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### Light Induced Spatial Structures in the Liquid Crystalline Azopolymers

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## Light Induced Spatial Structures in the Liquid Crystalline Azopolymers

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We studied the 3D distribution of azobenzene fragments in the films of two comb-like liquid crystalline azopolymers before and after irradiation by actinic UV light using a null ellipsometry technique. The polymer with an alkyl chain  $C_6H_{13}$  at the end of the azobenzene fragment forms structures with preferred homeotropic alignment of the fragments. Polarized UV light irradiation at normal beam incidence induces biaxial structures with a preference for out-of-plane alignment of azobenzene fragments. High UV doses induce highly ordered homeotropic alignment of the fragments. The second polymer with polar  $NO_2$  group at the end of the azobenzene moiety shows preferential in-plane orientation. Excitation with polarized light provides a highly ordered in-plane alignment of the azobenzene fragments perpendicular to the UV light polarization.

**Keywords:** azopolymer; light induced anisotropy; ellipsometry

### 1. INTRODUCTION

The phenomenon of light induced anisotropy refers to materials having ability to show birefringence and dichroism when they are illuminated

by actinic light. The parameters of the induced anisotropy depend on the irradiation conditions. The direction of the induced axis of anisotropy depends on the direction of polarization of the exciting light, while the value of the induced birefringence and dichroism depend on the irradiation dose. Materials featuring this phenomenon have found applications in optical data storage, holography and photo-switching of optical elements<sup>[1-4]</sup>. The effect of light induced anisotropy has also been applied for alignment of liquid crystals (LC)<sup>[5]</sup>.

Among a variety of photosensitive materials, azobenzene polymers demonstrate relatively high values of the induced birefringence and dichroism. They are characterized by fairly high photosensitivity and thermal stability of the anisotropy.

Photo-orientation mechanisms in azopolymers have been intensively studied in the present decade<sup>[1-4, 6-8]</sup>. It is believed that optical anisotropy in films of these polymers is due to photo-induced alignment of azobenzene fragments. As a result of multiple acts of light absorption followed by deactivation of the excited state, highly dichroic azobenzene fragments reorient in such a way that their optical dipole moments become perpendicular to the direction of polarization of the exciting light. In this case, light absorption by the fragments reaches a minimum. The photo-induced orientation of the azobenzene fragments can involve the non-absorbing fragments of the polymer in the reorientation process<sup>[2,3]</sup>. This effect is important for stability of the induced anisotropy<sup>[8]</sup>.

The vast majority of publications concerning light induced anisotropy in azopolymer films consider a two-dimensional distribution of the azobenzene fragments in the plane of the film. 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)<sup>[1-8]</sup>. However, it is natural to assume a three-dimensional (3D) distribution of azobenzene fragments<sup>[9,10]</sup>. Indeed, in case of irradiation with polarized light 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 fragments perpendicular to the film surface (an “out-of-plane” anisotropy) should be taken into account.

Prior to our work, the light induced structures formed in azopolymers were studied by absorption measurements<sup>[9,11]</sup>. The resultant data were applied for calculations of spectral order parameters. The authors used several approaches to estimate the spatial distribution of azobenzene fragments. However, these approaches are associated with strong physical approximations and have limited range of application.

In our work we studied the average 3D distribution of azobenzene fragments before and after irradiation by polarized UV light using birefringence measurements. The induced birefringence was measured with the testing light 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. The absolute values of the refractive indices needed for the calculations of birefringence were obtained using refractometry.

