Light induced structures in liquid crystalline side-chain polymers with azobenzene functional groups

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We applied ellipsometry to study the distribution of azobenzene fragments in the films of two types of comblike polymers with azobenzene moieties in the side chains before and after ultraviolet (UV) light irradiation. The polymer with an alkyl chain at the end of the azobenzene fragment forms structures with preferred homeotropic alignment of the fragments. Irradiation of this polymer with nonpolarized UV light at normal incidence induces a homeotropic alignment of azobenzene fragments. Oblique irradiation induces tilted structures. Polarized UV light irradiation at normal beam incidence induces biaxial structures with a fanlike distribution of azobenzene fragments and preferably out-of-plane alignment. The polymer with polar nitro group at the end of the azobenzene moiety shows preferential in-plane orientation. The degenerate in-plane alignment is retained for normal irradiation with nonpolarized UV light. Excitation with polarized light provides highly ordered in-plane alignment of the azobenzene fragments perpendicular to the UV light polarization. Re-orientation of the fragments. (© 2001 American Institute of Physics. [DOI: 10.1063/1.1351157]

I. INTRODUCTION

The phenomenon of light induced anisotropy refers to a material's ability to show birefringence and dichroism as a result of irradiation by actinic light. The parameters of induced anisotropy depend on the irradiation conditions; direction of the induced axis of anisotropy depends on the direction of polarization of exciting light, while the value of the induced birefringence and dichroism on the irradiation dose. Materials featuring this phenomenon have found applications in optical data storage, holography, and photo-switching of optical elements.^{1–4} The effect of light induced anisotropy was also applied for alignment of liquid crystals (LC).^{5,6}

Among a variety of photosensitive materials, azobenzene derivatives demonstrate relatively high values of the induced anisotropy that is caused by a high-absorption dichroism in its azobenzene units. Processes taking place during the irradiation of azobenzene compounds were extensively studied for different azobenzene containing media including viscous solutions of azobenzene molecules,⁷ Langmuir–Blodgett films,⁸ and polymers with azobenzene moieties that are chemically linked to a backbone (azopolymers).^{1–4,9–15} The latter materials have the advantage of high stability of the induced anisotropy.

In equilibrium the material consists mainly of azobenzene fragments in the lower energy trans conformational state. The trans isomers are elongated and may be considered approximately as rigid rods. A transition dipole moment for absorption of the trans isomers is oriented almost along the long molecular axis. The probability of light absorption is proportional to the projection of the isomer transition dipole moment on the electric vector of the incident light E. The azobenzene fragments that are oriented along the direction of the light polarization absorb light with much higher probability than the fragments oriented in all directions perpendicular to the light polarization. Light excitation of the dye fragments causes reversible trans-cis isomerizational transitions. The exited molecules relax to the lower energy trans state; however, the orientation of the molecules after the light absorption process is different from the original one. After the multiple acts of trans-cis transformations, the medium approaches a photo-steady state with azobenzene fragments oriented perpendicular to the direction of the exciting light polarization. Reaching this state, the molecules are excluded from the further reorientation. As a result, the vast majority of the azobenzene moieties reorient perpendicular to the vector E.

Being part of a polymer molecule, the azobenzene fragments influence the orientation of the polymer chains. The photo-induced orientation of the azobenzene fragments can

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involve the nonabsorbing fragments of the polymer in the reorientation process.^{10,11} This effect is important for the stability of induced anisotropy.¹²

A high polarizability along the long molecular axis of the azobenzene fragments in the *trans* conformation determines birefringence effects for the light outside the absorption band. The refractive index for the light polarized along the long molecular axis n_e is higher than the refractive indices in all the directions perpendicular to the long molecular axis n_o . Similar to low weight rodlike liquid crystals, the azobenzene moieties possess positive birefringence $\Delta n = n_e$ $-n_o > 0$, where n_e and n_o are the refractive indices for the extraordinary and ordinary waves, respectively.

