Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Investigation of Volume Absorption Anisotropy of Complex Anisotropic Structures

Anatoli Murauski [a] , Alexander Muravsky [a] & Vladimir Agabekov [a]
[a] Institute of Chemistry of New Materials NAS Belarus, Skariny St., 36, Minsk, Republic of Belarus
Version of record first published: 11 May 2012.

To cite this article: Anatoli Murauski , Alexander Muravsky & Vladimir Agabekov (2012): Investigation of Volume Absorption Anisotropy of Complex Anisotropic Structures, Molecular Crystals and Liquid Crystals, 559:1, 179-185

To link to this article: http://dx.doi.org/10.1080/15421406.2012.658707

Mol. Cryst. Liq. Cryst., Vol. 559: pp. 179–185, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.658707

Taylor & Francis
Taylor & Francis Group

Investigation of Volume Absorption Anisotropy of Complex Anisotropic Structures

ANATOLI MURAUSKI, ALEXANDER MURAVSKY,* AND VLADIMIR AGABEKOV

Institute of Chemistry of New Materials NAS Belarus, Skariny St., 36, Minsk, Republic of Belarus

Linear polyconjugated π-systems are rod-like molecular structures possessing mesogenic properties. Oriented layers of such materials demonstrate dichroic absorption of light. Prevailing absorption along long molecular axis of π-system, gives ground to study molecular distribution in the layer though polarizer light absorption. We derived equations to investigate light propagation in the layer with anisotropic absorption. If principle axes are known, series of polarized absorption spectra measurements in combination with sample rotation allow to measure volume absorption of the layer along x-, y-, z- axes to determine s_x, s_y, and s_z order parameters of complex anisotropic structure. We investigated molecular reorientation dynamic of azo dyes (Reversible Intermolecular Bonding photoalignment materials) upon polarized light exposure. According to experimental results, for layers with thickness below quarter wavelength of observation, the Pointing vector (light energy) propagate through absorbing anisotropic structure without refraction, while at thickness few times greater the wavelength of observation, refraction is observed.

Keywords Absorption anisotropy; anisotropic structure; volume anisotropy

Introduction

Analysis of light propagation in an anisotropic medium is a complicated problem. If the medium has an anisotropic absorption the problem of light propagation can be found in some special cases. The reverse problem for determination of absorption anisotropy and orientation of the principal axes in crystal is investigated in mineralogy for determination of absorbance ellipsoid indicatrix of electromagnetic radiation in anisotropic minerals [1,2]. The method was developed for crystal materials with weak absorbance. Another application of anisotropic absorbance is for the determination of molecular orientation in cases where small amounts of dye are dissolved in the tested material systems [3]. The example of such systems utilized for liquid crystal (LC) displays are thin film polarizers on the bases of uniaxial [4] or biaxial [5], like discotic, anisotropic materials. Development of photoalignment technology for LC display [6,7], thin film polarizers, retardation films require additional information on the absorption anisotropy inside the films and development of methods for

*Address correspondence to Alexander Muravsky, Institute of Chemistry of New Materials NAS Belarus, Skariny St., 36, Minsk, Republic of Belarus. E-mail: alexander.muravsky@ichnm.basnet.by

determination of the principal axes of absorption ellipsoid of the thin layers. In the case of thin layers, orientation of a principal axis is determined by the geometry of the film—one axis is oriented perpendicular to the surface, while the other two lay in the plane of the thin film. The common problem for such films is determination of the relation between the values of absorption along the principal axes. To solve this complex problem we developed new simple method for investigation of volume absorption anisotropy of thin film samples.

To investigate, we used linear polyconjugated π-systems with rod-like molecular structures possessing the mesogenic properties. Oriented layers of such materials demonstrate dichroic absorption of light. Prevalent absorption along long molecular axis of π-system, gives ground to study molecular distribution in the layer though polarized light absorption. Also we investigated the molecular reorientation dynamic of azo dyes (RIB photoalignment materials [8]) upon polarized light exposure and derived equations to investigate the light propagation in the layer with anisotropic absorption.

