heated to 95 °C for 15 min and quenched to room temperature.

The behavior shows that there is a certain threshold of the photoinduced order with respect to the competition between self-organization of the optically isotropic IsoSm* phase and the amplification of the photoinduced order.

In contrast to KW30, an intermediate UV preirradiation of the film does not result in higher values of anisotropy. In all cases, similar values of order are photoinduced by the subsequent UV and linearly polarized Vis irradiation compared to the irradiation of the virgin films (curve 2 in Figure 7), i.e., the effect of the sensitization does not occur. Since there is no restricting LC order, the UV step has no influence. The amplification of the photoinduced order by self-organization in that case is not so clearly pronounced but comparable to that one of the irradiated virgin film.

Furthermore, the thermo-assisted photorecording during cooling shows an unusual nonmonotonic evolution of the $D_{azo}$ value upon subsequent annealing in the darkness (Figure 7, curve 3): the degree of order reaches a minimum after 30−120 min of annealing but after that it grows steadily up to the starting value and even higher. The same behavior shows a freshly molten KM20 film, where the kinetically governed formation of the mesophase occurs at isothermal conditions (curve 4). We should note here that similar nonlinear behavior after switching off the irradiation (fast decrease followed by slow but remarkable increase) has been observed for the diffraction efficiency of holographic gratings recorded in ~30 $\mu$m thick films of a similar copolymer with higher concentration of azobenzene moieties, KM45.[29]

Such a nonmonotonic evolution of the photoinduced order should probably relate to a fast formation of the IsoSm* phase at higher temperatures resulting in a competition of the establishment of the system immanent LC order by self-organization and the amplification of the photoinduced order during irradiation and/or annealing, respectively. The established order strictly depends on which of both processes dominates under the irradiation conditions and the pre-history of the sample resulting either in a twisted layered structure or in macroscopically ordered films governed by the photoorientation process. The influence of interface conditions which seems to be of great importance for such thin films should be also taken into account. But a detailed explanation would require further investigations.

## IV. Conclusions

Spin-coated thin films of the studied photochromic, liquid crystalline copolymers with chiral moieties, KW30 and KM20, are optically isotropic. Irradiation with linearly polarized green light ($\lambda = 488$ nm) results in the induction of optical anisotropy. In the case of KW30, which establishes quite easily the chiral smectic order, the LC order restricts the induction of anisotropy. However, both film sensitization with UV light and the thermo-assisted recording result in a remarkable enhancement of the generation of anisotropy by photoorientation leading to values of the photoinduced dichroism of up to $D_{\mathrm{azo}} = 0.6$.

In contrast, the virgin films of KM20 which is characterized by a kinetically hidden formation of the IsoSm* phase, show already a high sensitivity to the photoorientation process compared to KW30. In the case of the second polymer, an intermediate UV irradiation, thermal shocking of the films, or irradiation of the films during the cooling process do not result in a higher photoinduced order.

The evolution of the photoinduced order in the LC copolymers depends on many poorly controlled factors, as, e.g., heat dissipation, film thickness, history of the sample, etc. The study shows that even in the case of IsoSm* polymers with microscopically ordered domains the competition of photoorientation and self-organization has to be considered. It can result in a restriction and/or an amplification of the light-induced ordering process depending on the irradiation conditions, the history of the films, and the ordering tendency of the polymers.

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## References and Notes

(1) *Applied Photochromic Polymer Systems*; McArdle, C. B., Ed.; Blackie & Son Ltd.: New York, 1992

(2) Läsker, L.; Stumpe, J.; Fischer, Th.; Kostromin, S.; Ivanov, S.; Shibaev, V.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *253* (1) 293.

(3) Stumpe, J.; Läsker, L.; Fischer, Th.; Rutloh, M.; Kostromin, S.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 371.

(4) Shibaev, V. P.; Kostromin, S. G.; Ivanov, S. A. Comb-Shaped Polymers with Mesogenic Side Groups as Electro- and Photooptical Active Media. In *Polymers as Electrooptical and Photooptical Active Media*; Shibaev, V. P., Ed.; Springer-Verlag: New York, 1996.

(5) Natansohn, A.; Rochon, P.; Meng, X.; Barrett, C.; Buffeteau, T.; Bonenfant, S.; Pézolet, M. *Macromolecules* **1998**, *31*, 1155.

