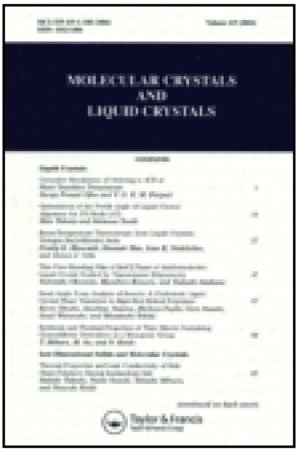

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Interdependence of Photoorientation and Thermotropic Self-Organization in Photochromic Liquid Crystalline Polymers

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To cite this article: Thomas Fischer, Lutz Läsker, Sylvia Czapla, Joachim Rübner & Joachim Stumpe (1997): Interdependence of Photoorientation and Thermotropic Self-Organization in Photochromic Liquid Crystalline Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 213-220

To link to this article: http://dx.doi.org/10.1080/10587259708036163

Mol. Cryst. Liq. Cryst., 1997, Vol. 298, pp. 213–220
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INTERDEPENDENCE OF PHOTOORIENTATION AND THERMOTROPIC SELF-ORGANIZATION IN PHOTOCHROMIC LIQUID CRYSTALLINE POLYMERS

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Abstract By irradiation with linearly polarized light optical anisotropy is generated in isotropic films of photochromic LCP's due to a photoorientation process. Generally, the efficiency is much higher in films of polymers with a high content of azobenzene moieties. On the other hand, the photochemically induced orientation of the photochromic side groups affects also the distribution of non-photochromic but mesogenic moieties. Furthermore, in initially isotropic films it 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. Investigating several polymers of the same general structure but with a different content of azobenzene side groups an interdependent behaviour was found for the photoorientation of the photochromic and the co-operative orientation of non-photochromic side groups.

INTRODUCTION

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[1]. 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]. Our previous studies on photoorientation processes in comb-shaped polymers were focused on materials which are situated at the border between liquid crystalline and amorphous polymers. The idea was to find an optimal combination of the advantages of both types, i.e. the high anisotropy of the molecular

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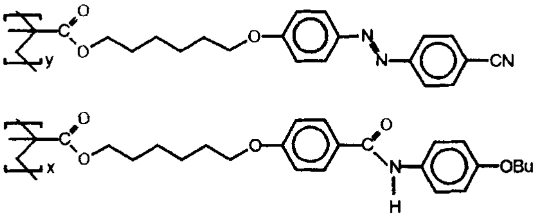
[#] Author to whom correspondence should be addressed polarizibility and the easy preparation of thin transparent films. We have shown that photoorientation can easily take place in amorphous films of such polymers whereas the reorientation of aligned LCP films requires a higher power density of the actinic light or a more sophisticated technique of irradiation, including a photochemical decoupling of the initial order which hinders or even suppresses an efficient photoorientation. However, it is very desirable to use both ordering tendencies, i.e. that of linearly polarized light interacting with rod-like photochromic groups and the thermotropic self-organization in one and the same orientation process instead of trying to prevent their interference. An attempt in this direction is shown in this paper.

POLYMERS AND METHODS

Synthesis and characterization

The synthesis of the azo-monomer was realized via 4-Hydroxy-4′-cyanoazobenzene in analogy to ref.[7]. The etherification with α,ω-dibromoalkanes and reaction with potassium methacrylate gave the monomer 4-[6-(2-methylpropenoyloxy)-hexyloxy]-4′-cyanoazobenzene. The synthesis of the amide-containing monomer is based on the synthesis of the corresponding ester compounds and was carried according to ref.[8]. The monomers and the monomer mixtures were polymerized with 2,2′-azo-isobutyronitrile as radicalic initiator at 70 °C and in N,N-dimethylformamide as solvent[7].

