Mol. Cryst. Liq. Cryst., Vol. 409, pp. 229–241, 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490431363

PHOTOINDUCED 3D ORIENTATIONAL ORDER IN LIQUID CRYSTALLINE AZOPOLYMERS STUDIED BY THE METHOD OF ATTENUATED TOTAL REFLECTION

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The attenuated total reflection (ATR) technique is applied to study 3D ordering in the films of liquid crystalline (LC) polymers. We used a series of LC side-chain polyesters differing by the tail substitutes (NO_2, OCH_3 and OC_4H_9) in azochromophore. The 3D order is studied in non-irradiated films as well as in the films irradiated by polarized light with $\lambda_{ex1} = 365\,nm$ or/and with $\lambda_{ex2} = 457\,nm$ strictly distinguished by absorption efficiency of azochromophores. The orientation under irradiation is compared to that after irradiation. Biaxial, uniaxial as well as isotropic 3D ordering of azochromophores is realized. The observed uniaxial spatial structures can be classified by analogy with crystal optics; 1) positive C films with preferential out-of-plane orientation of azochromophores; 2) negative C films with in-plane random orientation of azochromophores having symmetry axis in the film normal direction; 3) positive A films with in-plane uniaxial orientation, and 4) negative A films characterized by oblate orientational distribution having symmetry axis in-plane of the film. The initial states as well as the stationary states of the films are characterized by uniaxial order of azochromophores, except in the case of intensive pumping with 365 nm, which results in isotropic ordering. The change of the tail substitute in the succession $NO_2 \rightarrow OCH_3 \rightarrow OC_4H_9$ leads to orientation transition from the structure of negative C plate to the structure of positive C plate (non-irradiated films), increase of the tendency of isotropic ordering ($\lambda_{ex1} = 365\,nm$ irradiation), and transition from the

The studies were supported by personal NATO grant for Dr. O. Yaroshchuk.

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structure of positive A plate to the structure of negative A plate ($\lambda_{ex2} = 457\,nm$ irradiation).

Keywords: attenuated total reflection; azopolymer; photoinduced anisotropy; 3D order

1. INTRODUCTION

Azopolymers have induced a great interest over last few decades because of their potential for a number of photonic applications, such as optical data displaying, storage and processing, telecommunciation and holography [1,2]. The application capability of the azopolymers is associated with their unique properties. One of the most amazing features is a high efficiency of photoinduced ordering caused by a strong absorption dichroism of azochromophores. The irradiation corresponding to absorption range of azochromophores (actinic irradiation) causes E-Z isomerization of azochromophores and, possibly, their reorientation, perpendicularly to the polarization direction of the actinic irradiation. These processes cause big variety of spatial orientational configurations of azochromophores in irradiated films. The photoinduced 3D orientational order is of big importance for a number of applications (compensation films for LCD, optical retarders etc.). Furthermore, it is an exciting question of basic science.

Most of the experimental works of photoinduced ordering in azo-polymers are restricted to 2D measurements, because it is assumed that the material keeps the axial symmetry of the polarized actinic light. This assumption is valid in amorphous isotropic polymers, but many materials have a self-organization tendency, which competes with the symmetry of light. It is particularly the case of LC polymers, in which a 3D characterization of the structure is absolutely necessary.

The known methods suitable for the experimental study of the 3D ordering in polymer films are dealing with absorption coefficients or refractive indices, which are tensor parameters in general case. Analyzing various experimental approaches we concluded that the most efficient methods for this purpose are the methods operating with components of the refractive index tensor. The absorption methods are not universal but they can be successfully used in some experimental cases to estimate the components of order parameter tensor of azochromophores and other molecular fragments [3–6].

In the present studies we employ attenuated total reflection (ATR). This method was widely used before to study spatial order induced in amorphous azopolymers by actinic light and electrical polling [7–9]. With this research we extend the approach to investigate light induced ordering in LC azopolymers. These studies were carried out for two reasons: 1) since only few works devoted to the subject were found [10,11]; 2) we wanted to compare results obtained by ATR method and the method of null ellipsometry earlier applied for the same purpose [6,12,13]. In this research we consider the influence of the structure of azobenzene chromophore and the spectral content of the actinic light on the characteristics of photoinduced spatial ordering. The advantages and shortcomings of the ATR method in the studies of LC azopolymers are discussed.