Theory

Construction of the analytical dependence that successfully fit the experimental data requires utilization of certain reasonable models. Here it is necessary to note that, in the general case, the dye film is an anisotropic media, where all wave refractive indexes and absorption coefficients are different: $n_1 \neq n_2 \neq n_3$ and $\alpha_1 \neq \alpha_2 \neq \alpha_3$. Moreover, in contrast to the isotropic media, in anisotropic media the propagation direction of the light wave and the light ray that carries the energy (Poynting's vector) are not the same. This means that different types of equations formalize either a wave or ray optics approach, depending on the effect under investigation. The effects related to energy, like light absorption, should be described by the ray optics studying the light ray propagation. Thus the latter calculations are made for the Poynting vector related to the energy transfer.

Anisotropy absorption measurement techniques can be understood if the following optical problem is considered: absorption of polarized light with incident at angle γ_i by absorbing film of thickness d. Figure 1 shows the two possible geometries for s- and p-polarized incident light. Here we chose a sample rotation axis along the x-coordinate principle axis of the dye film, which is determined by the first exposure as described above. Let's relate the parameters of the medium with indexes 1, 2 and 3 to the x, y and z axes, respectively. The yz-plane is the plane of incidence. The electric vector of incident light coincides with the x-axes for s-polarization geometry. In this case, the refractive index and absorption coefficient do not change with the incident angle and are n_1 and α_1 respectively.

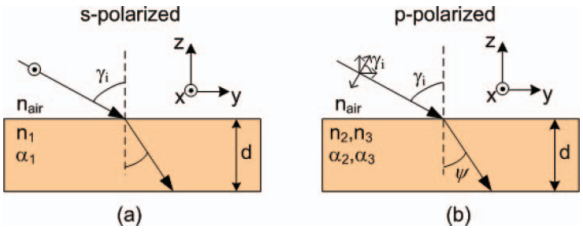

Figure 1. Absorption ellipsometry geometries for (a) s-polarized and (b) p-polarized light.

Absorption for s-polarized case for different incident angles is

$$A_s = \alpha_1 d \left[\cos\left(\arcsin\left(\frac{\sin\gamma_i}{n_1} \right) \right) \right]^{-1} \tag{1}$$

where γ_i – incident angle or the angle of substrate rotation; x-axis – rotation axis of ellipsometry; n_1, n_2, n_3 and α_1, α_2, α_3 – are the principle refractive indexes and absorption coefficients of light along x, y, z – directions, d – film thickness.

Remember that the wave refractive index and the ray refractive index are different in anisotropic medium. For the complex case of p-polarization geometry the ray refractive index is the next [9]:

$$n_r(\psi) = \sqrt{n_2^2 \sin^2\psi + n_3^2 \cos^2\psi} \tag{2}$$

where ψ – is the ray propagation angle in the uniaxial medium.
It can be shown using the Fermat principle that the Law of ray refraction at the interface of the uniform isotropic and the uniaxial anisotropic mediums is the next [8]

$$n_{air} \sin\gamma_i = \frac{n_2^2}{n_r(\psi)} \sin\psi \tag{3}$$

Due to absorption in the material the light ray dissipates its energy in two orthogonal directions, thus for p-polarized light absorption depends on the ray propagation angle as following:

$$A_p = (\alpha_2 \cos^2\psi + \alpha_3 \sin^2\psi)\frac{d}{\cos\psi} \tag{4}$$

$$A_p = \left[\alpha_2 \frac{n_r^2(\gamma_i)}{n_2^4} \sin^2\gamma_i + \alpha_3 \left(1 - \frac{n_r^2(\gamma_i)}{n_2^4} \sin^2\gamma_i \right) \right] \frac{d}{\sqrt{1 - \frac{n_r^2(\gamma_i)}{n_2^4} \sin^2\gamma_i}}$$

where nair = 1, $n_r(\gamma_i)$ is expressed from equations (2) and (3) as following:

$$n_r(\gamma_i) = \frac{n_2 n_3}{\sqrt{n_2^2 - \frac{n_2^2 - n_3^2}{n_2^2} \sin^2\gamma_i}} \tag{5}$$

In the case of linear dyes, the direction of E-field absorption coincides with the long molecular axis. The distribution of linear dyes in the layer with a xyz-coordination system is shown in Fig. 1. Average orientation of long molecular axes of all dye molecules is given by the unitary vector $\langle \vec{n} \rangle$ with components $\langle n_x \rangle$, $\langle n_y \rangle$ and $\langle n_z \rangle$, which are the mean projections of long molecular axes on x - ,y - and z - axis respectively. Note, the total absorption given as the sum of light absorptions along each axis is constant:

$$\alpha_x + \alpha_y + \alpha_z = const \tag{6}$$

Since light intensity is the square of E-field, normalized absorption of light intensity along x-axis is determined by mean square projection, as:

$$\frac{\alpha_x}{\alpha_x + \alpha_y + \alpha_z} = \langle n_x^2 \rangle \tag{7}$$

