

New Azodyes for LC Photoalignment and Optical Films

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ABSTRACT

New series of highly anisotropic azodyes with a strong absorption in the visible range is developed. The potential of these materials for LC photoalignment is studied and their utility for LCD optical films is discussed. The mechanisms of the molecular photoordering in the azodye films are considered.

1. INTRODUCTION

Presently, azodyes, at first used in textile industry, are of great interest for a number of photonic applications, such as non-linear optics, telecommunications, information displaying and storage. Among this variety of applications one can distinguish applications related to LCD, particularly LC alignment layers, polarizers and retardation films. All these LCD parts are based on anisotropic films. In addition to other methods, the anisotropy of azodye films can be generated by the actinic light action. This photochemical method of anisotropy generation attracts great attention because of avoidance of direct mechanical contact, simplicity and reproducibility.

As the aligning films for LCD, azodyes were at first proposed by Ichimura et al. [1]. They reported reversible homeotropic – planar alignment transition on the layers of azodye molecules chemically linked to the substrates. Later on, Gibbons and Shannon [2] observed excellent planar LC alignment on the films of azopolymers. As the third important stage, one can admit results of Chigrinov et al. [3] related to LC alignment on the thin azodye films, physically adsorbed on the boundary substrates. For this purpose, hydrophilic azodyes were selected to prevent dye solution in LC. By this way, uniform planar and tilt LC alignment was achieved. It was thermally and, more surprisingly, highly photostable, in spite of photosensitivity of azodyes.

In the other application, dichroic azodyes are used as materials for dichroic polarizers [4]. This application requires compounds with strong absorption dichroism in a whole visible range. In one more application, azodye materials can be used as retardation films for LCD. This application requires the films with strong optical birefringence.

In the present research we study new azodyes from the point of view of LCD applications mentioned above. We also discuss the photoordering model allowing us to explain experimental data.

2. EXPERIMENTAL

2.1. Aligning materials

The chemical formulas of azodyes used are presented in Fig. 1. The dyes Azo1-Azo3 are new synthesized dyes, while SD1 is a dye earlier intensively studied [3].

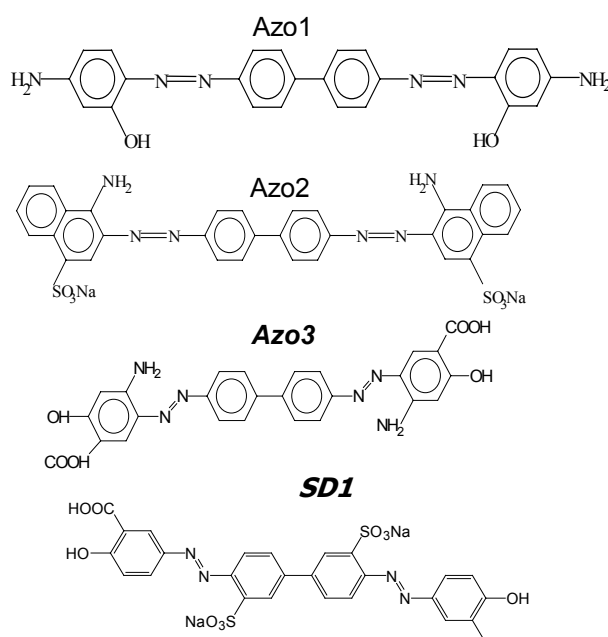


Fig. 1. Structural formula of azodyes

In contrast to SD1, new azodyes do not contain any side substitutes in a biphenyl core. Instead, they contain NH₂ fragment in the terminal aromatic rings, which can influence polarity of azofragments. The calculations show that Azo2 is strongly polar molecule, while Azo1 and Azo3 are substantially weaker polarized.

Fig. 2 shows UV/Vis spectra of the dye's films. One can see that, compared with SD1, spectra of Azo dyes are shifted to the visible range. The shift is especially strong for Azo2 having naphthalene terminal groups that enhance molecular π conjugation.

