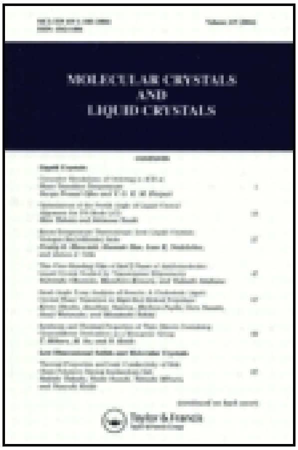

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Influence of Liquid Crystallinity and Aggregation on Photo-orientation

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Influence of Liquid Crystallinity and Aggregation on Photo-orientation

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The dependence of the Photo-orientation process on the liquid crystallinity and the molecular aggregation is studied. In the case of ordered films the photo-orientation is restricted, but this restriction can be overcome by a photochemical pre-treatment using UV light or by higher power density of the incident Vis light. The optical anisotropy increases with spacer length or the ordering tendency of the polymers.

Keywords: Photo-orientation; optical anisotropy; azobenzene; aggregation; liquid crystalline polyacrylate; photoisomerization; alignment

INTRODUCTION

The irradiation with linearly polarized light offers a new way to orient photochromic polymers [1-7]. In this way the optical properties of the films are modified reversibly changing the orientational distribution and/or the orientational direction of the photochromic moieties. Such Photo-orientation process is characterized as a photochemically induced (re)orientation process of the azobenzene groups in the glassy state of

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polymers upon irradiation with linearly polarized light [7]. It takes place via the repeated 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 groups become oriented perpendicular with respect to the electric field vector of the incident light. After switching off the illumination the initial state of the photochromic moiety is restored on the molecular level but the light-induced change of the orientational order remains stored long term stable in the glassy state.

The interaction between the ordering impact of the linearly polarized light and the thermotropic self-organisation is of special interest [8-11]. As shown recently in the case of homopolymers with azobenzene groups in the side chain, additional intermolecular interactions had to be taken into consideration caused by $\pi\pi$ stacking of the aromatic side groups [12]. In addition to the liquid crystalline self-organization, they cause specific ordering effects by aggregation. Dependent on their mutual arrangement H or J aggregates are formed [14-16].

The aim of the present study is to compare the Photo-orientation properties of a series of liquid crystalline homopolymers with azobenzene side groups modifing the liquid crystallinity and the glass transition temperature exclusively by the variation of the length of the alkyl spacer. The study should result in a more detailed insight to the relation between liquid crystallinity, molecular aggregation, molecular dynamics and Photo-orientation behaviour.

EXPERIMENTAL

The synthesis of the polyacrylates of the general structure shown in Figure 1 were described elsewhere [13].

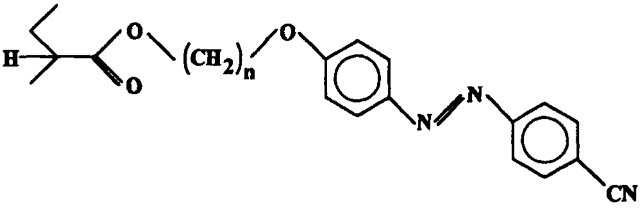

FIGURE 1 Structure of polymers with spacer lengths of n = 2 to 11.

Thin films were prepared by spin-coating on quartz glass substrates using THF as solvent (10 mg polymer in 1 ml solvent). The film thickness was approximately 0.2 µm. A hot stage (Lincam) has been applied for the annealing procedure. The irradiation with linearly polarized light was carried out using the 488 nm line of an Ar^+ laser (up to 100 mW/cm^2). In addition, a XBO lamp (1000 W) combined with a monochromator and a Glan-Thomson prism was used for polarized and, without the prism, for non-polarized irradiation. The UV/Vis measurements were carried out using a diode array spectrometer (Polytec XDAP V2.3). A Glan-Thomson prism with a computer-driven stepper was used for the angular-dependent measurements of absorbance. A turnable sample compartment was used for the polarized measurements.