## 2. EXPERIMENTAL DETAILS

### 2.1. Polymers.

We studied two types of azopolymers with chemical formulas presented in figure 1. Both materials are comb-like polymers with azobenzene fragments in side chains connected by flexible alkyl spacers to the polymer backbone. Side chains of the polymer P1 (figure 1a) contain polar  $\text{NO}_2$  groups. The side chains in polymer P2 (figure 1b) have

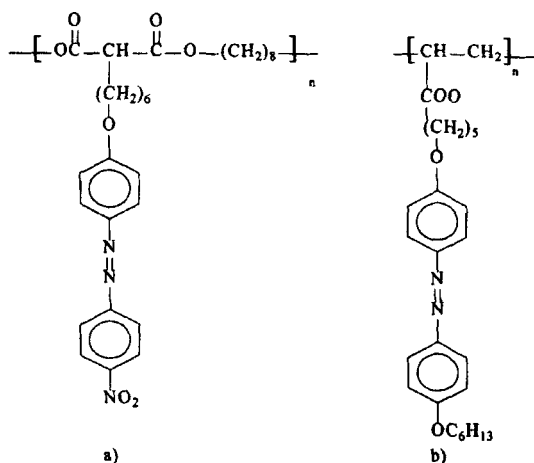


FIGURE 1. Chemical structure of polymers P1 (a) and P2 (b).

hydrophobic alkyl groups  $\text{C}_6\text{H}_{13}$  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

P1 form smectic A and nematic mesophases within the temperature range 44°-52°C and 52°-55°C, respectively. Polymer P2 demonstrates a reentrant nematic mesophase within the temperature interval 112°-140°C. Both polymers are solids at room temperature.

## 2.2. Sample Preparation.

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. The thickness of the films was measured with 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 density of polarized irradiation used in the experiments was 20 mW/cm<sup>2</sup> in the wavelength range of 326-400 nm. UV light was polarized using a dichroic UV polarizer supplied by Oriel Corporation and operable in the wavelength range of 230-770 nm.

## 2.3. Method and Experimental Setup.

To measure the light induced birefringence in polymer films, we used a transmission ellipsometry technique with fixed positions of a polarizer, quarter wave compensation plate and rotating analyzer (Figure 2)<sup>[12]</sup>. The quarter wave plate converts the elliptically polarized light passing through the sample into linearly polarized light. The rotation angle of the polarization plane of light after the phase plate can be found by rotation of the analyzer to a position of minimum light transmission at an angle

$\varphi$ . In case of the sample with dielectric axes  $x$ ,  $y$ , and  $z$  oriented, respectively, horizontally, vertically and along the direction of the incidence of the testing beam,  $\varphi$  is connected with the in-plane retardation of the sample  $(n_y - n_x)d$  as  $(n_y - n_x)d = \lambda\varphi/180$  ( $d$  and  $\lambda$  are film thickness and light wavelength, respectively).

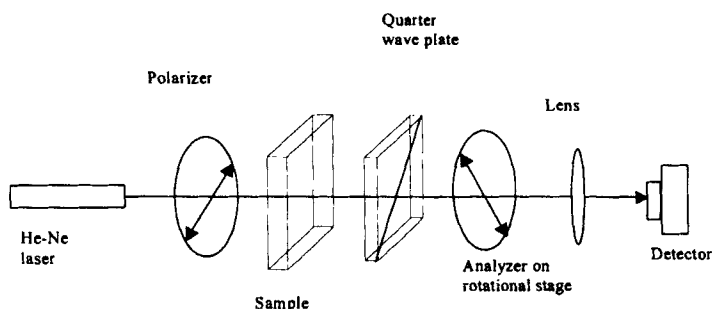


FIGURE 2. Ellipsometry setup.

This method used for in-plane birefringence measurements is known as the Senarmont technique. It can be extended for oblique light incidence. In this case, the angle  $\varphi$  depends on the in-plane retardation  $(n_y - n_x)d$ , 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  $\varphi$  can be calculated as a function of light incidence angles  $\theta$  of the testing beam assuming a particular optic axes distribution. Such calculations were carried out using Berreman's 4x4 matrix method<sup>[13]</sup>. The experimental curves  $\varphi(\theta)$  were fitted with the theoretical one. The absolute value of the refractive index measured by an Abbe refractometer was used in the fitting process.