TABLE 1:
Composition and properties of the studied polymers



polymer	azo content mol% found	$M_w/10^3$ in g/mol	$\frac{M_w}{M_n}$	Phase transition temperatures in °C	$\Delta H_{S_{Ad}\rightarrow I}$ in kJ/mol
P 1/100	0	149	5,4	G 75 K 128 S_{A1}/S_{Ad} 150 S_{A1} 162 I	5,03
P 2/10	8,4	290	3,9	G 63 S_{Ad} 166 I	4,25
P 2/25	23,5	247	4,0	G 56 S_{Ad} 169 I	3,90
P 2/50	49,6	216	3,7	G 52 S_{Ad} 168 I	2,35
P 2/75	73,1	139	2,7	G 51 S_{Ad} 162 I	1,87
P 2/90	89,4	96	2,3	G 48 S_{Ad} 162 I	1,75
P 2/100	100	40	2,3	G 51 S_{Ad} 166 I	2,35

The composition of the copolymers was determined from the N value of the elemental analysis for copolymers with a high azo content and by UV/VIS spectroscopy for copolymers with a low azo content. Yields between 72 and 90 % and a good agreement between initial comonomer ratio and copolymer composition were obtained. The results are summarized in Tab. 1. Since the degree of polymerization of all polymers is higher than 100, the phase behaviour can be considered as to be independent of the molecular weight. The phase transition temperatures were obtained by Differential Scanning Calorimetry (Perkin Elmer DSC 7, heating rate 20 K/min). The peak maximum of the second heating DSC–curve of the polymer samples was taken as the phase transition temperature. The glass transition (T_g) temperatures and the isotropization temperatures (T_{cl}) of all polymer samples exhibit only a weak dependency on composition (see fig. 1). The type of mesophases was detected by polarizing microscopy and X–ray diffraction.

In accordance with the phase behaviour of known combinations of monomers with acceptor– and donor tail groups[9] all polymer samples of the series exhibit smectic mesophases.

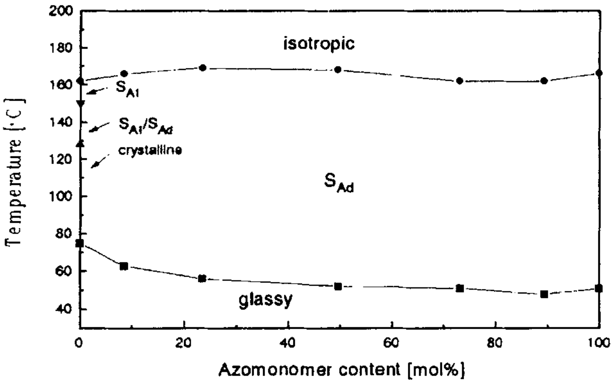


FIGURE 1:
Phase diagram of the copolymer system

Preparation of LCP films and Irradiation

The general structure of the studied polymers was chosen to combine donor– acceptor substitution and strong molecular interaction via H–bridge bonds with liquid crystalline properties offering a high rigidity and high transition enthalpies. In almost all cases of the studied copolymers, this combination of properties makes it impossible to prepare uniformly aligned films using common techniques. Isotropic films (≈0.2μm) have been prepared by spincoating from THF solutions. The films of the Liquid Crystalline Polymers 2 with different ratio of photochromic azobenzene side groups in the copolymer composition have been irradiated with the linearly polarized light of an Ar^+ laser (λ=488nm, P=200mW/cm^2) at room temperature, i.e. well in the glassy state. The optical anisotropy and the kinetics of its inducing has been determined by polarized UV 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. After irradiation the films have been annealed in the liquid crystalline phase 20K above the glass transition temperature for three days. After this procedure polarized spectra have been taken again.

RESULTS

As an example for the light-induced generation of orientational order figure 2 shows the absorbancies measured with light polarized parallel and perpendicular, respectively to the electric vector of the actinic light (90° in laboratory system) as well as the absorbance averaged over 36 measurements with light polarized from 0..175° in steps of 5°.

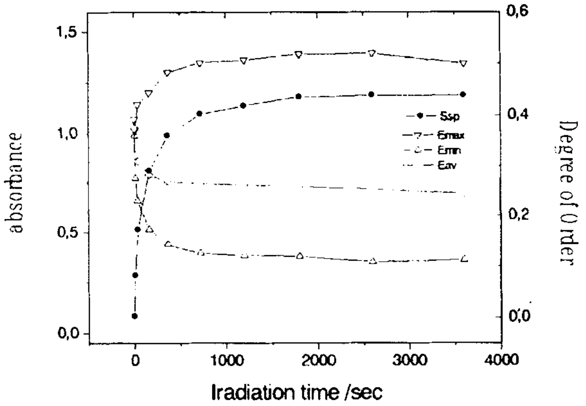


FIGURE 2:
P1/50 induced
dichroism (365nm)

