Structure effect and orientation distribution of azo dyes on optical anisotropy of dyed PVA-films

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Abstract. The derivatives of phenylazobenzoic, phenylazosalicylic acids and azobenzeneazonaphthalene were synthesized and employed to prepare polarizing films based on polyvinyl alcohol (PVA). The single-piece transmittance (T_0), polarizing efficiency (PE), dichroic ratio (R_d) of films and order parameter of dyes (S_{dye}) were calculated. It was found that parameters R_d and S_{dye} increased as electron-donating of substituents in molecules of phenylazobenzoic and phenylazosalicylic acids derivatives was grown, and the polarizing efficiency of film increased with increasing the order parameter of dye. Development of PVA films dyed with the derivatives of phenylazosalicylic acid and azobenzeneazonaphthalene allowed to obtain polarizers for near UV and visible range of spectrum, respectively. It was also developed a broadband polarizer for 300-610 nm.

Keywords: dichroic polarizers, polyvinyl alcohol, mono- and disazodyes, spectral-polarizing properties.

1. Introduction

Dichroic film polarizers are polymer uniaxially oriented films colored with molecular iodine or organic dyes. Polarizers based on polyvinyl alcohol (PVA) have the most practical application. The study of spectral properties of PVA films colored by different classes of dyes showed that the azocompounds can get film material with a high polarizing ability. However, the optical properties of these polarizers are dependent on many factors: the structure and the orientation distribution of the dye molecules in the polymer matrix, phase state and supramolecular structure of PVA, intermolecular interactions between dye molecules and macromolecules of the polymer [1 – 3].

In this work, the derivatives of phenylazobenzoic, phenylazosalicylic acids and azobenzeneazonaphthalene were synthesized, and then they were used for dyeing the PVA-films polarizing in near UV and visible regions of the spectrum. The purpose of this study is to determine the influence of the molecular structure (type and location of auxochrome group) of the synthesized compounds and the orientation distribution of dyes molecules in the polymer matrix on dichroism of PVA-films.

2. Experiment

Disazodyes:

M$_1$

M$_2$

M$_3$

IV

V

VI
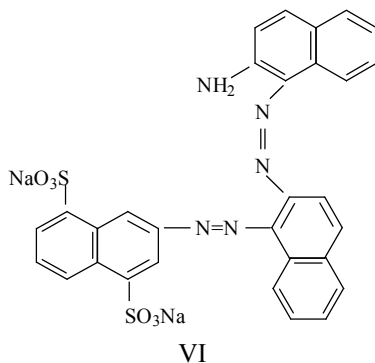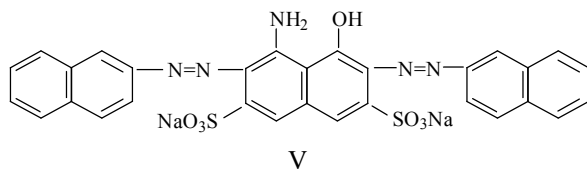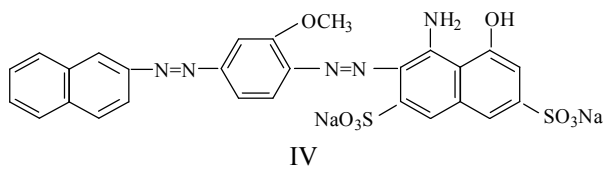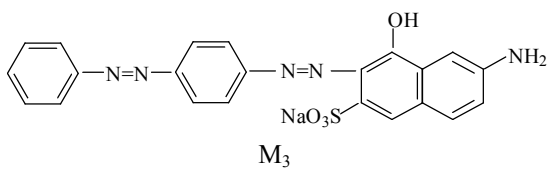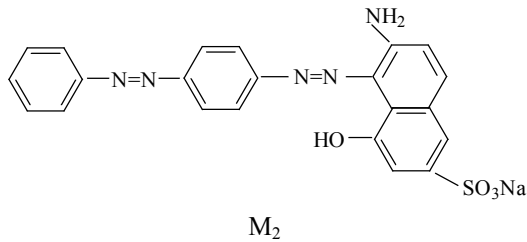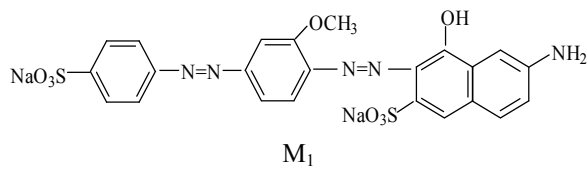
and monoazodyes (Table 2) of the general formula:
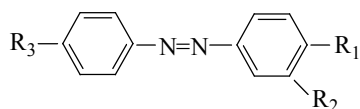
were synthesized in the form of free acids or their sodium salts by the diazotization of aromatic amines or diamines followed by azocoupling with salicylic, aminonaftolsulfo and acetoacetic acid in acidic or alkaline medium [4]. Preparation of polarizing films is described in [5].