The vast majority of publications concerning light induced anisotropy in azopolymer films consider a twodimensional distribution of the azobenzene fragments in the plane of the film. In fact, the polarized absorption and birefringence measurements used in these studies were carried out for normal incidence of the testing light beam. These methods allowed the authors to study the anisotropy induced in the plane of the films only (an ''in-plane'' anisotropy). $^{13-15,20-22}$ However, it is natural to assume a three-dimensional distribution of azobenzene fragments.^{16,17} Indeed, there are many directions perpendicular to the polarization direction of the exciting light. These directions form a plane that is perpendicular to the vector E. Thus, the ordering of the fragment perpendicular to the film surface (an "out-of-plane" anisotropy) should be taken into account. As an example, out-of-plane alignment of azobenzene fragments can be induced by nonpolarized UV light at normal beam incidence.^{18,19} In this case, the only direction that is perpendicular to the electric field vectors is the direction of the light propagation inside the polymer medium.

A three dimensional supramolecular ordering induced in azopolymers by light depends on a variety of factors, such as a chemical structure of the polymer molecules, interactions between polymer fragments and boundary conditions. We will show the influence of these factors on the distribution of the azobenzene fragments in two types of polymers.

In our work we studied the average spatial distribution of azobenzene fragments after irradiation by actinic UV light. The induced birefringence was measured with the light probe outside the absorption band of the polymer. We used a null ellipsometry technique to obtain differences between three principal refractive indices assuming an effective biaxiality of the films. The preferred orientation of the azobenzene fragments was estimated according to an assumption that the material possesses a higher polarizability and, hence, a higher refractive index for the extraordinary wave for the light polarized in the direction of the long molecular axis. At this point, we would like to stress that the induced structures can show an effective biaxiality, however, the molecules that form them are rod-shaped and exhibit uniaxial polarizabilities. The absolute values of the refractive indices needed for the calculations of birefringence were obtained using refractometry.



FIG. 1. Chemical structure of polymers P1 (a) and P2 (b), respectively.

II. EXPERIMENT

We studied two types of azopolymers with chemical formulas presented in Fig. 1. Both materials are comblike polymers with azobenzene fragments in side chains connected by flexible alkyl spacers to the polymer backbone. Side chains of the polymer *P*1 [Fig. 1(a)] contain polar NO₂ groups. The side chains in polymer *P*2 [Fig. 1(b)] have hydrophobic alkyl groups C₄H₉ attached to the azobenzene moiety. The difference in the chemical structure of the side chains was expected to influence the difference in the supramolecular structure of azobenzene moieties.

Due to flexibility of alkyl spacers, the azobenzene fragments can rotate relatively freely in the polymer matrix. Since their concentration in the polymer is high enough, they can form mesophases within some temperature intervals. Azobenzene fragments of polymer *P*1 form smectic *A* and nematic mesophases within the temperature range 44° –52 °C and 52°–55 °C, respectively. Polymer *P*2 demonstrates a reentrant nematic mesophase within the temperature interval 112°–140 °C. Both polymers are solids at room temperature.

The azopolymer films were fabricated by a spin coating technique. Polymers P1 and P2 were dissolved in toluene and dichloroethane, respectively, up to concentrations of 10% by weight. The solutions were spin coated on glass substrates at spinning speeds of 1500–3000 rpm. We used two types of substrates: Pre-cleaned microscope glass slides and the glass substrates covered with polyimide alignment layers. We studied the influence of different types of polyimide alignment layers on the orientation of the azobenzene fragments in the polymer films: The rubbed polyimide 3510 and nonrubbed polyimide 7511L, both from Nissan Corp. The thickness of the films was measured using a profilometer manufactured by Tencor Instruments.

To induce the anisotropy in the samples of azopolymers, we used the light of a Xe lamp from Oriel Corp. The irradiation density used in the experiments was 3, 20, or 90 mW/cm² in the wavelength range of 326-400 nm. To provide the irradiation of the samples with polarized light, we used a dichroic UV polarizer supplied by Oriel Corporation and operable in the wavelength range of 230-770 nm.



FIG. 2. Ellipsometry setup.

The light induced birefringence in the films was measured outside the polymer absorption band using an ellipsometry technique described in the following section. The setup included a low power He–Ne laser (λ =632.8 nm), two calcite Glan–Thompson polarizers mounted on rotational stages from Oriel Corp., a Babinet–Soleil compensator adjusted to produce the same retardation as a quarter wave plate for the light wavelength of λ =632.8 nm and a sample holder mounted on the rotational stage by Oriel Co. The light intensity was measured with a photodiode connected to a Keithley Instruments multimeter. The setup was automatically controlled by a personal computer. The rotation accuracy was better than 0.2°.

