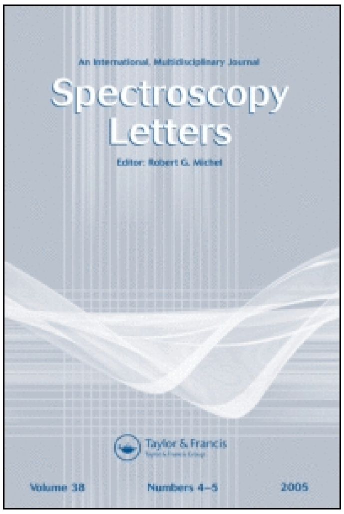

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Orientation of Dye Molecules in Skew Stretched Polyvinyl Alcohol Film

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Orientation of dye molecules in skew stretched polyvinyl alcohol film.

Key words: emission anisotropy, skew stretched film, polarized spectra, merocyanine dye.

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Introduction

The mutual orientation of pigments in living organisms, for example the antenna pigments in photosynthetizing organisms, have strong influence on molecular processes such as excitation energy transfer which are closely related to physiological function of photosynthetizing apparatus of plants, algae and bacteria [1].

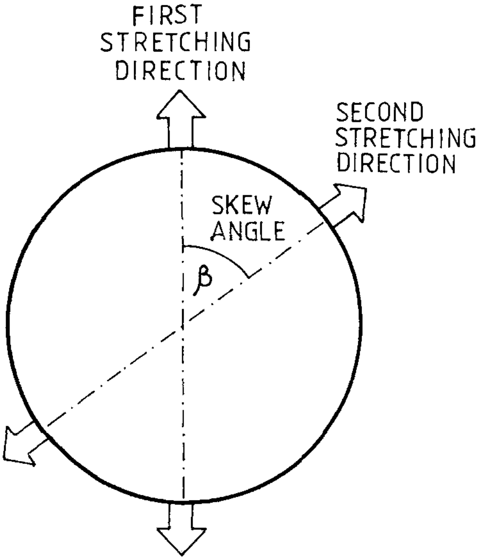
The structure of living organisms is very complex. It is therefore highly adventageous to investigate the mutual interactions between ordered molecules using model systems of known structure [2,3]. Several methods of pigment orientation can be used but for biological macromolecules very convenient is ordering by anisotropic matrix such as stretched polymer or squeezed gel [4]. It has been shown that polyvinyl alcohol can be suitable matrix for the orientation of photosynthetic pigments, pigment-protein complexes or even whole unicellular organisms [2,5-8].

There has been a long history of investigations of stretching polymer films to produce uniaxial or biaxial states of orientation [9-12]. However, little attention has been given to processes in which films are created using skew (i.e. non perpendicular) stretches such as in Fig.1. Lately Wu *et al.* [13] have reported about properties of skew stretched polyethylene tetephthalate films which have been analyzed using refractive index, infrared absorption and wide-angle X-ray diffraction. They have found that symmetry axes of sequential skew stretched films tend to move towards second stretching direction as increasing second stretching degree. At low second stretching degrees the samples exhibit a biaxial behaviour.

In this study the orientation of elongated dye molecules in skew stretched polyvinyl alcohol (PVA) film is shown. It seems that such type of pigment orientation can be very suitable for investigation of complex biological sample with many types of chromophores having similar absorption spectra but differently attached to macromolecule.

Material and methods.

The stilbazolium merocyanine (Fig. 1) 1- (6'-hydroxyhexyl) -4- [(4- oxocyclohexa -2,5-dienylidene) ethylidene] -1,4- dihydro -pyridine dye of elongated shape was used. The dye was synthesized as described [14] and was introduced into a polyvinyl alcohol film at the concentration 10^{-3} M/L. The



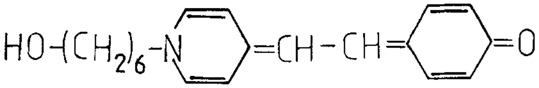


Fig. 1. The schematic representation of skew stretching mode and formulae of merocyanine dye.

