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## 3D Orientational Structures in Azopolymers Studied by UV Absorption Method

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UV absorption method supplemented by null ellipsometry technique is applied for the estimation of spatial orientational structures of azopolymer layers. The components of the order parameter tensor of azobenzene fragments are estimated for the non-irradiated state as well as for the various irradiation doses. The method is applicable for the polymers with short life-time of *cis* photoisomers and in-plane uniaxial structure at some moment of structural changes.

**Keywords:** azopolymer; photo-induced anisotropy; spatial orientation

### INTRODUCTION

The well known for azopolymers phenomenon of photoinduced optical anisotropy (POA) is associated with molecular ordering under the light action. Absorbing light dichroic azobenzene fragments aspire to reorient perpendicularly to the direction of light polarization  $E$  where its absorption reaches minimum. Considering spatial case, there are many directions being perpendicular to  $E$ . Preferable directions are formed as

result of many factors (chemical structure, film preparation, irradiation conditions and the like).

Photoinduced orientational 3D structures in photosensitive media are studied fairly poor because of the lack of effective experimental methods. Recently we suggested null ellipsometry technique as a method for investigation of 3D structures in azopolymers<sup>[1]</sup>. However, since ellipsometry method operates with birefringence indices, it is suitable only for the investigation of generalized structures, which summarize order of various molecular fragments. For the study of the orientational order of definite molecular groups the various absorption methods are usually applied. In this case a wavelength of the testing light is justified to absorption maximum of the desirable molecular fragments. The absorption methods were widely used for the study of in-plane orientational ordering<sup>[2-5]</sup>. The only authors of<sup>[6, 7]</sup> suggested to use results of the IR absorption measurements for the estimation of spatial order in polymer films. The approach developed in these publications could be applied only to systems having in-plane uniaxial structure at some moment of investigation.

The idea of our work is to combine the null ellipsometry method (NEM) with UV absorption measurements for the more complete study of 3D orientational distributions of the absorbing azobenzene fragments. The NEM gives the general structure of polymer film, which is mainly determined by the distribution of azobenzene fragments. In addition, the UV absorption measurements in the absorption maximum of azobenzene fragments could be used for estimation of its order parameter. The efficiency of this combination is demonstrated.

## EXPERIMENTAL

### Samples

We used poly{octyl{(4-hexyloxy-4'-nitro)azobenzene}malonate} synthesis of which is described in<sup>[8]</sup>. The polymer was solved in

dichloroethane and spincoated on the quartz slabs. The prepared films were kept at the room temperature for 24 h for the evaporation of solvent. Irradiation of the films was done with the polarised irradiation of mercury lamp ( $I=5 \text{ mW/cm}^2$ ) at the incidence direction of the light close to the film normal.

### Method

The UV/Vis absorption measurements were carried out using PC conjugated spectrometer KSVU (LOMO, Russia). A testing beam of deuterium lamp was polarized and directed normally to the film plane. At first UV/Vis spectrum of the original film was measured. Afterwards the wavelength of the testing light was justified to absorption maximum of azobenzene fragments. Absorption components in the direction of exciting light polarization  $E$  and perpendicularly to  $E$  were measured. We mark them  $D_x$  and  $D_y$ , respectively.

The out-of-plane absorption component  $D_z$  (imaginary component corresponding to propagation direction of the testing light lying in-plane of the film) was estimated using method proposed in [6, 7]. If at some moment  $t_0$  the sample has uniaxial structure with in-plane position of the axis of anisotropy, the equation  $D_z(t_0)=D_x(t_0)$  takes a place and the total (spatial) absorption could be estimated as

$$D_{total} \equiv D_x(t_0) + D_y(t_0) + D_z(t_0) = 2D_x(t_0) + D_y(t_0) \quad (1)$$

In case of conservation of the number of *trans* azobenzene units the total absorption is constant and value of  $D_z$  at each moment  $t$  can be determined as

$$D_z(t) = D_{total} - D_x(t) - D_y(t) \quad (2)$$

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

Kinetic dependencies of  $D_x$ ,  $D_y$  and  $D_z$  contain information about reorientation direction of azobenzene chromophores as well as its ordering rates as it is shown bellow.

## RESULTS AND DISCUSSION

The UV/Vis spectra of studied compound have intensive absorption band with the maximum at  $\lambda=377$  nm corresponding to  $\pi\pi^*$  transition of *trans* azobenzene fragments (Fig.1). The wavelength of the testing beam was justified at this value. The spectral changes induced by the actinic UV light were reversible with the time constant of about 5 min.