The absolute value of one of the refractive indices in the plane of the film was measured using Abbe refractometer. The measurements were taken with the light from a sodium lamp (λ =589.6 nm). In some cases, we have been able to measure three principal refractive indices independently. The calculated differences between three principal indices agreed with the birefringence data obtained by ellipsometry. The typical values for the ordinary ray of the smaller in-plane refractive index in the direction perpendicular to the polarization of the exciting UV light were $n_0 = n_x = 1.6$ and 1.58 for the polymers P1 and P2, respectively.

III. THE APPLICATION OF SENARMONT TECHNIQUE TO BIREFRINGENCE MEASUREMENTS

To measure the light induced birefringence in polymer films, we used a transmission ellipsometry (polarimetry) technique with fixed positions of a polarizer and a quarter wave compensation plate (Fig. 2).²³ The polarizer is fixed with its transmission axis at 45° to the horizontal direction. The analyzing part of the system consists of the quarter wave plate and the rotating analyzer. The optic axis of the quarter wave plate is parallel to the transmission axis of the polarizer. When the system does not contain the investigated sample, the analyzer is crossed with the polarizer producing no light leakage through the system. This is the starting position for the analyzer.

Let us consider a uniform film with two principal dielectric axes in the film plane and the third axis perpendicular to the film surface. n_x and n_y refer to the principal indices in the plane of the film along the horizontal and vertical, respectively, and n_z to that normal to the film. The light passing through the polarizer has two equal orthogonal components

along the vertical and horizontal directions. Entering the sample at normal incidence, the two components propagate through the sample as eigenmodes. Ellipticity (ratio of the lengths of major and minor axes of the ellipse of polarization) of light exiting the sample depends on the phase shift between the ordinary and extraordinary waves. The quarter wave plate converts the elliptically polarized light into linearly polarized light with the direction of polarization determined by the phase shift between the two eigenmodes. This direction is found by rotation of the analyzer to a position of minimum light transmission at an angle φ which is connected to the in-plane retardation of the sample $(n_y - n_x)d$ as $(n_v - n_x)d = \lambda \varphi/180$ (d and λ are film thickness and light wavelength, respectively) for the case of normal light incidence. This method used for the in-plane birefringence measurements only is known as the Senarmont technique. It can be extended for oblique light incidence. In this case, the angle φ depends on the in-plane retardation $(n_y - n_y)d$, the out of plane retardation $(n_z - n_x)d$ and the absolute value of one of the refractive indices of the biaxial film, for example, n_x . The angle φ can be calculated as a function of light incidence angles θ of the testing beam assuming a certain sample configuration. The results of optical calculations can be compared with the experimental data.

We performed calculations for the angle φ by using Berreman's 4×4 matrix method.²⁴ Maxwell's equations for the light propagation through the system of polarizer, sample and quarter wave plate were solved numerically. The result of the calculations is components of the electric field vector represented by four Stokes parameters. The measured value of φ is connected to the Stokes parameters S_1 and S_2 as φ $=45^{\circ}-\operatorname{atan}(S_2S_1)$. The problem has a unique solution for some strict sample geometries including biaxial films with the principal dielectric axes in the plane of sample and uniaxial films with arbitrary optic axis orientation. The sample can be considered as a stack of uniaxial or biaxial layers. This sample configuration allows one to study various optic axis distributions. The light coming out of the quarter wave plate is almost linear polarized when the system analyzes the phase shift between two orthogonal eigenmodes of the sample. To meet this requirement, the direction of n_x (or $n_{\rm v}$) has to be oriented along the horizontal (or vertical). In the case of the uniaxial film, the projection of its optic axis has to be aligned with horizontal direction.

We measured the phase shift versus incidence angle curves for two orthogonal geometries with n_x axis at horizontal and vertical direction, respectively. The in-plane retardation is directly calculated from head-on phase shift as $(n_y - n_x)d = \lambda \varphi_{\text{head-on}}/180$. The relationship between the inplane and out-of-plane indices influence the curvature of the measured φ versus θ curves. Thus, the only fitting parameter is the out-of-plane retardation $(n_z - n_x)d$. The best match for the experimental curve is considered to be a model for the crystallographic configuration.

The last step is to connect the estimated relationship between three principal refractive indices with the orientation of the azobenzene fragments. The highest index for the azobenzene fragment appears in the direction of the long molecular axis. Thus, the direction of highest index would



FIG. 3. Measured (\bullet) and modeled (solid line) curves for analyzer angle φ vs light incidence angle θ for polymer *P1* on untreated glass substrate (a) and correspondent distribution of azobenzene fragments (b).

coincide with the preferred orientation of the azobenzene fragments. In the next section, we apply this method to an analysis of three-dimensional (3D) structures induced in azopolymer films.