2. EXPERIMENTAL

2.1. Samples

In our studies we used a series of polymalonates differing by the end substitutes in the azochromophores (Fig. 1). The preparation of these compounds was carried out as described previously [14]. It based on the polycondensation of mesogenic diethylmalonates with 1,8-octanediol. The polyesters prepared were characterized by elemental analysis and 1H NMR spectrosocopy. The results are in agreement with the proposed structures. Molecular weights of the polymers were determined by gel permeation chromatography. These data are presented in Table 1.

The phase transitions in the polymers were studied by polarization microscopy and differential scanning calorimetry. By these studies, LC properties were revealed in all homologues of the series. The obtained phase transition temperatures are presented in Table 1.

The polymer films were prepared by spin coating of polymer solution in dichloroethane (2 wt.%). The films for the spectral studies were cast on quartz slides, while those for the ATR measurements were cast on glass slabs coated with a semitransparent gold layer. In the latter case the spin velocity has been varied to obtained films with a thickness of 1–2 μm, which is optimal for the ATR method. The UV/Vis absorption spectra of the films were carried out by silicone array spectrometer from Ocean Optics Inc. The spectra are presented in Figure 2. As can be seen, the position of the most

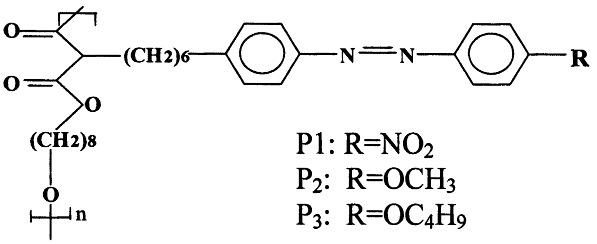

FIGURE 1 Structural formulas of azopolymers.

TABLE 1 Characterization of Polymers. The Symbols C, C_1 and C_2 Correspond to Crystalline Modifications, S and N, Respectively, to Smectic and Nematic Mesophase, I to the Isotropic Melt. M_n Designates a Number-Average Molar Mass

Polymer	R	M_n, g/mol	Transition temperatures, °C	Absorption max, nm
P1	NO_2	7000	C_1 32 C_2 44 S 52 N 55 I	375
P2	OCH_3	7519	C 58 N 62 I	351
P3	OC_4H_9	5820	C 63 N 75 I	318

intensive absorption band ($\pi\pi^*$ band) strongly depends on the end substitute of azochromophore. The wavelength of the maximal absorption, λ_{max}, increases in the order $OC_4H_9 \rightarrow OCH_3 \rightarrow NO_2$ and so is maximally shifted to the red for the chromophore with pronounced donor-acceptor properties. The value of λ_{max} is presented in Table 1 too.

The photo-ordering processes in films were initiated by the light of two different wavelengths;

1. $\lambda_{ex1} = 365\,nm$ from a mercury lamp, polarized with an UV dichroic polarizer. The light intensity in the sample position was about $20–80\,mW/cm^2$.
2. $\lambda_{ex2} = 457\,nm$ from an Ar^+ laser ($\leq 100\,mW/cm^2$).