2.2. Aligning films and their characterization

The dyes were dissolved in DMF at weight concentrations 0.5 %. The films were spin coated from these solutions on the glass slides at the conditions: 1,500 rpm, 80 s following with 2,500 rpm, 50 s. Before coating dye films, glass plates were thoroughly washed with a soap water, backed and subsequently cleaned in a ozone cleaner. According to our results, this cleaning procedure substantially improves adhesion and so quality of azodye films. After coating, the films were backed at 100 °C over 1 h to remove solvent remained.

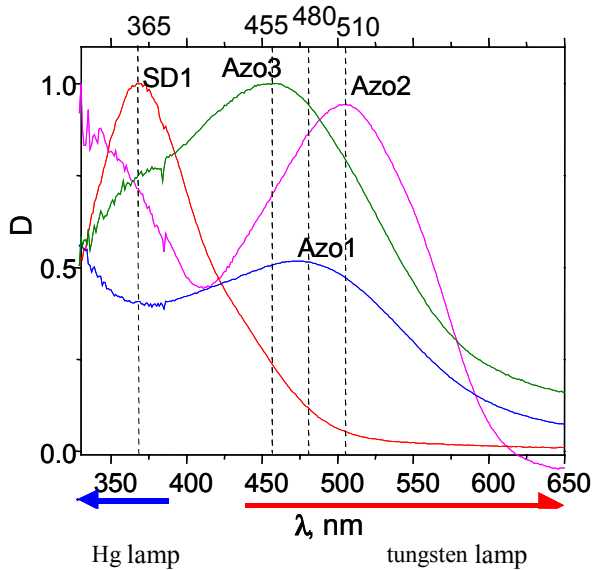


Fig. 2. UV/Vis spectra of azo dyes. Arrows below schematically represent spectral composition of exciting light.

For the induction of anisotropy in azodye films we used UV irradiation of Xe lamp (working with a cut off UV filter) or full spectrum irradiation of tungsten halogen lamp generating light in the visible (Vis) range. The intensity of polarized UV irradiation was 9-12 mW/cm². The azodye films were irradiated with the polarized light at the normal incidence. The spectral range of the exciting light, with respect to the absorption spectra of dyes, is schematically presented in Fig. 2.

The UV/Vis spectra of azodye films were measured by Perkin Elmer spectrometer. The photoinduced in-plane retardation in the films was measured using the method described in [5].

2.3. LC alignment tests

The LC cells were constructed by sandwiching the LC between a pair of glass/ITO substrates coated with azodye and irradiated as described above. Two types of LC cells have been used: (1) one substrate is dye coated substrate, while the second one has a rubbed polyimide layer (asymmetric cells); and (2) both substrates are dye coated and assembled in an antiparallel fashion (symmetric cells). The asymmetric cells were used to determine the direction of LC alignment and azimuthal anchoring on the dye containing substrate. The symmetric cells were used to measure LC pretilt angle by crystal rotation method. The cell gap was kept with spacers of 5.5 μm and 20 μm in diameter. We used LC K15 and MLC 5700-000 from Merck.

3. RESULTS AND DISCUSSION

3.1. Photoalignment tests

In case of UV irradiation, Azo2 films demonstrate good alignment comparable with that on SD1 films (Fig. 3). The pretilt angle on these films is close to zero, while azimuthal anchoring energy ranges 0.5-1.0 10⁻⁵ J/cm², i.e. comparable with the value for SD1. However, exposure dose required for good alignment in case of

Azo2 is two times higher then in case of SD1. The alignment achieved for Azo1 and Azo3 films was considerably poorer then for Azo2 films.