IV. RESULTS AND DISCUSSION

A. Structure of nonirradiated azopolymer films

Figure 3(a) shows the experimentally measured curves of the phase shift φ versus incidence angle θ for the polymer with nitro groups (P1) on an untreated glass substrate. There is no phase shift for normal light incidence (θ =0). This indicates equality of the two in-plane indices: $n_y = n_x$. However, the film possesses out of plane birefringence (n_z $-n_x$)d= -40 nm that causes a phase shift at oblique light incidence. Curve fitting gives the out-of-plane index n_z smaller than the two in-plane indices: $n_z < n_x = n_y$ and Δn_{zx} $= n_z - n_x \sim -0.08$. The film shows negative birefringence with the optic axis perpendicular to the film surface. The relationship between the three indices suggests that the azobenzene fragments are randomly distributed in the plane of the film with no preferred direction for their orientation (a degenerate in-plane distribution) [Fig. 3(b)].



FIG. 4. Measured (\bullet) and modeled (solid line) curves for analyzer angle φ vs light incidence angle θ for polymer *P2* on untreated glass substrate (a) and correspondent distribution of azobenzene fragments (b).

the polymer with alkyl groups (*P*2) coated on untreated glass substrates. Similar to the polymer *P*1, the in-plane birefringence is negligibly small $\Delta n_{yx} = n_y - n_x \approx 0$. Contrary to the previous case, the film is characterized by positive out-of-plane birefringence: $(n_z - n_x)d=35$ nm $(\Delta n_{zx} = n_z - n_x \sim 0.085)$ and $n_z > n_x = n_y$. The film of the polymer *P*2 is a positive uniaxial medium with the optic axis normal to the film surface featuring a homeotropic alignment of azobenzene fragments [Fig. 4(b)].

In order to elucidate the influence of the anchoring conditions, we studied the alignment of polymers on two types of alignment layers: Glass plates with rubbed PI 3510 and PI 7511L with no rubbing, respectively. The choice of these layers was determined by their strong anchoring of rodlike thermotropic liquid crystals. Our previous studies showed that the rubbed PI 3510 yields a planar alignment of cyanobiphenyl compounds contrarily to layers of nonrubbed PI 7511L that provide the homeotropic alignment.

The polymer with nitro groups (P1) shows a uniform in-plane distribution of azobenzene fragments on PI 7511L coating, while polymer with alkyl groups (P2) forms structures with preferable homeotropic alignment on both types of substrate. We detected in-plane birefringence $n_y - n_x = 0.2$ and $n_z - n_x = 0$ in polymer P1 films on rubbed PI 3510, indicating a uniaxial alignment of the azobenzene fragments along the rubbing direction.

The studies show that the influence of standard alignment layers on the orientation of azobenzene fragments is weak excluding the case when the in-plane orientational or-

Figure 4(a) shows the measured φ versus θ curves for

dering of the azobenzene fragments is induced in polymer with nitro groups (P1) by a rubbed polyimide substrate. We associate the preferable orientation of azobenzene fragments with interactions between the molecular fragments of the polymers. The in-plane distribution of azobenzene fragments in polymer P1 can be explained by assuming in-plane alignment of the backbones and a strong interaction of the polar nitro group of the azobenzene moiety with the main chain fragments. The preferred homeotropic alignment of the azobenzene fragments of the polymer with alkyl groups (P2) may possibly be determined by the hydrophobic functional group at the end of the moiety and its weak interactions with the polymer backbones.

B. Structures induced by nonpolarized light

In studies of structures in *P*1 and *P*2 induced by nonpolarized UV light, we distinguished 2 cases: Normal beam incidence and oblique beam incidence at the angle of 45° with respect to the film normal. The intensity of the recording beam varied from 11 to 90 mW/cm². The time of irradiation was 20 min.

The irradiation of polymer with nitro groups (P1) with nonpolarized light of low intensity does not change the degenerated in-plane distribution of azobenzene fragments (n_z $-n_x = -0.08$, $n_y - n_x = 0$). However, we observed the transition from planar to homeotropic structure in the case of a high-intensity actinic beam ($I=90 \text{ mW/cm}^2$). This result was anticipated according to a general consideration that the fragments should accumulate in the direction of light propagation.

