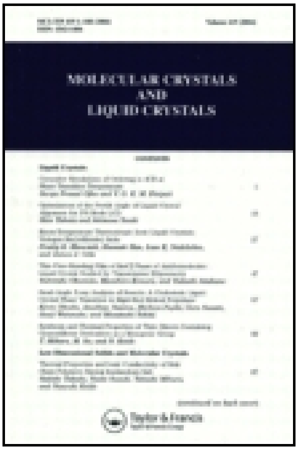

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3D Orientational Order in a Homologous Series of LC Polyesters With Azobenzene Side Groups and Different Lengths of the Alkylene Spacer in the Main Chain

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3D Orientational Order in a Homologous Series of LC Polyesters With Azobenzene Side Groups and Different Lengths of the Alkylene Spacer in the Main Chain

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The spatial orientational order of films of a series of LC polymalonates with 4-hexyloxy-4'-nitroazobenzene side groups which differ in the length of the alkylene spacer in the main chain are studied using null ellipsometry and UV/Vis spectroscopy. In the spin-coated films the azobenzene fragments strongly prefer a random in-plane alignment. Uniaxial as well as biaxial order of the azobenzene chromophore were detected in these films irradiating with linearly polarized UV light. Biaxiality is observed in the intermediate stages of irradiation whereas an uniaxial order is realized in the saturated state. Finally, it results in an in-plane structure with its optic axis perpendicular to the electric field vector of the incident light. The components of the tensor of the order parameter were estimated for each homologue as a function of the exposure dose. The scalar order parameters of the photosaturated states decrease monotonously with the increasing length of the alkylene spacer of the LC polymers. Variation of the azobenzene concentration, modification of the liquid crystallinity and peculiarities of the aggregation with the spacer length are considered as the reasons of the effect.

Keywords: LC polymers; azobenzene; photoisomerization; photoorientation; photoinduced anisotropy; aggregation

INTRODUCTION

Nowdays, azobenzene containing polymers are the most effective materials to generate photoinduced anisotropy (POA) [1-7]. The microscopic origin of this effect is the anisotropy of excitation of the rod-like azobenzene moiety whose transition moment is oriented approximately along the long molecular axis. As result of an unknown number of *trans-cis* photoisomerization cycles the azobenzene side group becomes oriented perpendicular to the electric field vector ***E*** of the linearly polarized light. Considering the spatial case, there are many directions perpendicular to ***E***. Some from them are preferable depending on the polymer structure, liquid crystal properties, influence of the substrate, irradiation conditions *etc*. It is a reason of a big variety of spatial orientational configurations in the polymer films.

The first attempt to estimate the 3D orientational order in the azobenzene containing polymer films during the photoorientation was done by Wiesner *et al.* [5] using IR absorption spectroscopy. The side chain ordering rates for the series of azobenzene containing copolymers at various irradiation stages were estimated. The weak point of the proposed approach is that it is applicable only for the special orientational configuration. Besides, it requires knowledge of the initial structure, which can be hardly studied using exclusively spectroscopic methods.

The present work is a first attempt of studies of the 3D orientational order depending on the constitution of the polymer backbone. In the study the spatial structures were investigated using UV/Vis spectroscopy supported by null ellipsometry [8-9]. The last method allows to estimate the type of the 3D orientational order before irradiation and after subsequent periods of irradiation. The combination of these methods was applied to study a homologous series of LC poly(malonates) with the same 4-hexyloxy-4'-nitroazobenzene side group and different lengths of the alkylene spacer in the main chain.

EXPERIMENTAL

1. Syntheses and characterization of the polymers.

A series of poly[m-{(4-hexyloxy-4'-nitro)azobenzene}malonates] was used having flexible alkylene spacers of different numbers of methylene groups in the main chain. The synthesis of the studied polyesters was described in [10]. The phase transitions of the LC polymers were studied by polarization microscopy and differential scanning calorimetry. Molecular weights were determined by gel permeation chromatography. The obtained results are summarized in Table 1.

Table 1 Characterization of the polymers

Polymer	m	Transition temperatures / °C	M_n, g/mol
P1	8	C_1 32 C_2 44 S 52 N 55 I	7 000
P2	9	C (G5 S 47N 55 I) 45 N 55 I	20 700
P3	10	C (N 51 I) 53 I	12 800
P4	12	C_1 (N 52 I) 68 C_2 76 I	21 800
P5	13	C (G 20 N 56 I) 46 N 56 I	8 600
P6	14	C (N 55 I) 57 I	9 300
P7	16	C 73 I	16 600

The symbols C, C_1 and C_2 correspond to crystalline modifications, G to glassy state, S and N, respectively, to smectic and nematic mesophase, I to the isotropic melt. M_n designates a number-avarage molar mass. The transition temperatures in the parentheses refer to the second heating followed after the first heating and subsequent cooling. It can be seen from Table 1, that all synthesized polymers form liquid crystalline phases except P7.