The setup included a low power He-Ne laser ( $\lambda=632.8$  nm), two calcite Glan-Thompson polarizers mounted on rotational stages from Oriel Corp., a Babinet-Soleil compensator adjusted to produce the retardation of a quarter wave for the light wavelength of  $\lambda=632.8$  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  $0.2^\circ$ .

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

#### 3.1. Structure of Non-Irradiated Films.

Figure 3a shows the experimentally measured curves  $\phi(\theta)$  for the P1 polymer film on an untreated glass substrate. There is no phase shift for normal light incidence ( $\theta=0$ ). 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  $n_z$  as smaller than the two in-plane indices:  $n_z < n_x = n_y$  and  $n_z - n_x \sim -0.08$ . 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).

Figure 4a shows the measured  $\phi(\theta)$  curves for the polymer P2 coated on untreated glass substrates. Similar to the polymer P1, the in-plane birefringence is negligibly small  $n_y - n_x \approx 0$ . Contrary to the previous

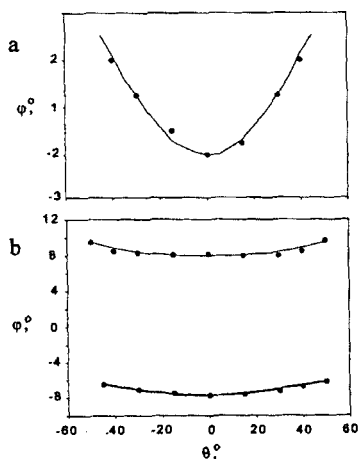


FIGURE 3. Curves  $\varphi(\theta)$  for P1 film before (a) and after (b) irradiation.

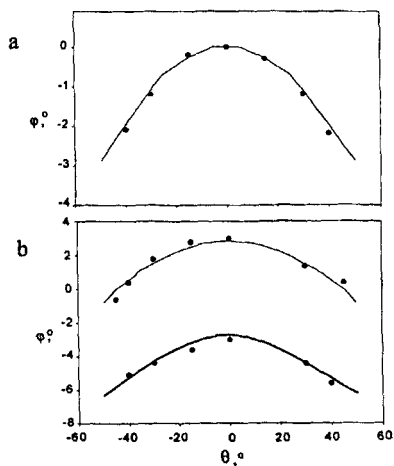


FIGURE 4. Curves  $\varphi(\theta)$  for P2 film before (a) and after (b) irradiation.

case, the film is characterized by positive out-of-plane birefringence :  $(n_z - n_x)d = 35 \text{ nm}$  ( $n_z - n_x \sim 0.085$ ) and  $n_z > n_x = n_y$ . The film of the polymer P2 is a positive uniaxial medium with the optic axis normal to the film surface featuring a preferred homeotropic alignment of azobenzene fragments.

We associate the preferred 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  $\text{NO}_2$  group of the azobenzene moiety with the

main chain fragments. The preferred homeotropic alignment of the azobenzene fragments of the polymer P2 may possibly be determined by the hydrophobic functional group at the end of the moiety and its weak interactions with the polymer backbones.

### 3.2. 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.

Fig. 3a and Fig.4a show the curves  $\varphi(\theta)$ , respectively, for P1 and P2 measured after 15 min of UV light irradiation with the intensity of 20 mW/cm<sup>2</sup>. 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 in-plane refractive index  $n_y$  perpendicular to UV light polarization and the lower in-plane index  $n_x$ . Curve fitting for P1 gives the following relationship between the three refractive indices:  $n_y - n_x = 0.3$  ( $(n_y - n_x)d \approx 30$  nm),  $(n_z - n_x)d = 0$  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 alignment perpendicular to the UV light polarization. For P2 film, similar to the film of P1, the higher index  $n_y$  is perpendicular to the direction of UV light polarization. However, the relationship between the three principal indices is different:  $n_y - n_x \approx 0.025$  ( $(n_y - n_x)d \approx 10$  nm) and  $n_z - n_x \approx 0.12$  ( $(n_z - n_x)d = 50$  nm),  $n_z > n_y > n_x$ . This suggests a biaxial structure characterized by a fan-like distribution of the azo-benzene fragments in the plane perpendicular to the direction of light