The irradiation of the polymer with alkyl groups (P2) increases the out-of-plane ordering of azobenzene fragments even in the case of low light intensity. The maximum induced out-of-plane birefringence reached $n_z - n_x = 0.27$ that is significantly higher than the initial value $n_z - n_x = 0.08$.

Figure 5(a) shows the measured φ versus θ curves for the film of the polymer with alkyl groups (P2) irradiated with a nonpolarized beam at an oblique incidence of 45°. The asymmetry of the curves suggests an oblique or splayed optic axis distribution of the positive uniaxial medium [Fig. 5(b)]. We modeled the optical behavior of this structure as a uniaxial film with an oblique optic axis. The calculated value of the birefringence according to the modeling is $n_e - n_o$ ~0.26. The optic axis is tilted in the plane of incidence of the excitation beam at the angle ~22° with respect to the film's normal. The tilt angle is much less than expected according to Snell's law. Thus, as a result of tilted irradiation of the azo-polymer P2 with nonpolarized light, the initial homeotropic orientation of the azobenzene fragments changes to a slightly tilted orientation.

The oblique irradiation of polymer *P1* films induced the structures that cannot be described within the applied models. The asymmetry of $\varphi(\theta)$ curves suggests complicated, possibly, tilted, distribution of azobenzene fragments.





FIG. 5. Measured (Φ, \bigcirc) and modeled (solid and dashed lines) curves for analyzer angle φ vs light incidence angle θ for polymer *P2* irradiated with nonpolarized UV light at oblique incidence (a) and correspondent distribution of azobenzene fragments (b). Curves correspond to two sample positions when the projection of optic axis is along vertical (1) and horizontal (2) directions, respectively.

C. Structures induced by polarized light

The irradiation of polymer films with polarized UV light at normal incidence induces in-plane birefringence and changes the relationship between the three principal refractive indices in both polymers.

Figure 6(a) shows the measured φ versus θ curves for the polymer with nitro groups (P1) after 15 min of UV light irradiation. The intensity of the recording beam was 11 mW/cm². Curves 1 and 2 correspond to vertical and horizontal azimuths of actinic UV light polarization, respectively. According to the modeling, positive phase shift corresponds to the axis in the horizontal direction having the higher inplane refractive index n_y perpendicular to UV light polarization and the lower in-plane index n_x . Curve fitting gives the following relationship between the three refractive indices: $n_y - n_x = 0.3 [(n_y - n_x)d \approx 30 \text{ nm}], (n_z - n_x)d = 0 \text{ nm}, n_y$ $> n_x = n_z$. The light induced structure is positive uniaxial with the optic axis perpendicular to the UV light polarization. In this case, the azobenzene fragments show planar



FIG. 6. Measured (Φ, \bigcirc) and modeled (solid and dashed lines) curves for analyzer angle φ vs light incidence angle θ for polymer *P1* irradiated with polarized UV light at normal incidence (a) and correspondent distribution of azobenzene fragments (b). Curves correspond to two sample positions when the direction of UV light polarization is along vertical (1) and horizontal (2) directions, respectively.

alignment perpendicular to the UV light polarization [Fig. 6(b)].

Figure 7 shows the measured φ vs θ curves for the polymer with alkyl groups (*P*2) irradiated under the same experimental conditions. Similar to the previous case, the higher index n_y is perpendicular to the direction of UV light polarization. However, the relationship between the three principal indices is different: $n_y - n_x \approx 0.025 [(n_y - n_x)d \approx 10 \text{ nm}]$ and $n_z - n_x \approx 0.12 [(n_z - n_x)d = 50 \text{ nm}]$, $n_z > n_y > n_x$. This suggests a fanlike distribution of the azobenzene fragments in the plane that is perpendicular to the direction of light polarization. However, the orientational order of the molecules giving rise to this in-plane birefringence is less than that for the homeotropic orientation discussed previously.