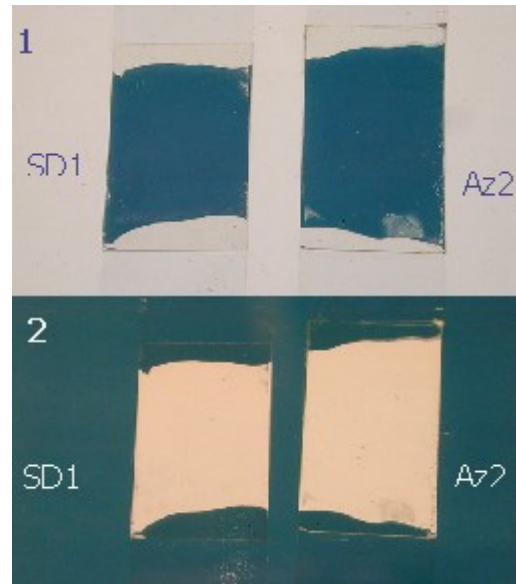


Fig. 3. Photos of two combined cells viewed between two polarizers. The cells have, respectively, SD1 and Azo2 photoaligning substrate. Cases (1) and (2) correspond to parallel and crossed polarizers, respectively. LC MLC 5700-000 is filled. d= 20 μm.

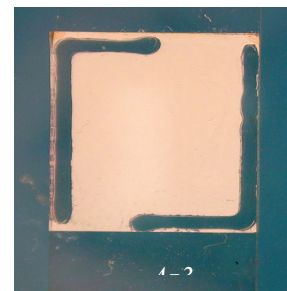


Fig. 4. Photo of symmetric cell based on Azo3 aligning films viewed between a pair of crossed polarizers. LC K15 is filled. d= 5.5 μm.

In case of Vis light irradiation, good alignment quality is achieved for Azo2 and Azo3 films (Fig. 4). The azimuthal anchoring coefficient is comparable with those for SD1. However, good alignment requires very long time of irradiation; about 1 h for Azo2 and Azo3 and 20 min for SD1. So, same as in UV irradiation case, new dyes require substantially higher dose of irradiation.

Let us discuss briefly possible reasons of the difference in irradiation dose for SD1 and Azo1-Azo3. Fig. 2 shows that Azo1-Azo3 dyes, in contrast to SD1, do not have intensive absorption bands in the UV range. Indeed, the most intensive $\pi\pi^*$ bands are in the visible range. In UV range, only Azo2 dye has second band that may explain its better aligning properties. It is more difficult to explain why alignment dose for SD1 is lower then for Azo1-Azo3 in case of Vis light excitation. To clarify the problem, the mechanisms of the molecular photoordering in azodye films have been studied.

3.2. Mechanisms of the Molecular Photoordering

Fig. 5 shows polarized spectra of SD1 and Azo1 films before and after irradiation with UV light. Before irradiation, the spectra corresponding to testing light.

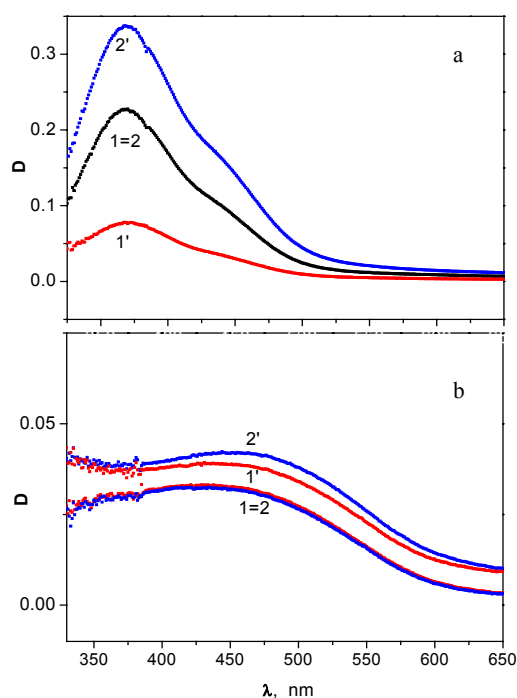


Fig. 5. Polarized UV/Vis spectra of SD1 (a) and Azo1 (b) before (1,2) and after (1',2') irradiation with linearly polarized UV light from Xe lamp. 1 and 1' correspond to $D_{||}$ polarization component, while 2 and 2' to D_{\perp} component.