polarization. We studied the kinetics of orientation of azobenzene fragments under polarized UV light irradiation with a light intensity of 20 mW/cm<sup>2</sup>. Birefringence measurements were taken at the same irradiation site after successive periods of irradiation. The time between the end of each irradiation step and the taking of the birefringence measurement was long enough to reach equilibrium. Figure 5 shows the measured values of induced in-plane and out-of-plane optical retardation  $(n_y - n_x)d$  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. 3a). 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. This process increases the difference between the two in-plane refractive indices. In the photo-saturated state,

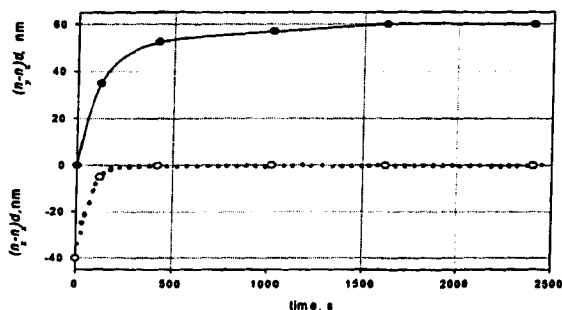


FIGURE 5. Birefringence kinetics in polymer P1 under polarized UV light irradiation.

the film is a positive uniaxial medium with the in-plane optic axis perpendicular to the UV light polarization  $n_y > n_x = n_z$ . The value of induced birefringence  $n_y - n_x$  is higher than 0.25. Figure 6 shows the kinetics for light induced ordering in polymer P2. The azobenzene fragments of the non-irradiated film have the preferred homeotropic alignment:  $n_z > n_y = n_x$ . 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 out-of-plane birefringence increases to  $n_z - n_x = 0.3$  ( $(n_z - n_x)d = 70$  nm). The photo-saturated state is characterized by a highly ordered uniaxial homeotropic alignment of the azobenzene fragments.

The studies of orientational kinetics in the two types of polymers under polarized UV light irradiation indicate the differences in orientational behavior of the azobenzene fragments depending on

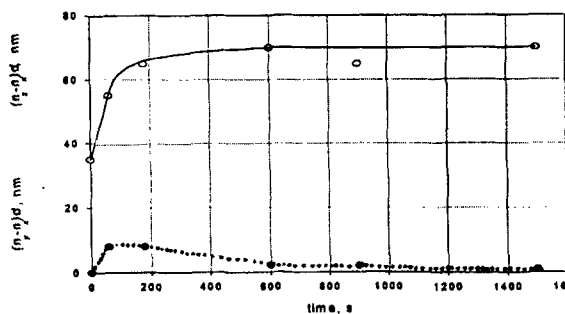


FIGURE 6. Birefringence kinetics in polymer P2 under polarized UV light irradiation.

chemical structure of main and side chains. The azobenzene fragments with polar groups retain their preferred in-plane alignment. Irradiation by polarized UV light induces planar alignment of the fragments in the direction perpendicular to the direction 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-saturated state for this polymer is characterized by highly ordered homeotropic alignment. Note that the photo-saturated state for both polymers is uniaxial. This uniaxiality could be connected with mesomorphic properties of the azobenzene fragments.

#### 4. CONCLUSIONS

We studied the 3D structures formed in the spin coated films of azobenzene polymers before and after polarized 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 a null ellipsometry technique.

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 group at the end of the azobenzene moiety (P1) possesses a preferential in-plane alignment.

The illumination of the films of P2 with polarized light induces fan-like 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 irradiation of the films of polymer P1 with polarized light provides planar alignment of the azobenzene fragments in the direction perpendicular to the UV light polarization featuring high in-plane birefringence.

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

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