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T. Fischer [a] , L. Läsker [a] , M. Rutloh [a] , S. Czapla [b] & J. Stumpe [a]

[a] Humboldt University, Institute of Chemistry, Erieseering 42, 10319, Berlin

[b] Technical University Berlin, Inst. of Technical Chemistry, Germany

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COMPETITION OF SELF-ORGANIZATION AND PHOTO-ORIENTATION IN LIQUID CRYSTALLINE POLYMERS

THOMAS FISCHER, LUTZ LÄSKER, MICHAEL RUTLOH,
SYLVIA CZAPLA* AND JOACHIM STUMPE#
Humboldt University, Institute of Chemistry, Erieseering 42, 10319 Berlin
*Technical University Berlin, Inst. of Technical Chemistry, Germany

Abstract Photoreorientation processes in photochromic LCP's are dependent on the supramolecular order. The efficiency is much higher in films of low order, which have been obtained by a suitable preparation or by an intermediate photochemical decoupling. On the other hand, a photochemically induced order in an initially isotropic film acts as initializing force, governing the direction of thermotropic self-organization. The combination of both ordering principles causes a significant amplification of the light-induced optical anisotropy.

INTRODUCTION

Photochromic liquid crystalline polymers (PLCP) are very promising for optical data storage because their optical properties may be changed by the photochemically induced variation of their supramolecular order[1]. The use of linearly polarized light offers a new way to orient moieties and in this way to modify optical anisotropy by photoorientation. Irradiation of polymer films containing azobenzene moieties causes a directed reorientation of rod-like side groups towards a direction perpendicular to the electric field vector of the incident light. In this way an optical axis is generated in the glassy state of initially isotropic films or rotated in aligned films. We have shown that this process occurs in differently ordered and amorphous polymer films[2-6]. In this paper the sophisticated relationship between the self-ordering and photoorientation will be discussed.

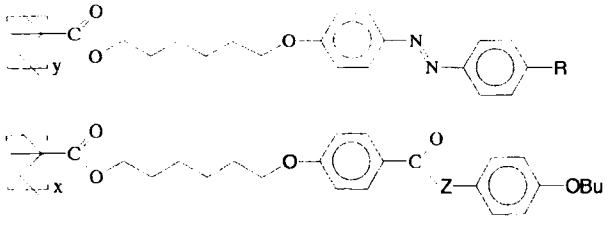
POLYMERS AND METHODS

Aligned films of the polymers have been prepared by filling their isotropic melts into cells designed for planar alignment of LC's (d=2μm) and subsequent slow cooling. Isotropic films have been prepared by spincoating from THF solutions (d=0.2μm). VIS irradiation was carried out with the linearly polarized beam of an Ar laser (λ=488nm). If not otherwise stated the time of irradiation was 1h with a power density P=200mW/cm^2 and a polarization of 45° with respect to the initial director of the LCP. The UV

Author to whom correspondence should be addressed

exposure was non-polarized (λ=365nm, P=0.7mW/cm^2, t=3600s). The in-plane anisotropy was examined by polarized spectroscopy. From the dichroic ratio R at a certain wavelength λ, the spectroscopic degree of order, $S_{sp,\lambda}=(R-1)/(R+2)$ was calculated. Moreover, the difference in optical path length, $\Gamma=\Delta n^*d$, was measured using an Ehringhaus compensator.

TABLE 1 Composition and properties of the studied polymers



Polymer	y	Z	R	T_g/°C	T_{lc}/°C	ΣΔH/Jg^{-1}	M_n/10^{3}gmol^{-1}
P1/50	0.50	-O-	-OBu	46	s_A 125 i	11.2	60
P2/10	0.10	-NH-	-CN	63	s_A 166 i	9.5	73
P2/25	0.25	-NH-	-CN	56	s_A 169 i	9.0	61
P2/50	0.50	-NH-	-CN	52	s_A 168 i	6.1	59
P2/75	0.75	-NH-	-CN	51	s_A 162 i	4.6	52
P2/90	0.90	-NH-	-CN	48	s_A 162 i	4.4	42
P2/100	1.00	-	-CN	51	s_A 166 i	6.0	17
P3/50	0.50	-NH-	-Ph	84	s_A 172 i	12,79	46

RESULTS

Films of different order have been irradiated with linearly polarized VIS light for 1 hour. Saturation has been achieved after this time for the studied light-induced processes.