As can be seen from Figure 2, the first irradiation line fall into the maximum of $\pi\pi^*$ absorption band of P1 and P2 chromophores and into

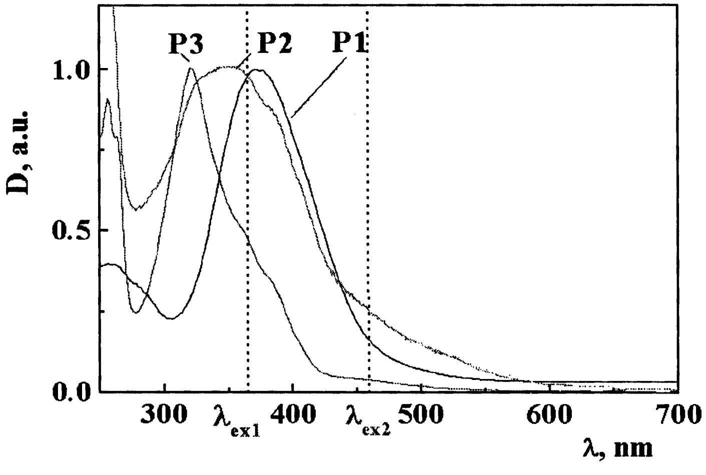

FIGURE 2 UV/Vis spectra of the films of P1-P3 polymers.

the edge $\pi\pi^*$ band of P3. The second line corresponds to the edge of $\pi\pi^*$ band of P1 and to weak $n\pi^*$ band of P3. The case of combined irradiation with λ_{ex1} and λ_{ex2} is also considered.

2.2. Method

The detailed description of the ATR method and experimental set-up can be found in previous publications [7–9,15]. The scheme of the method is presented in Figure 3. The glass slide, with an evaporated gold layer, is spin-coated with the polymer film and is put in optical contact with a half-sphere, through which the infrared laser beam ($\lambda = 829\,\text{nm}$) is reflected onto the sample. The laser is polarized at 45° from the plane of incidence. A Wollaston prism splits the reflected beam into TM and TE beam (polarized parallel and perpendicular to the plane of incidence, respectively), which are detected by two photodiodes. The laser and the detectors are mounted on the symmetric arms of a goniometer. This permits a simultaneous recording of TE and TM reflectivity, R^{TE} and R^{TM}, as functions of the incidence angle φ, in the range $\varphi = 8°–80°$. On $R^{TE}(\varphi)$ and $R^{TM}(\varphi)$ curves, a set of dips appears, corresponding to the successive TE and TM guided modes in the polymer films. The angular position of these two sets of modes are introduced in a computer fitting procedure which gives the thickness, d, and the three principal refractive indices n_x, n_y and n_z, where z is the normal to the sample and (x,z) is the plane of incidence. The set of these parameters determines the position of optical axes and the optical anisotropy of the studied films. Since azochomophores possess strong polarizability along the long molecular axis, we assumed that the highest index of refraction corresponds to direction of preferential alignment of the azochromophores.

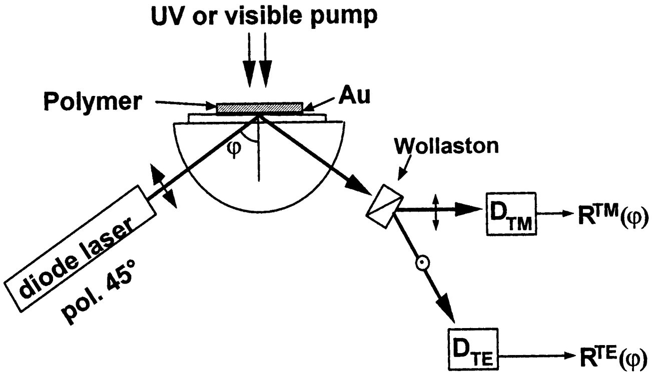

FIGURE 3 ATR experimental setup.

The measuring process takes several minutes depending on range of incidence angles and scanning speed, as determined by the desirable accuracy. It means that the method can be applied to films in a stationary state. During the pumping or the relaxation periods, the time variation of n_z are estimated by measuring the reflectivity of the sample, $R^{TM}(\varphi_1, t)$, at a fixed angle of incidence, φ_1, on the side of the TM mode of highest incidence. Knowing the shape of the mode, it is possible to calculate the time variations of the mode center, $\varphi^{TM}(t)$, which are, in first approximation, proportional to the variations of n_z. The saturation of this time dependence indicates that the stationary state of the film is reached.