2. *Sample preparation and irradiation procedure.*

The polymers were solved in dichloroethane with a concentration of about 40 g/l. The polymer films were obtained by spin-coating on slabs of fused quartz. The thickness of the films measured with a profilometer of Tencor Instruments was about 200-600 nm. The films were kept at room temperature for one day to evaporate the solvent.

Anisotropy was induced in the films upon irradiation using a Hg lamp in combination with an interference filter (365 nm). The intensity of the actinic light was about 1.0 mW. A Glan-Thomson polarizer was applied for the polarization of the UV light. Irradiation and spectroscopy was carried out in normal incidence. The geometry in the chosen laboratory frame is presented in Fig.1. The irradiation was provided in several steps carrying out the measurements approximately 20 min after finishing of every irradiation period.

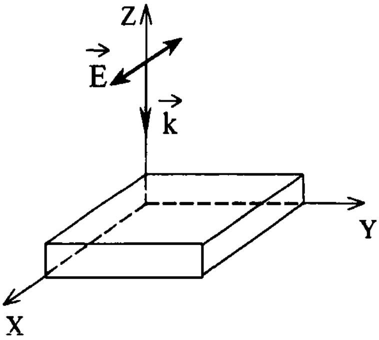

FIGURE 1 Irradiation geometry and principle axes of the film

3. Experimental methods

Null ellipsometry technique (Senarmont method [11]) was used to estimate both, the in-plane, $(n_y-n_x)d$, and the out-of-plane $(n_z-n_x)d$ optical path difference (n_x, n_y, and n_z are the principal refractive indices of the film (Fig.1)) using oblique incidence of the testing beam. Dependencies of the analyzer rotation angle φ on the incidence angle of the testing beam θ were measured for both, vertical and horizontal orientation of the x axis. The measurements were carried out for the polymer films before exposure as well as after different intervals of irradiation. The measured φ versus θ curves were fitted with the calculated one in the most probable configuration model. Alignment of the azobenzene fragments was derived from the obtained values of $(n_y-n_x)d$ and $(n_z-n_x)d$ assuming that the preferred direction of these fragments coincides with the direction of highest refractive index. A detailed description of the method can be found in our previous publication [8].

The UV/Vis absorption measurements were carried out using a diode array spectrometer (Polytec XDAP V2.3). The samples were set normally to the testing light. A Glan-Thomson prism with a computer-driven stepper was used for the polarization of the testing beam. The angular-dependent UV spectra of the original and irradiated films were measured every 5^0 in the spectral range of 220-450 nm rotating the polarizer stepwise.

RESULTS AND DISCUSSION

The shape of the curves $\varphi(\theta)$ measured with null ellipsometry was similar for the non-irradiated films of all homologues just after spin-coating. The experimental data obtained for vertical and horizontal

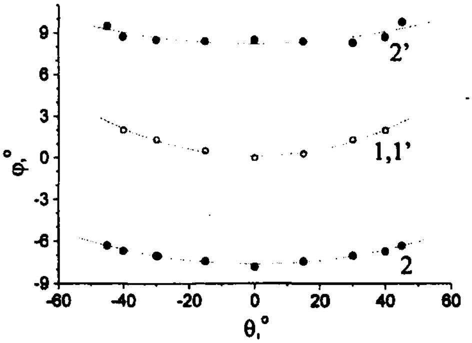

FIGURE 2 Curves for analyzer angle φ versus light incidence angle θ for polymer P1 on untreated glass substrate. 1,1'- non-irradiated film; 2, 2'-irradiated film.