RESULTS

Table 1 illustrates the phase diagram of the polyacrylates in dependence on the spacer length. Longer alkylene chains of the spacers result in decreasing glass transition temperatures, approximately constant clearing temperatures and increasing phase transition enthalpies. While the polymer with n=2 is nematic, those with n>3 have a S_A phase. But the polymers with n= 4 and 6 have a nematic phase in addition. Thus, the thermal properties are modified exclusively by the variation of the spacer length in this series, while the main chain and the photochromic moiety remain constant. This variation results in a polymer series of different liquid crystallinity, aggregation tendency and molecular dynamics.

Polymer CABO n PA	Tg (°C)	$T_{SA\text{-}N}$ (°C)	$T_{N\text{-}I}$ (°C)	ΔH (J/g)
2	85		115.2	0.9
3	61	107.1		0.6
4	53	91	129.1	1
5	38	101.1		2.5
6	33	99	110.5	3.8
7	29	111.1		4.3
8	25	121		4.6
9	25	117.5		4.3
10	29	121.9		4.6
11	28	113.6		4.4

TABLE 1 Phase behaviour of the polymers

In the case of long spacers the UV/Vis spectra of spin-coated films indicate the aggregation of the azobenzene side groups caused by ππ-stacking. While the polymer with n=2 is non-aggregated and that with n=3 forms H aggregates, the azobenzene moieties of polymers with longer alkylene chains are arranged in head-to-tail geometry. While the absorbance maximum of the H aggregates is hypsochromically shifted, those of the J aggregates is characterized by a bathochromic shift. The irradiation destroys the aggregates rebuilding the spectrum of non-aggregated chromophores, as shown in figure 2.

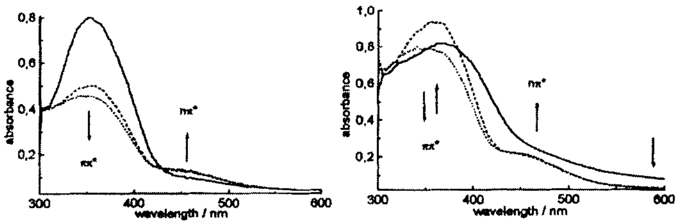

FIGURE 2 Spectral behaviour of polymer 2PA and 8PA upon UV irradiation (365 nm, P1 = 1mW/cm^2, P2 = 60 mW/cm^2; dashed line shows the steady state of the photoisomerization caused by P1 and the dotted line by P2; the arrows indicate the changes of absorbance during the photoreaction at different wavelengths).

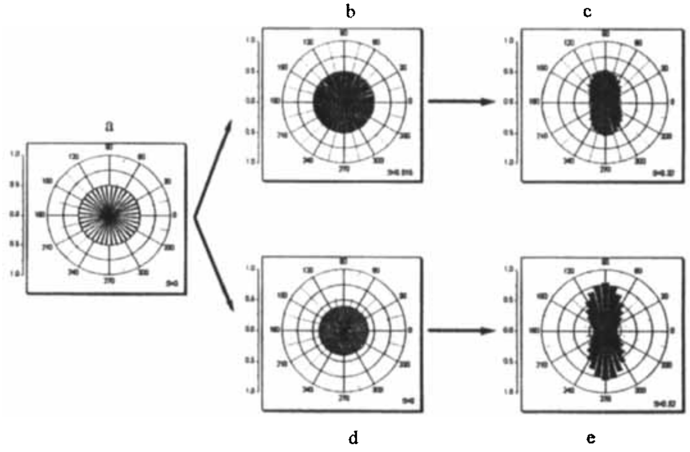

FIGURE 3 Photo-orientation of the polymer with n=10 a) initial film, b) after Vis irradiation (488nm, 0.5 mW/cm^2) c) subsequent Vis irridiation (50 mW/cm^2), d) after UV irradiation of the initial film (365nm, 1mW/cm^2) e) after subsequent Vis irradiation (0.5 mW/cm^2)

Irradiating the spin-coated films with linearly polarized light (488nm, 0.5mW/cm^2) dichroism is induced by Photo-orientation of the azobenzene moieties in films of polymers with short spacers (n=2 and 4) and high Tg values, respectively. But the process is strongly restricted by the aggregation of polymers with longer spacers and it is depressed in the case of the polymers with n=8 and 10 (see Table 2). But this restriction can be overcome by irradiating with increasing power density of the laser (Figure 3). In this way, much higher values of dichroism are induced even in the case of the polymers with longer spacer compared to the polymer n=2.