Reorientation of aligned films

The effect of linearly polarized VIS irradiation on aligned films of P1/50 ($S_{sp,410}$=0.67) depends strongly on the power density. For P≤200mW/cm^2 no modification of the orientational order could be observed by polarized spectroscopy. A slight re-alignment took place at 400mW and at P=800mW/cm^2 the director is reoriented by about 30°, i.e. the re-alignment is not complete (Figure 1). The order is decreased in all cases. This modification is stronger at higher values of P ($S_{sp,410}$=0.43 at P=800mW/cm^2).

A slightly different behaviour is observed by refractive measurements. Table 2 shows the optical path length difference of the final states of VIS irradiation measured along the expected new axis, Γ_{fin}, related to Γ_{init}, the values of the initial state along the axis of the aligned film. It can be seen that a weak reorientation has taken place at low power

densities although it could not be detected by spectroscopy. The ratio is a measure for the efficiency of the photoorientation. $\Gamma_{fin}=\Gamma_{init}$ holds in case of a photoinduced rotation of the director by 45° and an unchanged degree of order. Deviations are caused by both aspects, a director reorientation by a smaller angle and a decreased degree of order.

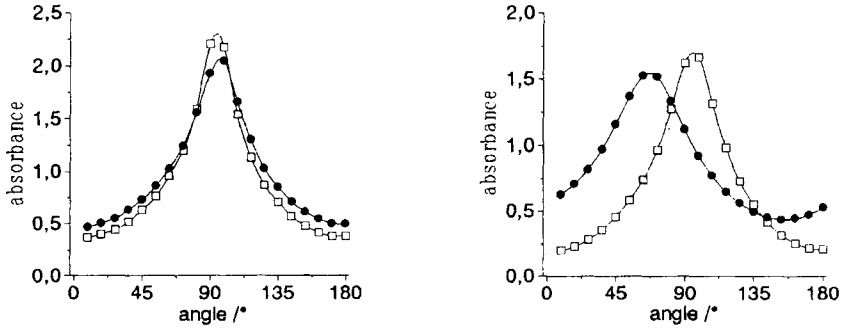


FIGURE 1 Angular-dependent absorbance (410nm) of P1/50 before (-□-) and after (-●-) VIS irradiation at 200 and 800mW/cm^2 (E vector 135°).

TABLE 2 Modification of optical anisotropy by irradiation of an aligned film of P1/50 with different power densities

P [mW/cm^2]	100	200	400	800
$\Gamma_{fin}/\Gamma_{init}$	0.093	0.21	0.23	0.64

It has to be noted that once the films were irradiated, there was no longer any "dark position" between crossed polarizers, i.e. the system is not longer uniaxial. Obviously the high initial order is strong enough to be kept partially even on irradiation with a comparatively high power density. To overcome these strong intermolecular interactions, the actual order of the films was decreased in different ways.

Photochemically Induced Disturbance

An identical film was exposured to non-polarized UV light before VIS irradiation. A photostationary equilibrium of the E⇌Z isomerization with a high proportion of the more crooked Z isomer is established destroying the liquid crystalline order.

The absorbance at 410nm is decreased by the photoreaction and its angular distribution is completely isotropic. Already one second of VIS irradiation establishes a new steady state of the photoreaction with a majority of E isomers. The absorbance averaged over all angles is approximately the same as in the initial state. The angular distribution is still isotropic at this stage. On continued irradiation a new orientational order of the azobenzene moieties is easily established . It is perpendicular to the electric vector of the actinic light. The spectroscopic degree of order in the final state ($S_{sp,410}=0.51$) is still

lower than that of the initial film which was aligned by surface interaction but it is significantly higher than that obtained without additional UV exposure (Figure 2a).

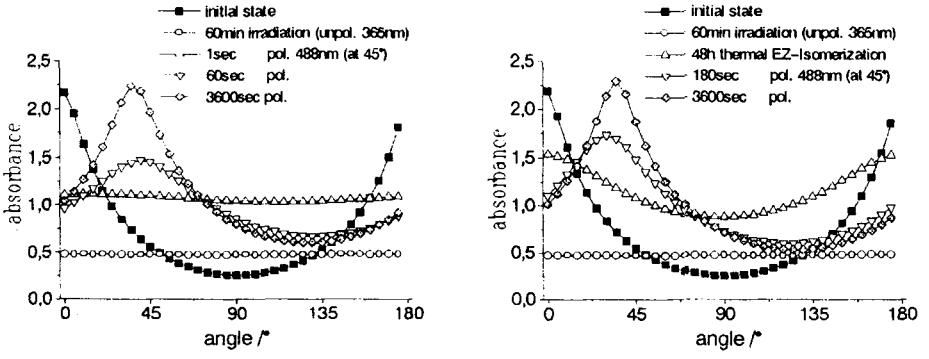


FIGURE 2 Photoorientation by VIS irradiation after photochemically induced disordering of aligned films of P1/50; a: immediately after UV exposure b: after UV exposure and thermal Z–E isomerization