By definition the order parameter of uniaxial dyes layer is given as [10]:

$$s = \frac{1}{2}(3\langle n^2\rangle - 1) \tag{8}$$

Uniaxial order parameters can be expressed from absorption coefficients in the next way:

$$s_x = \frac{1}{2}\left(\frac{2\alpha_x - \alpha_y - \alpha_z}{\alpha_x + \alpha_y + \alpha_z}\right); s_y = \frac{1}{2}\left(\frac{2\alpha_y - \alpha_x - \alpha_z}{\alpha_x + \alpha_y + \alpha_z}\right); s_z = \frac{1}{2}\left(\frac{2\alpha_z - \alpha_y - \alpha_x}{\alpha_x + \alpha_y + \alpha_z}\right) \tag{9}$$

Experiment

To investigate absorption anisotropy, three different types of films were used: a standard Iodine polarizer NPF-F1225DU from Nitto Denko, Japan (uniaxial absorbing film), a Discotic dye polarizer N015, Optiva, USA (biaxial absorbing film), and a thin film of photoaligned azo dye with thickness about 20 nm.

Optical schemes shown in Figs. 2 and 3 were implemented to perform measurements. Probing s- and p- polarized light with polarization parallel and perpendicular to the sample rotation axis, respectively, were used. Step motors rotated the sample with an accuracy of

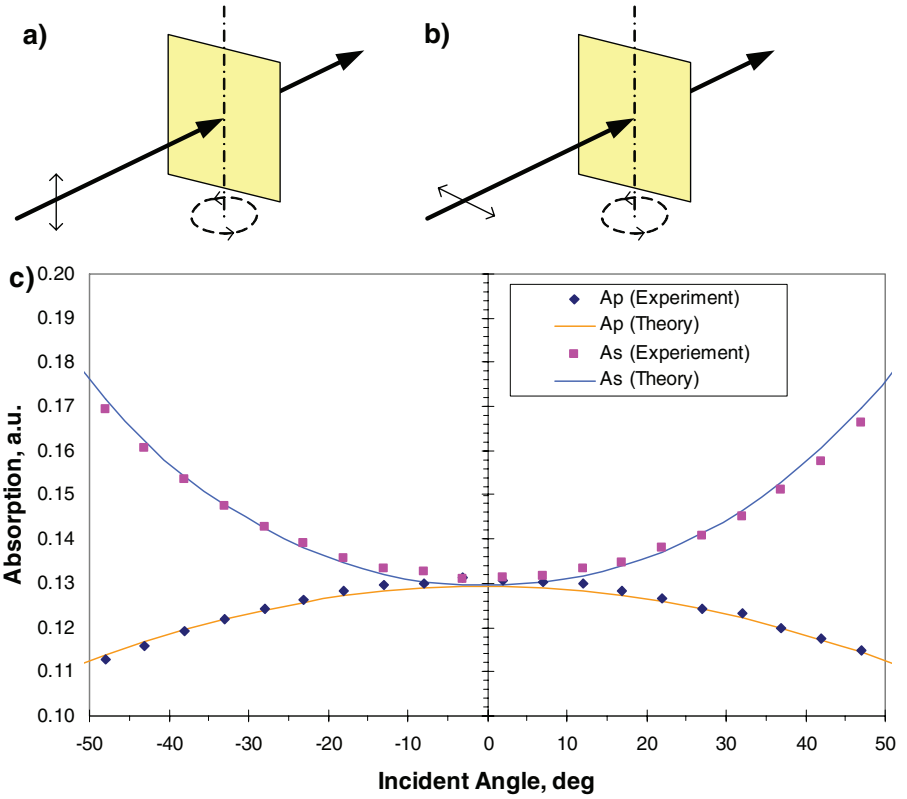

Figure 2. Experiment schemes: probing s- and p-polarized light with polarization parallel (a) and perpendicular (b) to the sample rotation axis; (c) angular dependence of probing polarized light absorption in the dye layer at the peak absorption wavelength.