Absorption and transmission spectra of films were measured using a UV-NIR Spectrometer HR4000CG (Ocean Optics, USA) equipped with wire-grid polarizer UBB01A (Moxtek, USA).

Optical properties of the polarizers were expressed in terms of such optical characteristics as the single-piece transmittance (T_0), polarizing efficiency (PE) and dichroic ratio (R_d) of dyed PVA-films. The order parameter (S_{dye}) characterized the degree of aligning dye molecules toward the orientation film axis. These parameters were calculated by means of the equations [6]:

$$T_0 = (T_\parallel + T_\perp)/2, \quad PE = \{(T_\perp - T_\parallel) / (T_\parallel + T_\perp)\} \cdot 100\%,$$

$$R_d = D_\parallel / D_\perp, \quad S_{dye} = (R_d - 1)/(R_d + 2),$$

where $D_\parallel$, $D_\perp$ – absorption and $T_\parallel$, $T_\perp$ – film transmittance of linearly polarized light in parallel ($\parallel$) and perpendicular ($\perp$) orientation of the electric vector of linearly polarized light towards the orientation axis of the film.

3. Results and discussion

Investigated PVA-films colored with mono- and disazodyes have a positive dichroism, which proves that the long-wave absorption dye oscillator is directed along its main molecular axis. The latter, in its turn, is oriented in the direction of the film orientation axis. Polarization efficiency of a film is determined primarily by the structure of dye molecules embedded in polymer. So, the samples obtained under identical conditions and polarized in the visible range of spectrum have the values of PE from 33 up to 98% (Table 1). Besides, the similar change of the order parameter S_{dye} can be seen.

Ab initio SCF MO LCAO RHF/MINI (3d) method was used in order to model the spatial structure of the dyes. It was found that the highest value of PE is inherent to the films colored with molecules that have a flat "extension" frame of two benzene and single naphthalene rings without volume substitutes causing steric hindrance for the alignment of dye molecules along the polymer chains and towards the drawing direction (compounds M$_1$, M$_2$ and M$_3$).
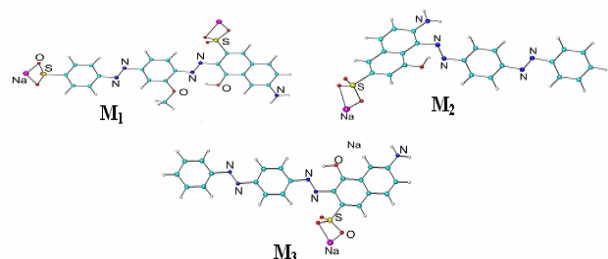
Table 1. S_{dye} and PE for films dyed with disazodyes. The dye concentration is 0.2-0.4 mas.%. The film thickness is 60 μm.

| Dye	λ_{max}, nm	$D_{\parallel}$	$D_{\perp}$	R_d	S_{dye}	PE, %
M_1	595	1.52	0.15	10.1	0.75	92
M_2	585	2.22	0.50	4.4	0.53	96
M_3	580	2.19	0.26	8.4	0.71	98
IV	495	1.57	0.40	3.9	0.49	87
V	570	0.80	0.46	1.7	0.19	61
VI	507	0.62	0.33	1.9	0.23	33