methods of film preparation have been described previously [5]. Samples were placed in film stretcher. There were two stretching steps to make skew stretched films. In the first step the isotropic film with dissolved merocyanine dye was uniaxially stretched tree times of initial length (l_o) ($\Delta l/l_o$= 200 %). In a second step film was stretched under axis forming 60° skew angle with initial axis till twice elongation ($\Delta l/l_o$= 100 %) (Fig. 1). Elongeted film was silted to the frame to prevent the changes in deformation in time. The processing temperature was 50 ^{0}. For comparison, films elongated uniaxially (200 %) were also prepared.

Polarized absorption spectra were measured using M40 Specord (Carl Zeiss) spectrophotometer and polarized emission spectra on home-built spectrophotometer [15].

Results and discussion.

Figs. 2 and 3 show the examples of polarized absorption and fluorescence spectra of investigated merocyanine dye in biaxial and uniaxial stretched PVA films. The investigated dye occurs in PVA predominantly in protonated form with the maximum of absorption at about 400 nm, but some admixture of free base form (with the absorption in a region of 525 nm) is also observed [16]. The emission is mostly observed for aggregated form (aggregates of ground state and excimers) of the dye [16-20]. As it follows from our erlier study [16] the emmision of this merocyanine which is observed at 500 and 575 nm is related to different states of dye aggregation and protonation.

As it follows, from polarized absorption spectra (Fig. 2) and from the dependence of the degree of orientation S_{γ}

$$S_{\gamma} = (A_{\parallel}-A_{\perp})/(A_{\parallel}+ 2A_{\perp}) \qquad (1)$$

[$A_{\parallel}$ parallel and $A_{\perp}$ perpendicular polarized absorption components] on an angle γ between direction of the first film stretching and an electric vector of light polarization (Fig. 4), in "parallel" absorption component the degree of pigment orientation S_{γ} calculated in respect to the second axis of stretching is much higher than that obtained at the angle $\gamma = 0^{\circ}$ at stretching only in respect to primary axis. After second stretching the S_{γ} value in respect to $\gamma = 0^{\circ}$ axis is negative

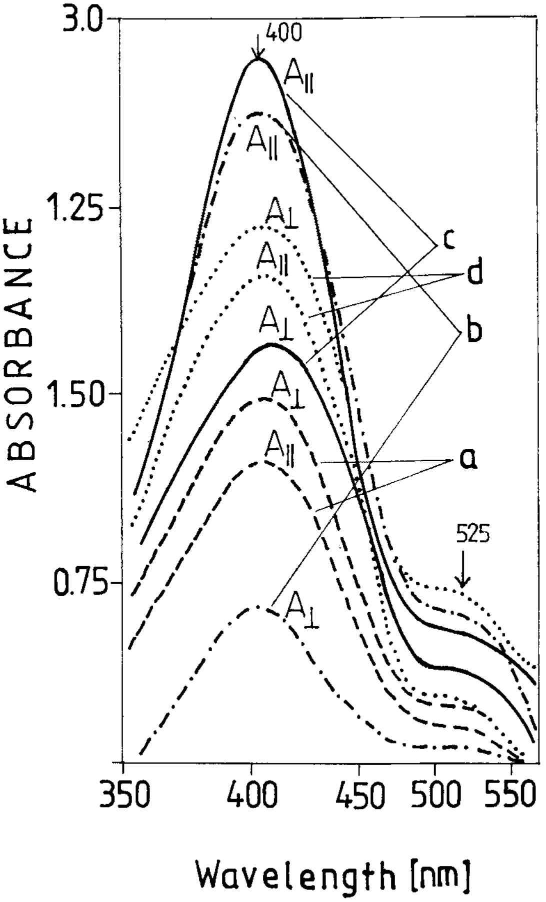


Fig. 2. Polarized absorption spectra of merocyanine in PVA films: a,b/biaxially stretched and measured at $\gamma = 0^{\circ}$ and 60°, c,d/uniaxially stretched and measured at $\gamma = 0^{\circ}$ and 60°.