Polymer	Photo-orientation without photochemical pretreatment			Photo-orientation after photochemical pretreatment	
mW/cm^2	0.5	10	50	0.5	10
2PA	0.135			0.14	0.14
4PA	0.31	0.43		0.33	0.4
8PA	0.01	0.2	0.225	0.51	0.53
10PA	0.08	0.16	0.32	0.52	

TABLE 2 Photoinduced dichroism in dependence on power density (488nm) without and with initial UV irradiation (365nm, 1 mW/cm^2)

A second, very efficient method to overcome this restriction caused by the initial order is the photochemical decoupling by UV irradiation destroying aggregation and any orientational order of LC domains. While the photoinduced anisotropy is constant for polymer n=2 under all conditions, the photoinduced anisotropy increases significantly in the case of the other polymers after such photochemical pretreatment. Starting from such an isotropic, non-aggregated film the saturation value of the order parameter increases with the spacer length from 0.14

for n=2 to 0.53 for n=8 as show in Table 2. This is caused by the faster dynamics by the decoupling of the mesogenic moiety from the backbone and the larger thermotropic ordering tendency of the polymers with the longer spacer. It results in a higher efficiency of the Photo-orientation process shown in figure 4.

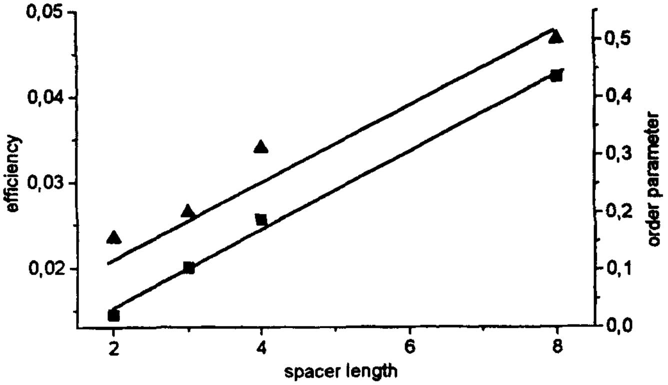

FIGURE 4 Efficiency (square) and the order parameter (up triangle) of Photo-orientation versus the spacer length.

The threshold of order parameter versus time can be described as a monoexponential function in form of S(t)=1-exp(-efficiency*t)+S. The estimated efficiency versus spacer lengths shows a linear slope.

Annealing of the photo-oriented film of the nematic polymer with n=2 above Tg, results in a significant amplification of the optical anisotropy from S= 0.14 to S= 0.34. The orientational order photo-generated in the glassy state acts as an initializing force for the thermotropic self-organization of the polymers in the mesophase, as shown recently for some copolymers [10,11]. So, a "Command" effect is created, which result in an efficient planar alignment. The director of these LC monodomain films is governed by the electric field vector of the incident light. But in the case of the smectic polymers with n>3 the in-plane anisotropy becomes erased and the average absorbance is significantly decreased. This indicates that the annealing process results in a homeotropic alignment of the LC polymers.

CONCLUSION

There is a strong dependence of ordering and Photo-orientation in a series of homopolymers with very similar composition in which the molecular dynamics and the liquid crystallinity are varied exclusively by the spacer lengths. The study shows that molecular aggregation and liquid crystallinity have a strong influence on the light-induced anisotropy generated by Photo-orientation. In the case of aggregation and liquid crystalline domains efficient Photo-orientation can be achieved by decreasing the intermolecular interactions by a temporary photochemical de-coupling of the supramolecular order. In this case Photo-orientation and liquidcrystalline ordering are interactive and result in increasing anisotropy with longer spacers or higher thermotropic ordering tendency.

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