The $R^{TE}(\varphi)$ and $R^{TM}(\varphi)$ curves for all films were measured before irradiation, in the stationary state of irradiation and after irradiation. The TE polarization was chosen for the pumping light (along the x axis). In the case of slow relaxation of the induced orientation (in polymers P2 and P3), the estimation of principle refractive indices has been carried out for various periods of relaxation.

3. RESULTS AND DISCUSSION

Since qualitatively the experimental curves $R^{TE}(\varphi)$ and $R^{TM}(\varphi)$ obtained for different polymers are fairly similar, we bring only the results for polymer P1, mainly for demonstration of the method. Curves 1 and 1′ in Figure 4 correspond to the initial state of a P1 film, curves 2 and 2′ have been

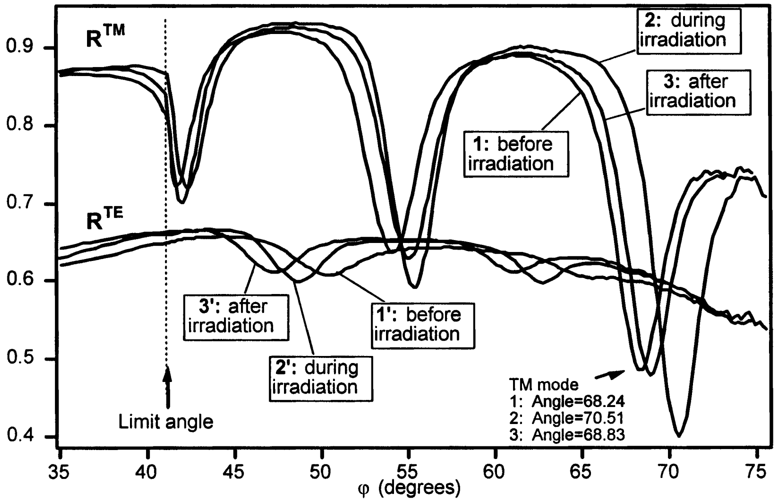

FIGURE 4 TM and TE reflectivity versus the incidence angle for P1 film.

recorded on the same spot of this P1 film in a stationary state of UV irradiation and curves 3 and 3′ after relaxation in dark for 50 minutes. The dynamics of the reorientation intiated by UV light was monitored by recording $R^{TM}(\varphi_1,t)$ at a fixed angle φ_1, on the side of the TM mode near 70°. As the mode moves a lot, we were obliged to change φ_1 stepwise during the record: this was performed automatically by the computer driving the experiment. Figure 5 shows the calculated position of the mode center, $\varphi^{TM}(t)$.

The fitting results for polymers P1, P2 and P3 for non-irradiated state as well as for various irradiation situations (stationary and quasi-stationary states) are summarized in Table 2, Table 3 and Table 4, correspondingly.

Let us analyze the data with regard to conditions of film treatment. The estimation of the orientational structure of the *non-irradiated films* was the biggest challenge in our experiments. The matter is that the LC polymers, in big contrast to amorphous polymers, form polydomain films characterized by a fairly poor optical homogeneity. For demonstration, Figure 6 shows texture of P1 film observed with a polarizing microscope. The polydomain structure appears at the film thickness d > 500 nm, i.e. at the thickness closed to the optimized thickness for ATR method. To meet conditions of transparency, for the ATR method, the films were carefully selected. In spite of that, the ATR modes were often very broad (especially for P2 and P3 films) that reduced accuracy of our measurements. For some polymers, the results obtained for different non-irradiated films suggested different types of orientation. For the non-irradiated P1 films, the observed ratios, $n_x \approx n_y > n_z$, correspond to the random in-plane alignment of