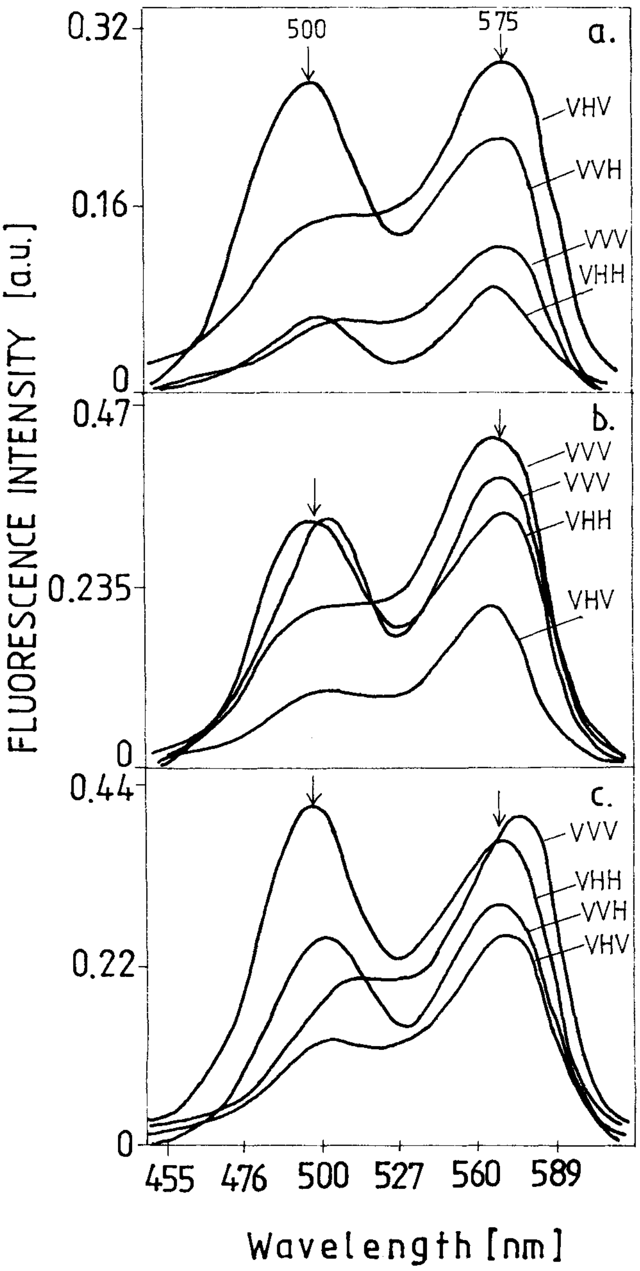


Fig. 3. Polarized emission spectra of merocyanine in PVA films: a,b/biaxially stretched and measured at $\gamma = 0^{\circ}$ and 60°, c/uniaxially stretched and measured at $\gamma = 0^{\circ}$.