Polarization, E_t , parallel and perpendicular to the polarization of excitation light, E_{ex} ($D_{||}$ and D_{\perp} components, respectively) overlap. This means that initially both films are in-plane isotropic. Due to the polarized UV irradiation $D_{||}$ and D_{\perp} polarization components split, but this splitting is different for SD1 and dyes from Azo series. In case of SD1, D_{\perp} grows, while $D_{||}$ falls down. This reflects reorientation of azodye molecules in the direction perpendicular to E_{ex} (angular redistribution mechanism of the photoinduced anisotropy (PIA) [6]). In Azo1 film, UV irradiation leads to the increase of $\pi\pi^*$ absorption band for both polarizations, but $D_{\perp} > D_{||}$. The increase of $\pi\pi^*$ absorption reflects the increase of the number of *trans* isomers due to the *cis-trans* photoisomerization. The simultaneous increase (decrease) of $D_{||}$ and D_{\perp} components is typical for the photoselection mechanism of PIA [6]. The ratio $D_{\perp} > D_{||}$ implies preferable alignment of *trans* isomers perpendicularly to E_{ex} . It is not consistent with the *cis-trans* photoselection, which results in $D_{||} > D_{\perp}$. This disagreement might be explained by the influence of photoreorientation increasing part of *trans* isomers in the direction perpendicular to E_{ex} .

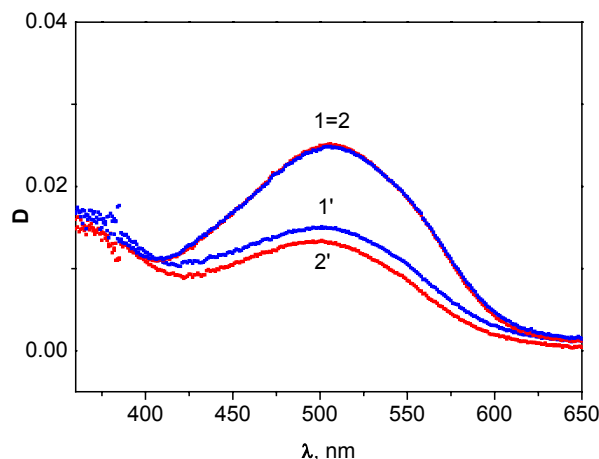


Fig. 6. Polarized UV/Vis spectra of Azo2 before (1,2) and after (1',2') 1h irradiation with linearly polarized Vis light from tungsten halogen lamp. 1 and 1' correspond to $D_{||}$ polarization component, while 2 and 2' to D_{\perp} component.

In case of Vis excitation, spectral changes in SD1 film are rather similar to the UV excitation case; they show photoreorientation of SD1 molecules perpendicularly to E_{ex} . In Azo1 film, both $D_{||}$ and D_{\perp} components decrease, at that $D_{\perp} > D_{||}$. This corresponds to the photoselection mechanism of PIA.

The additional information about photoordering in the azodye films gives the phase retardation kinetic. Fig. 7 presents such kinetic curves for the case of Vis excitation. In SD1 film, monotonous change of the photoinduced phase retardation is observed (decrease in our coordinate system). The shutting down of excitation results in enhancement of the phase changes, similarly to the results described for some azopolymers [7]. In the Azo1 film, the induced phase retardation changes non-monotonously: it rapidly grows, reaches maximum and then gradually decreases changing a sign. In the first period of irradiation, the induced changes fully relax after shutting down the light. With the increase of irradiation dose, phase retardation level, reached in the process of relaxation, is lower than before irradiation. These regularities might be explained assuming two ordering mechanisms with different signs and characteristic times. First of them, characterized by the molecular orientation perpendicular to E_{ex} , slow recording and relaxation, might be connected with the *trans-cis* excitation and accompanying photoselection. This agrees well with spectral changes in Fig. 6. The second mechanism, characterized by the molecular orientation along E_{ex} , as well as by the fast recording and relaxation, is not completely clear. It might be connected with *cis-trans* or other photoselection, photoinduces absorption/desorption, thermal activation, etc.