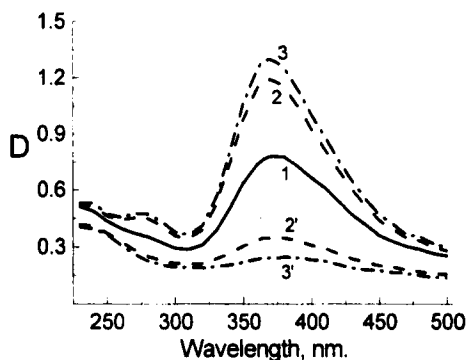


FIGURE 1 UV spectra of azo-polymer film measured: 1-before irradiation, 2, 2' - just after irradiation, 3, 3' - in 20 min after irradiation. Curves 2, 3 corresponds for the component  $D_y$ , 2', 3' -  $D_x$ .

Measurements of the components  $D_x$  and  $D_y$  were carried out in 15 min after finishing of each irradiation period in order to obtain complete relaxation of azobenzene units to initial state.

The experimentally measured absorption components  $D_x$  and  $D_y$  corresponding to different irradiation doses are presented in

Fig.2a. Kinetic of  $D_x$

and  $D_y$  is typical for reorientation mechanism of azobenzene units <sup>[9]</sup>. Both curves  $D_x(t)$  and  $D_y(t)$  demonstrate saturation. As it was earlier shown by null ellipsometry method <sup>[11]</sup> the saturated state of the film of studied polymer is fitted as uniaxial structure with the in-plane orientation of the axis of anisotropy. In this case  $D_z = D_x$  and the method described in <sup>[7, 8]</sup> could be applied for estimation of  $D_z$  at various irradiation doses. The values of  $D_z$  calculated using (1)-(2) are presented in Fig.2a. Analyzing dependencies  $D_x(t)$ ,  $D_y(t)$  and  $D_z(t)$  one can conclude that the photoinduced ordering arises first of all from the in-

plane reorientation of azobenzene fragments in the  $y$  direction. In addition, slight reorientation from  $z$  to  $y$  direction takes a place.

The orientational structure in a general case is describable by the tensor  $S_{ij}$ , which has a diagonal form when the coordinate axes coincide with the principle axes of the film. The diagonal terms  $S_{xx}$ ,  $S_{yy}$  and  $S_{zz}$  are connected with the absorption components  $D_x$ ,  $D_y$  and  $D_z$  [6]. For example

$$S_{xx} = \frac{D_x - \frac{1}{2}(D_y + D_z)}{D_x + D_y + D_z} \quad (3)$$

The components  $S_{yy}$  and  $S_{zz}$  can be obtained from (3) by the cyclic permutation in expression (3).

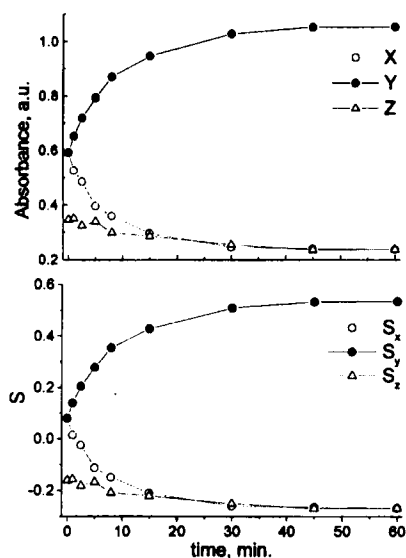


FIGURE 2 Dependencies of the principle absorption coefficients (a) and components of the order parameter (b) on irradiation time.

The values of  $S_{xx}$ ,  $S_{yy}$  and  $S_{zz}$  calculated using equation (3) are presented in Fig.2b. One can conclude that the initial stage of irradiation is characterized by biaxiality, whereas the photosaturated stage by uniaxial orientation with order parameter close to 0.7. As it was assumed in [1], uniaxiality in the saturated state could be caused by mesomorphic properties of azobenzene fragments. The action of actinic light can be considered as a factor stimulated selforganization peculiar to mesophases.

From this point of view the realized structure is a result of photoreorientation and selfassembling processes in the film.

## CONCLUSION

Thus, UV absorption method supplemented by the null ellipsometry technique is effective tool for investigation of the features of spatial ordering in azopolymer films demonstrating preferable in-plane alignment of azobenzene fragments. This method clearly detects spatial rearrangement of chromophores under irradiation. More of that, it allows to calculate the order parameter components of the original structures of the films as well as structures at various stages of irradiation.

## Acknowledgement

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