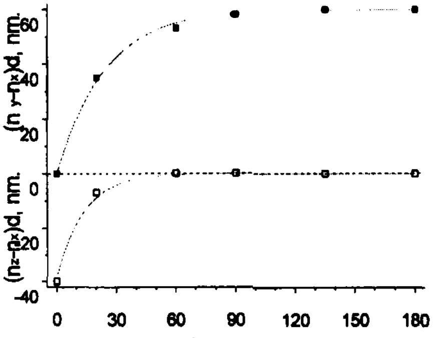

FIGURE 3 Birefringence kinetics in polymer P1 under polarized UV light irradiation.

position of the sample axis *x* (curves 1 and 1' in Fig.2) are practically in coincidence. This demonstrates the in-plane isotropy of the initial films. The fitting gives the correlation $n_x=n_y>n_z$ reflecting the preferential in-plane alignment of the azobenzene units and their random distribution in the azimuthal plane. The curves $\varphi(\theta)$ measured for the irradiated films do not coincide anymore (curves 2 and 2'). The irradiation process causes a gradual increase of the distance between the curves and a curvature of the dependence $\varphi(\theta)$. The photoinduced changes saturated at values, which depend on the irradiation condition. The most pronounced changes were observed for the homologues with the short spacer (m=8). The fitted values of the in-plane, n_y-n_x, and out-of-plane, n_z-n_x, birefringence of the

P1 film corresponding to different times of irradiation are presented in Fig.3. In the first period the principal refractive indices are different with the following correlation $n_z<n_x<n_y$. The in-plane birefringence monotonously increases with increasing exposure time establishing saturated states. Simultaneously, the difference between n_x and n_z decreases. So, in the intermediate stages of irradiation the film acquires biaxiality, whereas the photosaturated state is characterized by uniaxial order. The optic axis lies in the film plane parallel to the y direction. The same tendency was observed for the other homologues.

Since the ellipsometry method operates with refractive indices, it is suitable only for the investigation of generalized structures, which summarize the order of the complete ensemble. For the study of the orientational order of definite molecular groups the various spectroscopic methods can be used. Angular-dependent UV/Vis absorption measurements were carried out at the wavelength of the absorption maximum of the azobenzene group to estimate the order parameter.

In the general case of biaxial films the order parameter is a tensor S_{ij} having diagonal form when the coordinate axes coincide with the principle axes of the film (Fig.1). The diagonal terms S_{xx}, S_{yy} and S_{zz} are connected with the absorption components D_x, D_y and D_z [5]. For example

$$S_{xx}=\frac{D_x-\frac{1}{2}(D_y+D_z)}{D_x+D_y+D_z} \tag{1}$$

The components S_{yy} and S_{zz} can be obtained from (1) by cyclic permutation in expression (1). The in-plane components D_x and D_y can be easily measured at normal incidence of the testing beam. In general, it is difficult to estimate the component D_z. However as admitted in [5], the problem simplifies if at some moment t_0 the sample has uniaxial order with an in-plane position of the axis of anisotropy. In this case $D_z(t_0)=D_x(t_0)$ and the total (spatial) absorption can be estimated by

$$D_{total} = D_x(t_0) + D_y(t_0) + D_z(t_0) = 2D_x(t_0) + D_y(t_0) \quad (2)$$

The total absorption is constant if the number of the absorbing units remains constant. In this case a value of D_z at each moment t can be estimated as

$$D_z(t) = D_{total} - D_x(t) - D_y(t) \quad (3)$$

where $D_x(t)$ and $D_y(t)$ are experimentally measured parameters.

The requirements for the application of this method are satisfied in the case of the studied films. Indeed, in-plane uniaxial order corresponds to the photosaturated state. Besides, the lifetime of the *cis* isomer is less than 1 s, so the number of the *trans* isomers is constant during the measurements. The values of D_x and D_y (experimentally measured) and D_z (calculated using (2)- (3)) for P1 at various irradiation times are presented in Fig.4a.

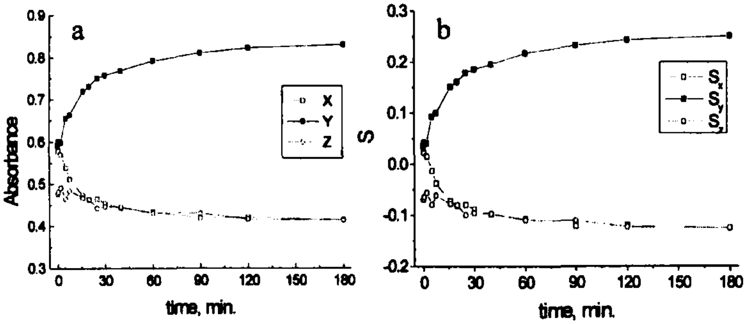

FIGURE 4 Kinetic of D_x, D_y, D_z (a) and S_{xx}, S_{yy}, S_{zz} (b) for polymer P1.