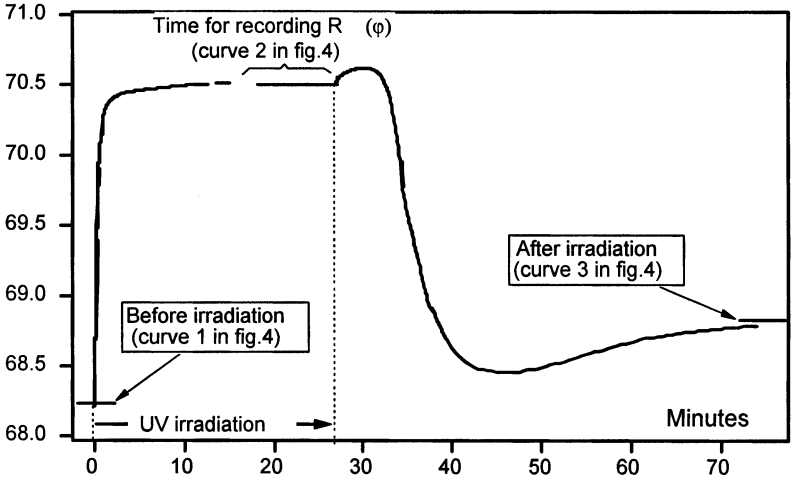

FIGURE 5 Angular position of the TM mode of P1 film versus pumping time.

TABLE 2 The Fitting Results and the Corresponding 3D Orientational Structures Obtained for P1 Films

Film	Film irradiation conditions	Film parameters					Film structure
		d, μm	n_x	n_y	n_z	$\langle n \rangle$	
P1: irradiation with $\lambda = 365$ nm (x polarization)							
P1-1	Before irradiation	1.319	1.612	1.600	1.557	1.591	negative C film
	Under irradiation (365 nm, 50 mWcm^{-2})	1.340	1.578	1.607	1.566	1.584	positive A film
	Under irradiation (365 nm, 80 mWcm^{-2})	1.348	1.577	1.584	1.577	1.579	isotropic film
	After irradiation	1.339	1.562	1.625	1.554	1.581	positive A film
P1: irradiation with $\lambda = 457$ nm (x polarization)							
P1-2	Before irradiation	1.331	1.637	1.628	1.556	1.606	negative C film
	Under irradiation (457 nm, 100 mWcm^{-2})	1.358	1.560	1.632	1.566	1.586	positive A film
	After irradiation	1.358	1.560	1.634	1.565	1.586	positive A film

azochromophores. Following terminology used in crystal optics, this structure corresponds to the structure of negative C plate. In case of P2 films, we obtain $n_x \geq n_y > n_z$ which corresponds to either structure of the negative C plate or to local biaxial orientation. In both cases, in-plane alignment of azochromophores is preferred. Finally, for P3 films $n_x \approx n_y > n_z$ which shows uniaxial alignment of azochromophores in the direction of the film normal. Optically, this type of orientation corresponds to the positive C plate.

As it was noted before, ATR method can be successively used to study only strongly homogeneous films. For this reason, ATR studies of non-irradiated films were supplied by the transmission null ellipsommetry method [5,6], which is less critical to the optical quality of samples. The ellipsommetry studies have confirmed the results obtained with ATR method.

During and after irradiation, all films exhibit good ATR modes, corresponding to a better homogeneity. The latter conclusion was confirmed by the film observation in polarizing microscope.

To analyze the structures related to *irradiated films* one should distinguish two states:

1. the structure of the films in the stationary state of irradiation.
2. the structure of the irradiated films after irradiation process.

TABLE 3 The Fitting Results and the Corresponding 3D Orientational Structures Obtained for P2 Films

		Film parameters					
Film	Film irradiation conditions	d, μm	n_x	n_y	n_z	$\langle n \rangle$	Film structure
Irradiation with $\lambda = 365$ nm (x polarization)							
P2-1	Before irradiation	1.448	1.569	1.574	1.540	1.561	negative C film
	Under irradiation (365 nm, 30 mWcm^{-2})	1.441	1.549	1.566	1.547	1.554	positive A film
	After irradiation	1.455	1.551	1.550	1.549	1.55	isotropic film
Irradiation with $\lambda = 457$ nm (x polarization)							
P2-2	Before irradiation	1.408	1.621	1.555	1.517	1.564	locally biaxial
	Under irradiation (457 nm, 100 mWcm^{-2})	1.408	1.529	1.652	1.531	1.571	positive A film
	After irradiation	1.403	1.535	1.652	1.533	1.573	positive A film
Combined irradiation with $\lambda = 365$ nm and $\lambda = 457$ nm							
P2-1	Irradiation with $\lambda = 365$ nm (non-polarized, 30 mWcm^{-1}, 30 min) and, subsequently, with $\lambda = 457$ nm (100 mWcm^{-2}, 30 min, x polarized).	1.457	1.525	1.655	1.525	1.568	positive A film