Table 2. Order parameter and spectral-polarization characteristics of the films dyed by monoazodyes. The dye concentration is 0.2 to 0.3 mas.%. The film thickness is close to 50…60 μm.

| Substituent	Cipher of dye	λ_{max}, nm	$T_{\perp}$ %	$T_{\parallel}$ %	$D_{\perp}$	$D_{\parallel}$	T_0, %	R_d	S_{dye}	PE, %
R_1= COONa, R_2 = H, R_3= COONa	VII	351	75.6	2.8	0.122	1.553	39.2	12.7	0.80	93
R_1= COOH, R_2 = H, R_3= COOH	VIII	351	91.4	11.5	0.039	0.939	51.4	24.0	0.89	78
R_1= OH, R_2 = COONa, R_3= CH_3-C(O)	IX	381	43.0	1.4	0.367	1.854	22.2	5.1	0.58	94
R_1= OH, R_2 = COOH, R_3= CH_3-C(O)	X	381	42.5	0.5	0.372	2.301	21.5	6.2	0.63	98
R_1= OH, R_2 = COONa, R_3= CH_3-C(O)-NH	XI	376	28.6	0.01	0.544	4.000	14.3	7.4	0.68	99
R_1= OH, R_2 = COONa, R_3= NaOOC	XII	380	78.1	4.2	0.107	1.377	41.1	12.9	0.80	90
R_1= OH, R_2 = COONa, R_3= NH_2	XIII	399	64.7	0.5	0.189	2.301	32.6	12.2	0.79	99
R_1= OH, R_2 = COONa, R_3= CH_3O-C_6H_4-C_2H_2-C(O)	XIV	386	51.4	1.3	0.289	1.886	26.4	6.5	0.65	95
R_1= OH, R_2 = COOH, R_3= CH_3O-C_6H_4-C_2H_2-C(O)	XV	382	41.7	0.6	0.380	2.222	21.2	5.8	0.61	97

Sulfo-groups do not violate flatness of molecules M_1 and M_3. Violation of coplanarity of the dye molecules IV and V reduces the intensity of the long-wave absorption bands and decrease values of S_{dye} and PE. Molecules of dye VI, the length of which is comparable with their width, are oriented in polymer matrix with different angles of deviation of its main absorption axis along the drawing axis, which is the reason for the low polarizing ability of dyed PVA-film.

Monoazoderivatives of benzoic and salicylic acid are effective dichroic components of films polarizing in the near UV range of the spectrum (Table 2).

The nature of substituents in the dye molecule affects not only on the position and intensity of the long-wave absorption band of the film, but also on its dichroism. "Delete" from the conjugation one of the NaO(O)C-group in the dye VII and the introduction of the *e*-supplying group OH on its place:

VII
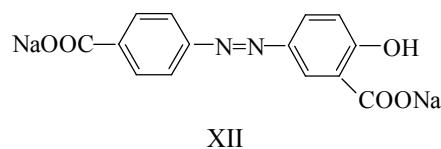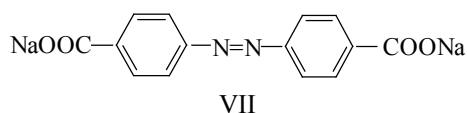
does not practically change the value of the order parameter R_d, but replacing the second NaO(O)C-group on *e*-withdrawing substituent R = $CH_3C(O)$ – (IX), $CH_3C(O)NH$- (XI), $CH_3(O)Ar$-CH = CH – C(O) – (XIV)
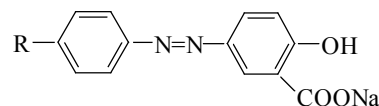
reduces R_d from 12.2…12.7 to ~5-7. With the *e*-supplying group NH_2:

XII

XIII
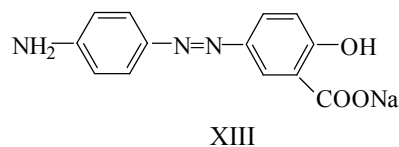
R_d returned to 12.2. In general, with increase of electron-donating of substituents the value of dichroic ratio increases:

R: NH_2- > $CH_3C(O)NH$- > $CH_3(O)Ar$-CH=CH-$C(O)$- > $CH_3C(O)$
R_d: 12.2 > 7.4 > 6.5 > 5.1

The value of S_{dye} (Table 2) also depends on the structure of dye and for the compounds VII-XV is:

R: $NaO(O)C$-NH_2-$CH_3C(O)NH$-$CH_3(O)Ar$-CH-CH=CH-$C(O)$- $CH_3C(O)$
S_{cr}: 0.80 0.79 0.68 0.65 0.63

Since the orientation of the dye strongly depends on the spatial structure of its molecules [7], introduction of larger volume substituents $CH_3C(O)NH$-, $CH_3(O)Ar$-CH=CH-$C(O)$- and $CH_3C(O)$ compared to groups $NaO(O)C$- and NH_2- reduces S_{dye}.

The order parameter S_{dye} decreases with increasing the dye concentration (C) in the film. For example, the increase of C for dye IX from 0.15 up to 0.30 mas.% reduces the value of S_{dye} from 0.63 to 0.58, and in the case of dye XIII the growth of C from 0.2 up to 0.4 mas.% causes the decrease in S_{dye} from 0.88 down to 0.71. This dependence $S_{dye} - C$ was predicted using the mathematical model worked out to describe the spectral-polarizing properties of dyed PVA films and was experimentally proved with film samples containing azo dye "direct blue"[6].

The orientation degree of the dye molecules increases in films with a quasi-crystalline structure of PVA that is formed after the heat treatment of the PVA-film and the processing by "cross-linking" agent (boric acid) [5]. This structure is characterized by a highly ordered polymer chains with respect to the drawing axis of the film, and as a result increase the degree of orientation of the dye molecules in the polymer matrix. For example, the parameter S_{dye} of the dye M_1 in films untreated and treated with boric acid is equal to 0.63 and 0.78, respectively [5].

Studying the optical properties of PVA-films dyed by (M_3H) obtained by treatment of dye M_3 with hydrochloric acid, we found that M_3H is an effective dichroic component of films polarizing in near UV and visible ranges of spectrum (Fig. 1). The polarization efficiency of this film is 92 to 99% (300…400 nm) and 96 to 99% (400…610 nm).
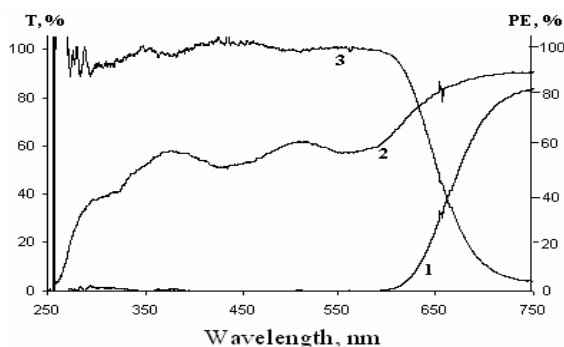

Fig. 1. Transmission spectra and polarizing ability of PVA-film dyed by M_3H. *1 – T_∥, 2 – T⊥, 3 –* PE; film thickness is 60 μm; dye concentration is 0.4 mas.%.

4. Conclusion

The structure of molecules of derivatives of phenylazobenzoic and phenylazosalicylic acids as well as azobenzeneazonaphtalene influences on optical properties of polarizing PVA films and orientation alignment of azodyes in polymeric matrix. With rising electron-donating of the substituents conjugated with the chain of double bonds in derivatives of phenylazobenzoic and phenylazosalicylic acids, the dichroic ratio of film and the order parameter of dye (a degree of dye orientation in polymer matrix) increase. The polarizing ability of films grows with rising the order parameter of dye, the value of which depends on the concentration of dye and the supramolecular structure of polymer matrix. From PVA dyed by synthesized mono- and disazodyes we obtained the polarizers for UV and visible ranges of the spectrum as well as the broadband polarizer for the range 300…610 nm.

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