We studied kinetics of orientation of azobenzene fragments under polarized UV light irradiation with a light intensity of 20 mW/cm². Birefringence measurements were taken at the same irradiation site after successive periods of irradiation. The time between the finish of each irradiation step and taking the birefringence measurement was long enough to reach equilibrium. Figure 8 shows the measured values of induced in-plane and out-of-plane optical retarda-



FIG. 7. Measured (\bullet, \bigcirc) and modeled (solid and dashed lines) curves for analyzer angle φ vs light incidence angle θ for polymer *P*2 irradiated with polarized UV light at normal incidence. Curves correspond to two sample positions when the direction of UV light polarization is along vertical (1) and horizontal (2) directions, respectively.

tion $(n_y - n_x)d$ and $(n_z - n_x)d$, respectively, versus time of irradiation for the polymer P1. Before the UV light was applied, the azobenzene fragments were distributed uniformly in the plane of the film $(n_z < n_x = n_y)$ [Fig. 3(b)]. The irradiation of the polymer P1 redistributes the fragments in the plane of the film such that they align perpendicular to the direction of UV light polarization [Fig. 6(b)]. This process increases the difference between two in-plane refractive indices. At the photo-steady state, the film is a positive uniaxial medium with the optic axis perpendicular to the UV light polarization $n_y > n_x = n_z$ [Fig. 6(b)]. The value of induced birefringence Δn_{yx} is higher than 0.25.

Figure 9 shows kinetics for light induced ordering in polymer P2. The azobenzene fragments of the nonirradiated film have the preferred homeotropic alignment: $n_z > n_y = n_x$ [Fig. 4(b)]. Contrary to the polymer P1, the UV light induces relatively low in-plane birefringence with the maximal value $n_y - n_x = 0.045$ [$(n_y - n_x)d \approx 10$ nm]. Simultaneously, the



FIG. 8. Birefringence kinetics in polymer *P*1 under polarized UV light irradiation: Measured curves for in-plane (1) and out-of-plane (2) optical retardation, respectively.

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FIG. 9. Birefringence kinetics in polymer P2 under polarized UV light irradiation: Measured curves for out-of-plane (1) and in-plane (2) optical retardation, respectively.

out-of-plane birefringence increases to $n_z - n_x = 0.3$ [$(n_z - n_x)d = 70$ nm]. The photo-steady state is characterized by the high ordered uniaxial homeotropic alignment of the azobenzene fragments.

The studies of kinetics of orientation in the two types of polymers under polarized UV light irradiation indicate the differences in orientational behavior of the azobenzene fragments depending on chemical structure of main and side chains. The azobenzene fragments with polar nitro groups retain their preferred in-plane alignment. Irradiation by polarized UV light induces planar alignment of the fragments in the direction perpendicular to the projection of light polarization. The azobenzene fragments with alkyl functional groups prefer the homeotropic alignment. Small in-plane birefringence induced by low dose polarized light is transient. The photo-steady state for this polymer is characterized by highly ordered homeotropic alignment. The photo-steady state for both polymers is uniaxial. This uniaxiality of photosteady structures may be a consequence of mesomorphic properties of the azobenzene fragments.

D. Re-orientation phenomena

To study the re-orientation of the azobenzene fragments, we initially irradiated the films of polymers P1 and P2 with polarized UV light. The time of the irradiation was adjusted to get maximum possible in-plane birefringence for the given film. After the process was completed, we rotated the polarizer in the azimuthal plane and continued irradiation process. We took the birefringence measurements at the same irradiation site after subsequent irradiation steps.

Rotation of the UV light polarization by the azimuthal angle of 90° destroys the in-plane ordering in the polymer with alkyl function groups (*P*2). Homeotropic ordering of azobenzene fragments increases with increase of irradiation dose similar to the case of prolonged nonpolarized UV light irradiation.

The process of re-orientation of the azobenzene fragments in the polymer with nitro groups (P1) depends on the azimuthal angle between the initial and the new direction of



FIG. 10. Re-orientation kinetics in polymer P1 under polarized UV light irradiation: Measured curves for out-of-plane (1) and in-plane (2) optical retardation, respectively.

the UV light polarization. If this angle is 45°, the optic axis of the film gradually rotates 45° in the plane of the film. This process takes place without significant changes in the film's texture and without change of planar alignment.