The conditions at which the films where measured after irradiation depended on several factors. The measurement of $R^{TM}(\varphi_1,t)$ after turning off the pump light reveals that relaxation strongly depends on the polymer structure as well as on the irradiation conditions. In all polymers, after $\lambda_{ex2} = 457\,\text{nm}$ irradiation, the relaxation is very weak (modes shift is small). In contrast, in the case of $\lambda_{ex2} = 365$ nm irradiation, the relaxation process is quite important, as it can be seen in Figures 4 and 5. The relaxation time τ obtained from $R^{TM}(\varphi_1,t)$ curve was strongly dependant on polymer: for polymer P1, $\tau \leq 10$ min, whereas for polymers P2 and P3 $\tau > 2\,\text{h}$. The time constants τ should be determined by the lifetime of unstable Z form and the orientational relaxation of polymer chains. Taking into account the obtained values of τ, P1 films were tested 15 min after irradiation when equilibrium state is established. P2 and P3 films were measured 10 min after irradiation, and for different delays, several hours after, since relaxation times are substantially longer than measuring time.

TABLE 4 The Fitting Results and the Corresponding 3D Orientational Structures Obtained for P3 Films

		Film parameters					
Film	Film irradiation conditions	d, μm	n_x	n_y	n_z	$\langle n \rangle$	Film structure
Irradiation with $\lambda = 365$ nm (x polarization).							
P3-1	Before irradiation	3.338	1.620	1.627	1.645	1.631	positive C film
	Under irradiation with $\lambda = 365$ nm, 50 mWcm^{-1}	3.451	1.601	1.604	1.609	1.605	isotropic film
	After irradiation	3.420	1.613	1.616	1.621	1.617	isotropic film
Irradiation with $\lambda = 457$ nm (x polarization)							
P3-2	Before irradiation	1.737	1.538	1.534	1.555	1.542	positive C film
	After irradiation with $\lambda = 457$ nm (100 mWcm^{-1})	1.758	1.521	1.577	1.580	1.559	negative A film
Combined irradiation with $\lambda = 365$ nm and $\lambda = 457$ nm							
P3-2	Irradiation with $\lambda = 365$ nm (non-polarized, 30 mWcm^{-1}, 30 min) and, subsequently, with $\lambda = 457$ nm (100 mWcm^{-2}, 30 min, x polarized).	1.722	1.512	1.571	1.582	1.555	negative A film

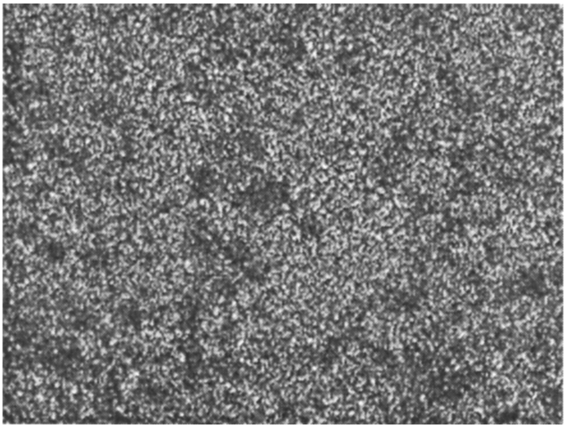

FIGURE 6 Photomicrograph of P1 film showing its optical texture. Angle between polarizer and analyzer is 90°. Magnification x400.