Figure 2b demonstrates that the easier reorientation is actually caused by a decreased order rather than by a high concentration of Z isomers: In this experiment the azobenzene moieties were allowed to relax back to the E isomers thermally (48 hrs., 25°C). As a result of this process the initial direction of the orientational order is rebuilt. However, the degree of order which can be achieved in the glassy state ($S_{sp,410}$=0.18) is much lower as that after annealing in the viscous–elastic state. The irradiation of such weakly ordered system results in a re–alignment within a comparable time and yielding a comparable order as in the case of VIS irradiation immediately after UV exposure.

Disturbance by thermal treatment

Another attempt was aimed to get a thick isotropic film by cooling the sample quickly from the isotropic melt into the glassy state. Earlier we used this procedure successfully for different series of LCP's[2,3,5]. In the present case, however, a scattering polydomain structure was obtained because of the strong tendency of the polymers to establish LC phases. But it could be transformed into a non–scattering, isotropic film by UV exposure. These properties were maintained even after thermal Z–E isomerization. Subsequent polarized VIS irradiation generates the new orientational order within the same time and with the same order as in the experiments shown in Figure 2.

Spincoated films

Isotropic, non–scattering thin films may be prepared by spincoating. Figure 3a shows the isotropic orientational distribution of the azobenzene and benzanilide side groups of a film of P1/25 as detected by polarized UV/Vis spectroscopy. The π–π^* transitions of

the azobenzene (365nm) and the benzanilide chromophores (280nm) are polarized along the long molecular axises. In the shorter wavelength region, both aromatic system have some other transitions with deviating directions of the transition moment which contribute to the absorbance. On VIS irradiation an orientation perpendicular to the electric vector of the actinic light is generated with $S_{sp,365}$=0.18 and $S_{sp,280}$=0.23 (Figure 3b). This shows clearly that not only the photochromic moieties but all rod-like side groups of the copolymer have been aligned by photoorientation.

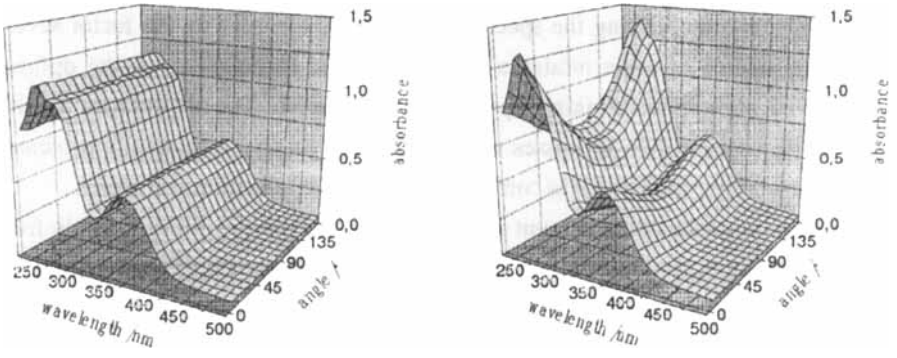


FIGURE 3 Polarized UV/Vis-spectra of a spincoated film of P2/25 before (left) and after (right) VIS irradiation

Co-operativity and Amplification

To study the co-operative effect in more detail, spincoated films of the **P2** polymers with different content of azobenzene moieties have been aligned by polarized VIS irradiation in the glassy state. The resulting spectroscopic degrees of order shown in the left part of table 3 suggest a high co-operativity of the process. $S_{sp,365}$ increases with the azobenzene content up to 50% and is almost constant at higher concentrations. Obviously a more ordered molecular environment stabilizes the orientational order of the photochromic groups. The relation $S_{sp,365}<S_{sp,280}$ for 10% and 25% azobenzene side

TABLE 3 Spectroscopic degree of order induced by VIS irradiation and subsequent annealing of spincoated films of P2 polymers

y(azobenzene)	irradiated		annealed	
	$S_{sp,365}$	$S_{sp,280}$	$S_{sp,365}$	$S_{sp,280}$
0.10	0,039	0,042	0,12	0.28
0.25	0,18	0,23	0,61	0.51
0.50	0,37	0,34	0,56	0.41
0.75	0,32	0,31	0,47	0.41
0.90	0,38	0,32	0,57	0.44
1.00	0,40	0,33	0,46	0.39

groups is turned with increasing azobenzene concentrations because the contribution of transitions with moments deviating from the long molecular axis to the absorbance at 280nm becomes more dominant in comparison to that of the benzanilide chromophore.