The re-orientation of the azobenzene fragments of the polymer with nitro groups (P1) is more complicated when the direction of the UV light polarization makes an angle of 90° to the initial one. Figure 10 shows the curves for the in-plane $(n_y - n_x)d$ and out-of-plane $(n_z - n_x)d$ retardation values versus irradiation time. The initial film has the optic axis along y direction and in-plane retardation $(n_y - n_x)d$ = 58 nm, $(n_z - n_x)d = 0$ nm. Pumping of the film with light polarized along the y direction decreases the in-plane and increases the out-of-plane birefringence. The point of the intersection of the two curves $(n_y - n_x)d = (n_z - n_x)d$ (n_x) $\langle n_{y} = n_{z} \rangle$ corresponds to a negative uniaxial film with the optic axis along the x direction. This indicates the degenerate distribution of the azobenzene fragments in the plane yoz that is perpendicular to the direction of the initial UV light polarization. Further pumping decreases the in-plane birefringence $(n_v - n_x)d$ to zero in a favor of the out-of-plane refractive index $n_z:(n_v-n_x)d=0$ nm, $(n_z-n_x)d=50$ nm $(n_x = n_y < n_z)$. At this point the film is positive uniaxial with homeotropic alignment of the azobenzene fragments. The following increase of the irradiation dose decreases the outof-plane birefringence $n_z - n_x$. At the same time, the absolute value of in-plane birefringence $n_y - n_x$ increases and changes sign. This indicates the in-plane alignment of some of the azobenzene fragments. The order of molecules giving rise to in-plane birefringence is less than that for the preferred homeotropic alignment. The structures are similar to the fan-like distribution of the azobenzene fragments observed in polymer P2 after low dose polarized irradiation. The reorientation process involves out-of-plane rotations of the azobenzene fragments that is not observed during the initial orientation.

During the re-orientation, the texture of the sample changes significantly from the uniform planar alignment to a grainy polydomain structure. We observed light scattering typical for transition phenomena. The process provokes strong distortions of the alignment of the azobenzene fragments. It can produce different biaxial structures. Figure 10 depicts schematically the main features of the process; however, it lacks accuracy of detail because of the huge distortions.

The re-orientation phenomena observed in the film of the polymer with alkyl groups (P1) under polarized UV light irradiation are similar to the reorientation of low-molecular weight liquid crystals (LCs) induced by electric field.²⁵ In the latter case, the reorientation is a process without a threshold if the angle between the LC director and an external field is less than 90°. However, when the director of the liquid crystal makes a 90° angle with respect to the direction of the electric field, strong director distortions occur. The process is accompanied by strong light scattering typical for transient phenomena.

V. CONCLUSIONS

We studied the spatial structures formed in films of azobenzene polymers by polarized and nonpolarized UV light irradiation. The method we employed uses light outside the absorption band of the polymers and involves measurements of the in-plane and out-of-plane birefringence using the null ellipsometry technique. The distribution of the azobenzene moieties were obtained assuming that the refractive index for the light polarized along the long molecular axis is higher than the refractive indices in all perpendicular directions.

The structure of the spin-coated films strongly depends on the chemical structure of polymers molecules. The polymer with the alkyl functional group at the end of the azobenzene fragment (P2) forms structures with preferred homeotropic alignment of the fragments. The polymer with the polar nitro group at the end of the azobenzene moiety (P1) possesses a preference of in-plane alignment.

Homeotropic and tilted uniaxial structures were realized in the films of polymer with alkyl groups (P2) at normal and oblique incidence of nonpolarized light, respectively. The structures induced in the films of P1 under oblique irradiation display some optical characteristics of tilted structures but cannot be described as simple uniaxial films with tilted optic axis. The irradiation of the P1 films at the normal incidence does not change the original in-plane degenerate alignment. Homeotropic structures were induced only at the maximal intensities of the UV light used in our experiments.

The irradiation of the films of polymer with nitro groups (P1) with polarized light provides planar alignment of the azobenzene fragments in the direction perpendicular to the UV light polarization.

The irradiation of the films of polymer with alkyl groups (P2) with polarized light induces fanlike structures with small in-plane birefringence and preferred out-of-plane alignment of the azobenzene fragments. The illumination of this polymer with high UV doses provides highly ordered homeotropic alignment featuring high out-of-plane birefringence.

The process of the induction of anisotropy has saturation behavior. The photo-steady structures observed in both polymers are uniaxial. This could be connected with the mesogenic properties of studied polymers.

The reorientation of the azobenzene fragments of polymer with nitro groups (P1) with UV light polarization that is perpendicular to the initial polarization involves some outof-plane rotation of the fragments. The unfavorable out-ofplane movement of the azobenzene fragments in this polymer (''planar-homeotropic'' transition) was observed at high doses of UV light irradiation.

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