Independently of the wavelength of pumping light, P1 films *after irradiation*, show properties of positive A plate having their optic axis oriented in-plane of the film. This means that azochromophores are uniaxially aligned in the film plane. Their ordering axis is perpendicular to the polarization direction of pumping light. This conclusion is in full agreement with that obtained for P1 polymer by null ellipsommetry method [5,6]. As can be concluded from Table 2, the orientation realized under irradiation with $\lambda_{ex1} = 365$ nm strongly depends on the pumping intensity. The uniaxial in-plane alignment is generated when $I < 50$ mWcm^{-2}, whereas the film is spatially isotropic under the pumping with $I > 80$ mWcm^{-2}. The isotropic state seems to be influenced by the high concentration of non-mesogenic Z isomers destroying orientational order. The quite interesting phenomenon is a restoration of strong orientational order in P1 films after relaxation, even if they were isotropic under irradiation. This phenomenon implies some orientational memory more likely to be caused by ordering of polymer matrix, which persists even when the order of azochromophores is destroyed [16].

The difference in the orientational order under irradiation and just after irradiation is not so pronounced for P2 and P3 films. However, in big contrast to P1 films, the induced orientation strongly differs for the two pumping conditions: the P2 films irradiated with $\lambda_{ex1} = 365\,\text{nm}$ are isotropic, while they exhibit in plane uniaxial orientation (structure of positive A plate) with $\lambda_{ex2} = 457\,\text{nm}$ irradiation. The P3 films also have isotropic structure after $\lambda_{ex1} = 365\,\text{nm}$ irradiation. However, the $\lambda_{ex2} = 457\,\text{nm}$ irradiation induces a negative A plate structure. In this case the azochromophores are oriented randomly in the plane perpendicular to polarization direction of pumping light. The kind of structure should be expected when light factor plays dominant role in the ordering process, like in amorphous polymers. The different structure (the structure of positive A plate) realized in P1 and P2 polymers, suggests that, in these LC materials, the actinic light initiates strong self-ordering processes, which might be influenced by the boundary conditions.

The results presented in Tables 3 and 4 show that preliminarily irradiation of P2 and P3 films with non-polarized UV light ($\lambda_{ex1} = 365\,\text{nm}$) does not influence the order induced with $\lambda_{ex2} = 457\,\text{nm}$ (the order of positive A plate and negative A plate, respectively). This implies that the order (disorder) preliminarily induced with UV light is completely erased and the resulted order determines by the last irradiation process.

4. CONCLUSIONS

Thus, ATR method is an effective tool for the study of 3D orientational order in LC azopolymers. It permits the estimation of the orientation of azochromophores in any stationary or quasi-stationary state reached before, after or under irradiation. The results obtained with ATR method are in full agreement with those earlier obtained with the null ellipsommetry. This confirms their high reliability.

Some of the ordering regularities we observed for the studied polymers are listed bellow:

1. the structures corresponding to stationary states of the studied films (realized before, during and after irradiation) are uniaxial or spatially isotropic. The latter case corresponds only to intensively pumped polymers.
2. the order induced in a photo-stationary state can be substantially different from that in a stationary state reached after irradiation.
3. the tail substitutes in azochromophore strongly influence 3D orientation. The change of the tail substitute in the order $NO_2 \rightarrow OCH_3 \rightarrow OC_4H_9$ leads to a) transition from the structure of negative C plate to the structure of positive C plate (non-irradiated films), b) increase of the tendency of isotropic ordering (by $\lambda_{ex1} = 365\,\mathrm{nm}$ irradiation), and C) transition from the structure of positive A plate to the structure of negative A plate (by $\lambda_{ex2} = 457\,\mathrm{nm}$ irradiation).
4. in case of multi-step irradiation, the resultant stationary 3D orientation is determined by the last irradiation process.

The observed spatial order is a result of a number of factors, such as irradiation conditions, polymers structure determining photochemistry and self-ordering properties of polymers, and, probably, other factors not well studied yet (interfacial interaction, film preparation conditions *etc.*). The detailed analysis of these factors will be given in a forthcoming paper.

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