After irradiation the films have been annealed 20 K above T_g for 3 days. In all cases the photoinduced orientational direction was maintained and the spectroscopic degree of order was significantly increased. The smaller the content of photochromic groups, the stronger is the relative increase of anisotropy by this procedure. Thus, 10% are sufficient to force the thermotropic self-organization in the direction controlled by the polarization of the light and amplifying the spectroscopic degree of order by the factor seven. With 25% the degree of order attains a maximum. This polymer shows the optimal combination of photoinduced anisotropy and LC potential. The importance of this potential for photoorientation processes was stressed previously.[5] The results presented here confirm our suggestion that it is correlated to the phase transition enthalpies.

To study the influence of the amount of photoinduced anisotropy independently from the chemical structure, the VIS irradiation of 4 spincoated films of **P3/50** was stopped at different stages of the photoorientation process (Figure 4a). The photoinduced order was amplified by annealing at 104°C for 3 days. Figure 4b demonstrates that the strongest amplification has taken place when only 16% of the saturation value were photoinduced. An order parameter as high as 0.81 has been achieved by annealing when 50% of the saturation value were photoinduced, whereas the weak amplification after the saturated photoinduction has resulted only in value of 0.64, a fact which is under further investigation.

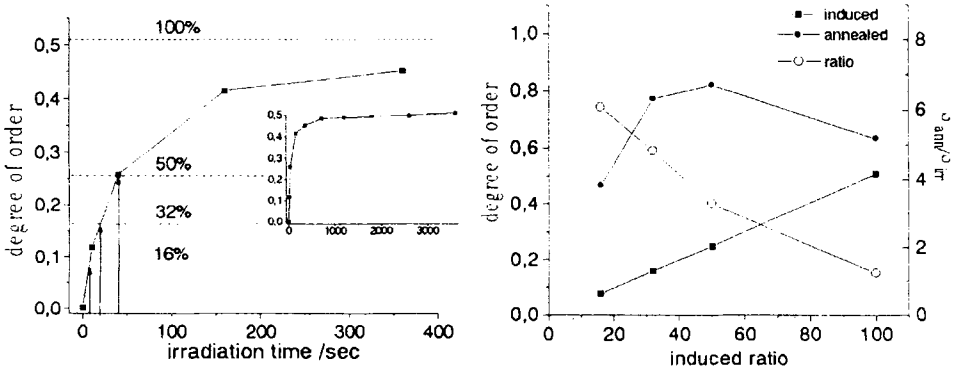


FIGURE 4: a: Photoorientation process in P3/50 films and different stops,
b: $S_{sp,365}$ after photoinduction and after annealing as well as the ratio of amplification in dependence of the photoinduced proportion from saturation value

SUMMARY

On irradiation of aligned films of PLCP a competition between two principles of order takes place – the self-organization of mesogenic side groups and the photoorientation process. Thus, the initial order of the film may restrict the ordering tendency of the linearly polarized light. The restriction can be overcome by lowering the order permanently or temporarily, e.g. by preparing spincoating films or supercooled isotropic melts. A new method is introduced in this paper: The photochemical transformation of rod-like photochromic groups into non-mesogenic moieties. The liquid crystalline order of planarly aligned films can be destroyed or considerably lowered by this intermediate light-induced decoupling of the anisotropic intermolecular interactions.

In PLPC films of such low actual order optical anisotropy can be generated by photoorientation as easy as in amorphous polymers but with a much larger values and a higher stability. Moreover, the self-organization of mesogenic moieties in the viscoelastic state amplifies the light-induced optical anisotropy. The orientational order generated by photoorientation in the glassy state acts as an initializing force in the process of establishing a more perfect alignment at temperatures above the glass transition. This combination of both ordering principles represents a new method to align LCP's.

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