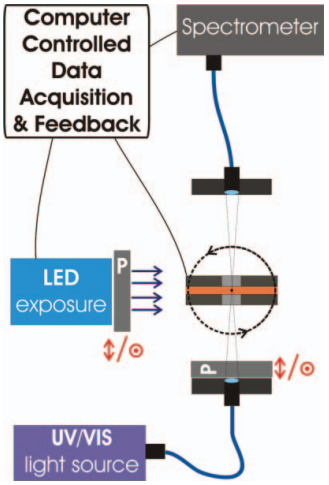

Figure 3. Equivalent optical scheme of the measurement setup for determination of volume absorption anisotropy and photo-orientation dynamics.

0.01 degrees. The dependence of the absorbance coefficient on incident angle for s- and p- polarization is shown in Fig. 2(c).

Least square fitting was applied to the experimental data. With that aim, absorption values given by formulae (1) and (4) for s- and p-polarization cases, respectively, were calculated for each incident angle setting used in the experiment. Next, the sum of the square deviations of experimental data from the theory was computed. Fitting procedure includes minimization of the sum of square deviations for s- and p-polarizations, where n_1 and α_1 were used as fitting parameters for s-polarization geometry and n_2, n_3, α_2 and α_3 were used as fitting parameters for p-polarization case. The data extracted from the each set of rotation measurements are the absorptions coefficients: α_1, α_2 and α_3, which correspond to absorption of light polarized along x, z, y – directions, computed according to equations (1) and (4).

The resulting measurement for the s-polarization case does not depend on the absorption anisotropy because the polarization vector is perpendicular to the incident plane. The length of ray propagation in the investigated film determines the angular dependence of absorption, which is subject to the ray refractive index. While for the p-polarization case, when the incident angle increases, the absorption coefficient is larger (than for s-polarization) if dye molecules oriented vertical to plane of the film; and is smaller if molecules are oriented in the film plane. We used this method for the investigation of reorientation dynamics of the photoaligned film (Fig. 4).

Measurement results for different types of films are shown in Table 1. We can see that for a uniaxial film, absorption is maximal in one direction. For discotic materials, we expected that absorption is equal in x- and z- directions (in the plane of orientation of molecular discs), but we determined that absorption ellipsoid is biaxial with maximal absorption for x-direction, while absorption in z-direction is smaller than in x-direction, but still greater than the lowest absorption in the y-direction.

In the case of photoaligned dye, the layer thickness is much smaller than the wavelength (see Table 1). We observed that the effective values of the refractive indexes are close to one, meaning that the light does not change the direction of propagation in such films. The