The spectroscopic results show that the concentration of the rod-like moieties oriented along the 90° direction is decreased. The enrichment in the perpendicular direction within the plane of the film is not adequate. This behaviour suggests, that a certain proportion of the side groups is forced to move out of this plane. The change of the ratio of the average absorbance at 250nm and at 350nm caused by polarized irradiation gives an additional hint for such a behaviour. This fact will be discussed in a forthcoming paper. 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. Both aromatic system have some other transitions with deviating directions of the transition moment which contribute to the absorbance in the shorter wavelength region. On polarized 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 as a result of the photoorientation.

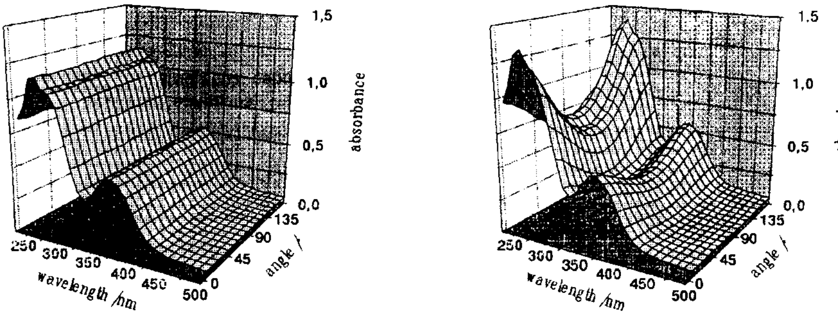


FIGURE 3 Polarized UV/Vis–spectra of a spincoated film of P2/25 before (left) and after (right) VIS irradiation

Co–operativity and interdependence of the photoorientation process

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 2 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.

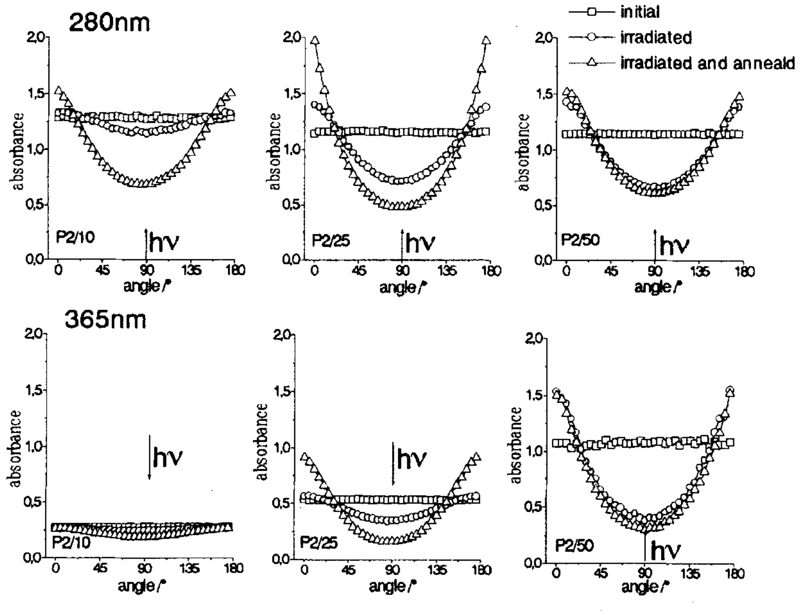


FIGURE 4: Angular distribution of absorbance before and after irradiation and after annealing for the copolymers P2/10, P2/25 and P2/50

Thus, an interdepent behaviour can be stated for the photoorientation process in these polymers. The dichroism induced at the π–π^* transition band of the azobenzene is very similar to that found for the benzanilide transition. For the same photochromic moiety the strength of induced anisotropy differs considerably. That means, the non–

photochromic groups are not only oriented by the azobenzene side groups, but they determine also the degree of orientation, which the photochromic groups can achieve. Such a dependence seems to be to strong for a short range or local interaction. The later should result in a much weaker dependence of the dichroism of the photochromic moiety on the copolymer composition because of the identity of the chromophores and hence of the transition moments. Furthermore the decrease of the dichroism of the non-photochromic groups with decreasing content of azobenzene side chains should be stronger as that found for the photochromic groups. In our experiments the values of induced dichroism are very similar for both types of side groups over the whole range of copolymer composition. Obviously the two types of mesogenic side groups acts as an anisotropic environment, which takes a stabilizing influence, when its uniformity is improved within the process of photoorientation. With a higher proportion of photoactive groups, the anisotropic power of the photoorientation becomes stronger. For contents of 50% and higher it dominates the system totally. The relation $S_{sp,365}<S_{sp,280}$ for 10% and 25% azobenzene side 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.