(6) Rasmussen, P. H.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 4738.

(7) Fischer, Th.; Stumpe, J.; Läsker, L.; Kostromin, S. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 453.

(8) Shibaev, V. P. *Mol. Cryst. Liq. Cryst.* **1994**, *243*, 201.

(9) Stumpe, J.; Läsker, L.; Fischer, Th.; Kostromin, S.; Ruhmann, R. *Thin Solid Films* **1996**, *284*, 252.

(10) Fischer, Th.; Läsker, L.; Rutloh, M.; Czapla, S.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *299*, 293.

(11) Fukuda, T.; Matsuda, H.; Shiraga, T.; Kimura, T.; Kato, M.; Wiswanathan, N. K.; Kumar, J.; Tripathy, S. K. *Macromolecules* **2000**, *33*, 4220.

(12) Han, M.; Morino, S.; Ichimura, K. *Macromolecules* **2000**, *33*, 6360.

(13) Kozlovsky, M. V.; Blinov, L. M.; Haase, W. Chiral Polymers with Photoaffected Phase Behavior for Optical Data Storage. In *Photoreactive organic thin films*; Sekkat, Z., Knoll, W., Eds.; Academic Press: New York, 2002; pp 145−177.

(14) Bata, L.; Fodor-Csorba, K.; Szabon, J.; Kozlovsky, M. V.; Holly, S. *Ferroelectrics* **1991**, *122*, 149.

(15) Kozlovsky, M. V.; Haase, W.; Kuball, H.-G. In *6th European Conference on Liquid Crystals, March 25−30, 2001, Halle (Saale), Germany*; Abstracts, 5-P14

(16) Kozlovsky, M. V.; Haase, W.; Stakhanov, A.; Shibaev, V. P. *Mol. Cryst. Liq. Cryst.* **1998**, *321*, 177.

(17) Demikhov, E.; Kozlovsky, M. V. *Liquid Crystals* **1995**, *18*, 911.

(18) Goodby, J. W.; Waugh, M. A.; Stein, S. M.; Chin, E.; Pindak, R.; Patel, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 8119.

(19) Kitzerow, H. Twist Grain Boundary Phases. In *Chirality in Liquid Crystals*; Bahr, C., Kitzerow, H., Eds.; Springer-Verlag: New York, 2000; p 297.

(20) Kozlovsky, M. V.; Haase, W. *Macromol. Symp.* **1999**, *137*, 47.

(21) Kozlovsky, M. V.; Meier, J. G.; Stumpe, J. *Macromol. Chem. Phys.* **2000**, *201*, 2377.

(22) The photochemistry and the thermal behavior of a 790 nm thick film of KM20 show the same trends as observed in the case of the thinner films of KM20, so that an influence of the film thickness with respect to the described behavior in KM20 films can be neglected.

(23) The spin-coated films were stored at least for 1 day at RT in order to evaporate the solvent from the films. In the case of KW30, this results already in the formation of the IsoSm* phase. As described above, the formation of the IsoSm* phase needs up to 24 h in the case of KM20. The comparison of the thin spin-coated film and the solvent spectra indicates that the IsoSm* phase is not completely formed even after this time.

(24) Blinov, L. M.; Gipparone, G.; Kozlovsky, M. V.; Lazarev, V. V.; Scaramuzza, N. *Opt. Commun.* **2000**, *73*, 137.

(25) Zebger, I.; Rutloh, M.; Hoffmann, U.; Stumpe, J.; Siesler, H. W.; Hvilsted, S. *J. Phys. Chem. A* **2002**, *106*, 3454.

(26) Fischer, Th.; Läsker, L.; Czapla, S.; Rübner, J.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *298*, 213.

(27) Stumpe, J.; Fischer, Th.; Rutloh, M.; Rosenhauer, R.; Meier, J. G. *Proc. SPIE Liquid Crystals III* **1999**, *3800*, 150.

(28) Rosenhauer, R.; Fischer, Th.; Czapla, S.; Stumpe, J.; Vinuales, A.; Pinol, M.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **2001**, *364*, 295.

(29) Podgornov, F.; Kozlovsky, M. V.; Haase, W.; Lazarev, V. In *MRS 2001 Fall Meeting, November 26−30, Boston, MA*; Abstracts, CC5.17.