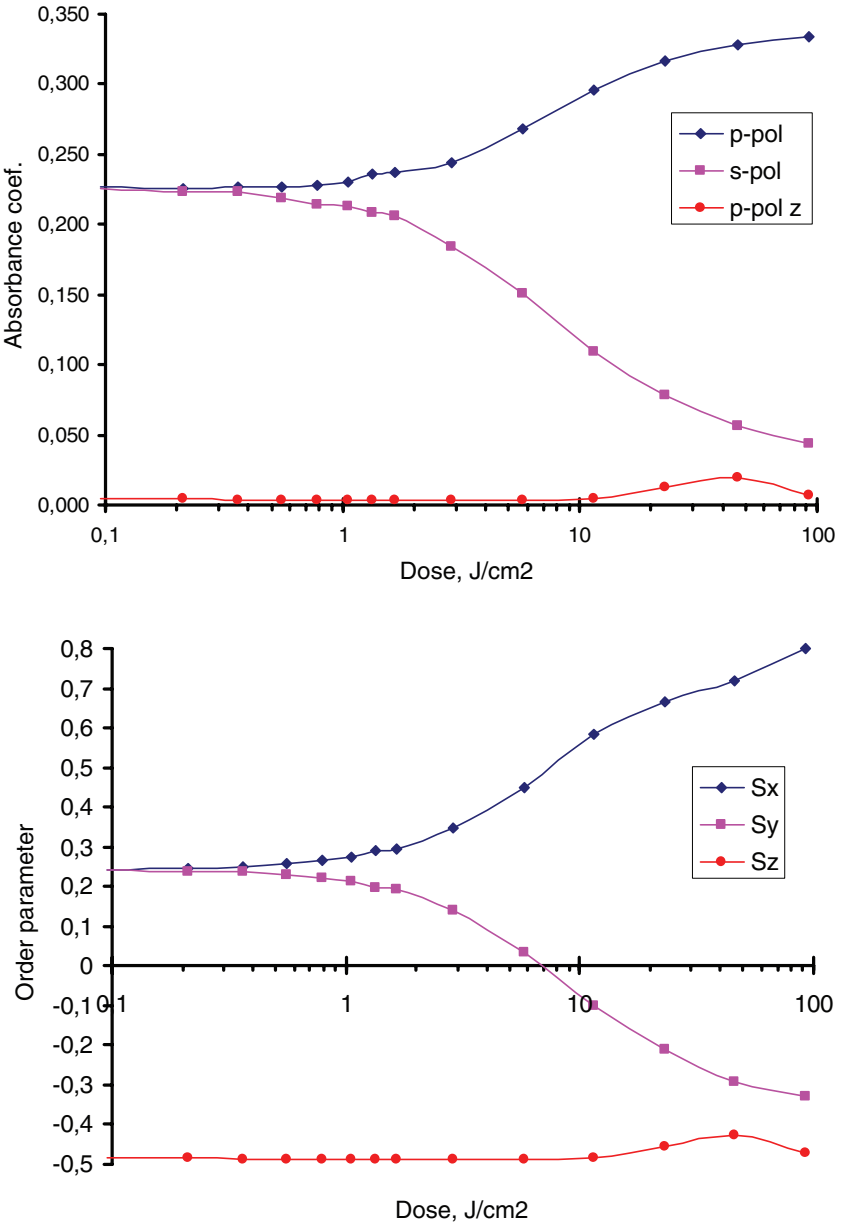

Figure 4. Absorbance coefficient and order parameter of the photoaligned azo dye in dependence dose of the polarized light.

latter is clear from the physical point of view, as refractive index of the medium is the result of interaction of light with the medium. The result of such interactions becomes noticeable after certain distance (interaction thickness), which is probably comparable to or greater than the wavelength of observation. In the limit of zero thickness effective refractive index should be equal to one.

Table 1. Properties of the different films with anisotropic absorbance

	Nitto Denko NPF-F1225DU	Optiva NO15	Photoaligned dye
$\alpha_x : \alpha_y : \alpha_z$	27 : 1 : 1	16 : 1 : 1.6	dose dependant
$n_x : n_y : n_z$	1.62 : 1.52 : 1.42	1.7 : 1.4 : 1.3	$\approx$1
thickness	190 μm	1 μm	20 nm

Conclusions

This paper presented a novel method for the measurement of volume absorption anisotropy. It gives experimental data to investigate complex optical effects, such as absorption of anisotropic thin layers via direct light propagation through organic and inorganic thin films. This method is suitable for the determination of molecular order parameters and investigation of anisotropic organic layers for use in organic electronic devices. An interesting measurement result is that for layers with thickness below wavelength of observation, the Pointing vector (light energy) propagates through absorbing anisotropic structure with effective refraction index that depends on the layer thickness, while if the thickness is a few times greater the wavelength of observation, refraction is constant and does not depends on thickness of the investigated layer.

References

[1] Sambridge, M., Gerald, J. F., Kovács, I., O'Neill, H. St. C., & Hermann, J. (2008). *American Mineralogist*, *93*, 751.
[2] Kovács. I., Hermann. J., O'Neill, H. St. C., Gerald. J. F., Sambridge, M., & Horvát, G. (2008). *American Mineralogist*, *93*, 765.
[3] Collings, P.J., Ratna, B. R., & Shashidhar, R. (2003). *Phys. Rev. E. 67*, 021705.
[4] Land, E. H. (1951). *J. Opt. Soc. Am.*, *41*, 957
[5] Yeh, P., & Paukshto, M. (2000). *Molecular Materials*, *14*, 1.
[6] Su, L., Wang, B., West, J., & Reznikov, Y. (2001). *Mol. Cryst. Liq. Cryst.*, *359*(1), 147.
[7] Chigrinov V., Prudnikova, E., Kozenkov, V., & Kwok, H.-S. (2002). *Liquid Crystals*, *29*(10), 1321.
[8] Muravsky, A. (2009). *Next Generation of Photoalignment*, VDM Verlag Dr. Müller: Germany.
[9] Kriezis, E. E., Chrissoulidis, D. P., & Papagiannakis, A. G. (1992). *Electromagnetics and Optics*, World Scientific Publishing: Singapore.
[10] Chandrasekhar, S. (1977). *Liquid Crystals*, Cambridge University Press: Cambridge.