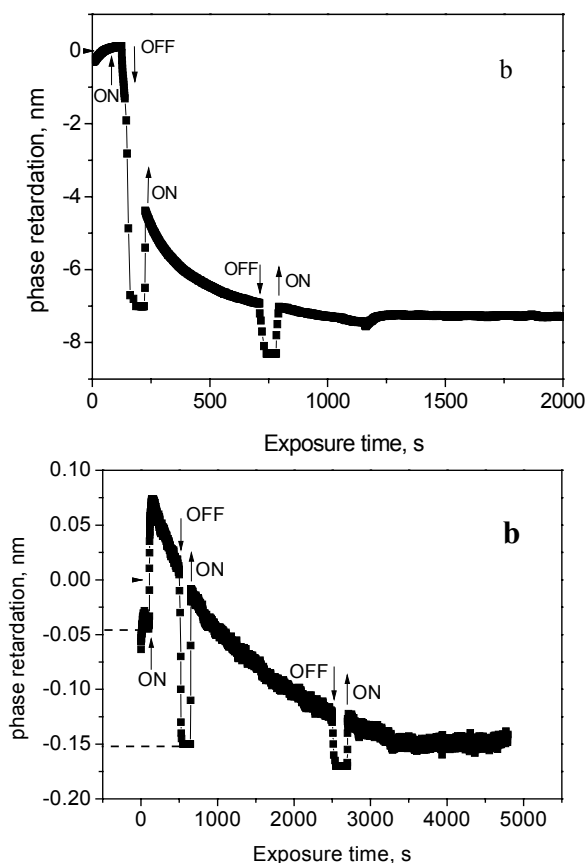


Fig. 7. Recording and relaxation kinetics of the photoinduced phase retardation in SD1 (a) and Azo1 (b) films. The films are irradiated with Vis polarized irradiation of tungsten lamp.

As a general conclusion, the anisotropy in SD1 films is preferably induced due to the mechanism of photoreorientation, while in the Azo1-Azo3 films the photoselection mechanism prevails. The reason of this is unclear yet and, possibly, it is connected with the chemical structure of the dyes. Noteworthy that SD1 contains NaSO_3 groups in the biphenyl core, while dyes of Azo series have non-substituted biphenyl core. This may influence adhesion of dye molecules to the glass substrate, character of photoisomerization, and so ordering peculiarities in the thin films.

4. CONCLUSIONS

The dyes of Azo series demonstrate good LC aligning properties. However, exposure dose for the achieving good alignment is 2-3 times higher than for SD1. This might be caused by different mechanisms of the molecular photoordering in Azo1-Azo3 and SD1 dyes. The photoordering in SD1 is realized through the photoreorientation yielding high ordering rate. The major ordering mechanism in Azo dyes is photoselection associated with a poorer order compared with the photoreorientation [7]. In spite of this difference in the ordering rate, the Azo dyes provide excellent LC alignment with strong azimuthal anchoring comparable with LC anchoring on SD1. The higher irradiation dose in case of Azo dyes is a result of non-proper excitation. As we believe, in case the wavelength of excitation is adjusted at the $\pi\pi^*$ absorption maximum of Azo dyes, the photoreorientation ordering mechanism will be realized

and the exposure dose for good alignment will be reduced. The realization of photoreorientation may substantially increase absorption dichroism and birefringence of Azo films and so its attraction for the dichroic polarizer and optical retarder applications. These advantages might be achieved by substituting traditional irradiation sources (e.g., Hg and Xe lamps) by the non-traditional ones, for instance lasers generating intensive lines in the visible range.

The other way to realize a highly ordered state of Azo dyes is its alignment in anisotropic matrices (LC, stretched polymers, etc.). This method allows to avoid adjustment of the excitation spectrum to the absorption spectrum of Azo dye. By this way one can also increase thickness of the film and so phase retardation and/or optical density to optimize them for certain application (compensation film, dichroic film polarizer, etc.).

The results for Azo series show how the intensive absorption of azodyes in the Vis range can be achieved. Particularly, it can be realized by substituting terminal aryl fragments by the fragments of naphthalene type. This might be quite important for the development of broad band dichroic polarizers for the Vis range.

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