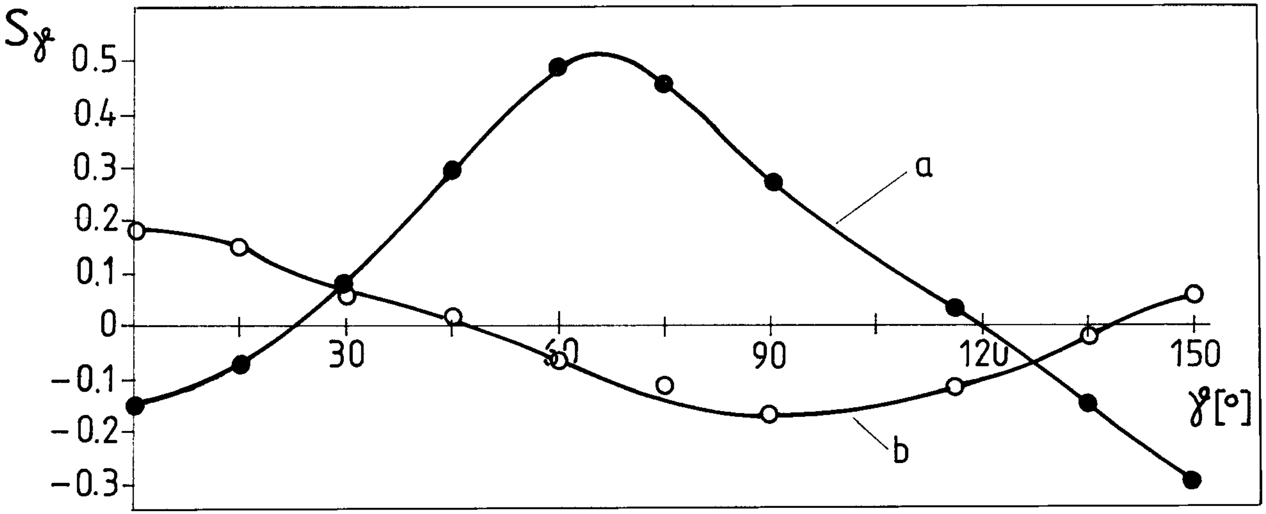


Fig. 4. The distribution of order parameter S_γ *versus* γ angle for merocyanine dye in PVA films: a/biaxially stretched, b/uniaxially stretched.

and rather low in absolute value. Also half wide of S_γ distribution became narrower after twice applied procedure of stretching than after uniaxial deformation. Therefore skew stretching can improve the resolution of the contributions of the molecules with transition moments of absorption directed mutually under low angles.

Fig. 3 presents four polarized components of merocyanine emission spectra measured for the samples stretched bi- ($\gamma = 0^o$ and 60^o) and uniaxially ($\gamma = 0^o$). Components are marked V-vertical, H-horizontal in sequence: polarization of excitation, sample axis, polarization of emission. The excitation was at 400 nm (in the region of absorption of the protonated form). The fluorescence spectra exhibit two maxima, one at 500 and the other at 575 nm. From comparison of the spectra in Fig. 3 it follows that the ratio of polarized emission at about 500 nm and in a region 550-590 nm depends on film stretching axes. Also position of longwavelength maximum is shifted as a result of the change in light polarization and stretching axis. Similar components of polarized emission of merocyanine were measured for both uni- and biaxially stretched samples at several values of the angle γ. On the basis of four polarized *components (such as in Fig. 3) the parameters* characterizing the emission anisotropy of dye molecules in anisotropic media can be defined [20].

Two of them

$$r_a = [(VVV/VOV)-(VVH/VOH)]/[(VVV/VOV)+2(VVH/VOH)] \quad (2)$$

and

$$r_b = [(VHV/VOV)-(VHH/VOH)]/[(VHV/VOV)+2(VHH/VOH)] \quad (3)$$

describe the anisotropy of emission of two pools of molecules : one with small and the other with large angles between the