Annealing of the irradiated film and Amplification dichroism

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.

TABLE 2 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

The smaller the content of photochromic groups, the stronger is the relative increase of anisotropy by this procedure (see fig. 5).The amplification of the induced dichroism is shown in figure 6. Thus, 10% of photochromic groups 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 obtained by irradiation and subsequent annealing attains a maximum. This polymer shows the optimal combination of photoinduced anisotropy and LC potential. On the other hand the amplification due to the annealing procedure decreases with the increasing content of azobenzene side groups, although these polymers posses comparatively high transition enthalpies too. Obviously the anisotropic interactions which result in a more perfect alignment act mainly in the process of irradiation, whereas in the case of lower contents they have to be stimulated by the annealing procedure.

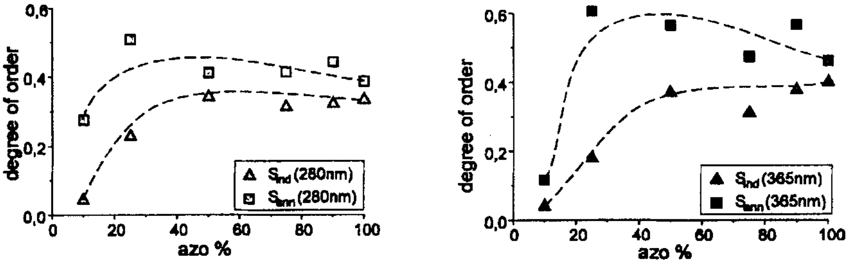


FIGURE 5: Induced dichroism before and after annealing at 280nm and 365nm

The strong amplification of the induced dichroism of polymers with a low azobenzene content leads to similar or even higher values of dichroism as those found for polymers with a high content. The orientation of the side groups is improved by establishing a liquid crystalline like ordered state.

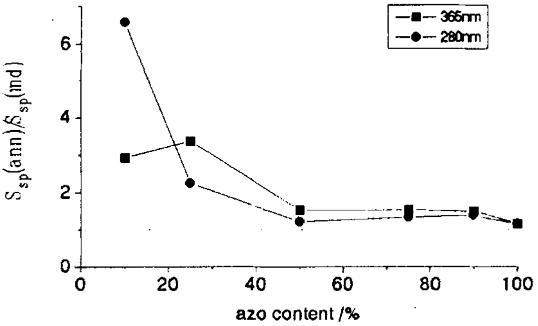


FIGURE 6: Amplification of induced dichroism by annealing

Thus, the photoorientation acts as an aligning force. In combination with the annealing procedure, this technique offers a new way to orient films of such type of PLCP. This is of special interest, if all conventional methods like external fields or surface forces fail to prepare uniformly aligned films. The importance of the LC potential for photoorientation processes was stressed previously.[5] The results presented here confirm our suggestion that it is correlated to the phase transition enthalpies.

SUMMARY

In spincoating films of PLCP with strong liquid crystalline potential, optical anisotropy can be generated by photoorientation as easy as in amorphous polymers and the values which can be obtained are even higher. The photoorientation process in such type of PLCP leads to an interdependent orientation of both types of side groups. On the one hand the photochromic groups orient the non-photochromic ones and on the other hand the non-photochromic, mesogenic side groups influence the amount of light induced dichroism. Moreover, the self-organization of mesogenic moieties in the visco-elastic state amplifies the light-induced optical anisotropy. Using this effect, a high LC potential turns to be an advantage for inducing high values of optical anisotropy by photoorientation. Furthermore, 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. The combination of both ordering principles represents a new method to align LCP's. This technique is especially helpful if all conventional aligning methods fail to orient such type of PLCP. Moreover it offers the possibility to align other non-photochromic groups using a modified polymer design.

ACKNOWLEDGEMENT: We thank the DFG for financial support.

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