The data $D_x(t)$, $D_y(t)$ and $D_z(t)$ were used for the estimation of the kinetic curves of order parameter components S_{xx}, S_{yy} and S_{zz}. The dependencies $S_{xx}(t)$, $S_{yy}(t)$ and $S_{zz}(t)$ are presented in Fig.4b. As one can see from Fig.4b, the order is biaxial only in the first period of the irradiation. This is in agreement with the result obtained with the null ellipsometry method. The saturation part of the curves $S_{xx}(t)$, $S_{yy}(t)$ and $S_{zz}(t)$ describe the uniaxial orientation along the y axis. In this case $S_{yy} \equiv S$ and the correlation between the order parameter components is $S_{xx} = S_{zz} = -0.5\,S_{yy}$.

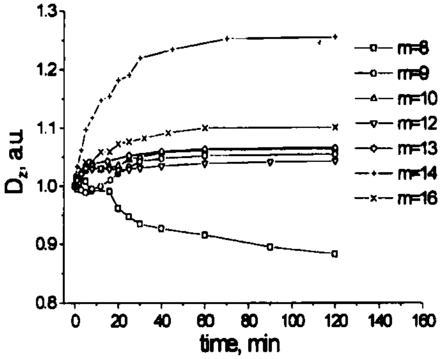

FIGURE 5 Calculated dependencies D_z on irradiation time for different homologous.

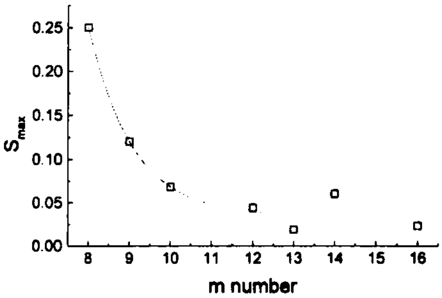

FIGURE 6 Order parameter *S* versus *m* number of polymer.

The procedure described for polymer P1 was applied to the other polymers of this series. In spite of qualitative similarity of the experimental curves $D_x(t)$ and $D_y(t)$, results obtained for different polymers were strongly depended on the homologue number. In Fig.5 there are presented results of the calculation of $D_z(t)$. As can be seen, in the first period of irradiation, reorientation in the polar plane occurs. For the homologue with m=8 the azobenzene fragments aspire to reorient from homeotropic direction into the film plane. The chromophores in homologues with m=9, 10, 13 demonstrate practically pure in-plane reorientation. In the homologues with m=14, 16 the out-of-plane photoinduced reorientation occur. So, lengthening of the main chain spacer leads to the tendency of the out-of-plane alignment of azobenzene units. Simultaneously, monotonously decreases the uniaxial order induced in the photostationary state (Fig.6).

These results allow to make several conclusions. Firstly, the strong absorption anisotropy of the photosensitive moiety is not the only one factor influencing its ordering rate at irradiation with linearly polarized light. Indeed, in spite of all studied polymers contain the same azobenzene group they demonstrate different rate of the photo-induced order. Secondly, the strong increase of S with the shortening of the spacer is an evidence that interaction of the azobenzene units and the resulting aggregation [12,13] are important factors for the photoorientation process. In the case of these polymers it can not be excluded that the polarized light provokes only the process of the self-organization resulting in a preferential direction of orientation as recently found for the photoorientation of other LC polymers [4,14,15]. The strong dichroic interaction of azobenzene units partially aligned with the light should cause a more effective order. Another feature of the self-organization is the involvement of non-absorbing fragments from side and main polymer chains in the orientational process [2, 3, 7].

In addition, the role of the liquid crystallinity in the induction of 3D orientational order should be discussed. The uniaxial order induced in all polymers of this series can be explained easily assuming that the linearly polarized UV light provokes a thermotropic self-organization. Indeed, the uniaxiality should be the final state of self-organisation of mesomorphic systems, since the uniaxial order of liquid crystalline materials in the equilibrium state is a well known fact [16].

CONCLUSIONS

Thus, using the combination of null ellipsometry and UV/Vis absorption spectroscopy the following peculiarities of the 3D orientational order in a series of 4-alkoxy-4'-nitroazobenzene polyesters were established. The azobenzene units in the spin-coated films demonstrate random in-plane alignment. Irradiation with the polarized UV light causes its preferential in-plane reorientation with alignment direction perpendicular to vector $\boldsymbol{E}$ of the exciting light. The biaxial structures correspond to the initial period of irradiation, whereas a photosteady state is characterized by uniaxial orientation. The components of the order parameter tensor S_{ij} are estimated for different irradiation doses. The ordering rate decreases with the lengthening alkylene spacer. Simultaneously, the tendency of the out-of-plane reorientation of the chromophores increases. The photoinduced self-organization having characteristic features of liquid crystalline compounds is an important factor causing the 3D orientational order in the films.

Acknowledgments

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