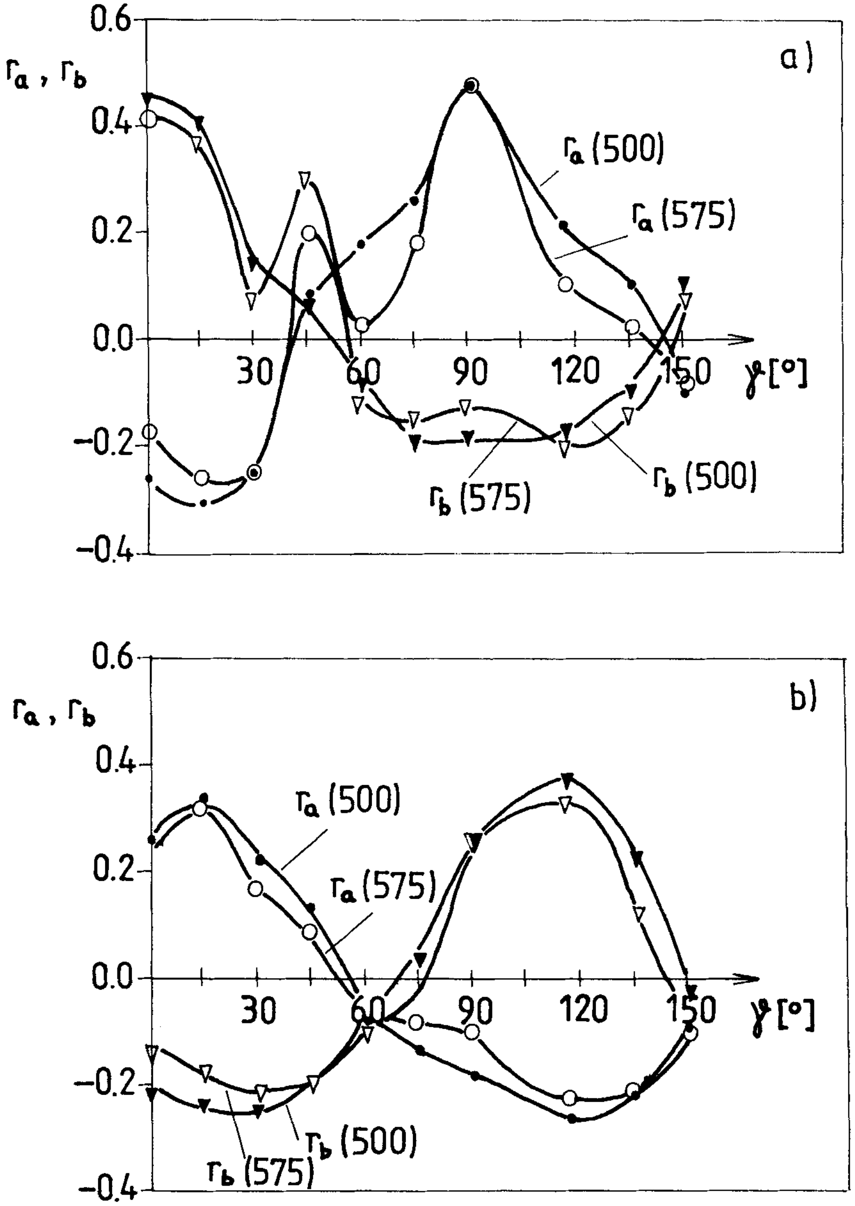


Fig. 5. The distributions of emission anisotropies r_a and r_b at two emission maxima (500 and 575 nm) *versus* γ angle for merocyanine dye in PVA films: a/ biaxially stretched, b/uniaxially stretched.

emission transition moments and electric vector of exciting light (VOV and VOH are components obtained for unstretched samples for the same experimental geometry in order to normalization can be performed). These two parameters as a function of the angle γ for both emission maxima in both uniaxially and skew stretched film cases are presented in Fig. 5. The increase in the absolute maximal value of emission anisotropy is observed in skew samplesbut, what it is more important in a case of biological systems, with several chromophores, the distribution of emission anisotropies *versus* γ for various type of dye forms are different. This gives an opportunity to investigate the emission properties of various forms separately. The maxima of emission anisotropy in both type of PVA films are shifted in γ scale in respect to maxima of absorption anisotropy what shows that absorption and emission transition moments are not exactly parallel to each other. In a case of biaxial stretched sample is clearly shown that longwavelength emission band contains the contribution from different pools of molecules (two maxima for r_a at $\gamma = 0^o$ and 45^o and for r_b at 45^o and 90^o). Generally, the distributions of r_a and r_b *versus* γ angle exhibit better resolution in both emission bands for biaxial stretched samples than that for uniaxial stretched.

On the basis of presented results seems that skew stretching of polymer film can be a promissing method, which can give a new additional opportunity in investigation of artificially oriented biological samples.

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