

BRIEF COMMUNICATIONS

SPECTRAL AND POLARIZING PROPERTIES OF ANISOTROPIC FILMS BASED ON POLYVINYL ALCOHOL AND 4,4'-BIS[4-(PHENYLAMINO)-6-(METHOXY-1,3,5-TRIAZIN-2-YL)AMINO]STILBENE-2,2'-DISULFONIC ACID

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The spectral and polarization characteristics of optically anisotropic polyvinyl alcohol (PVA) films containing 4,4'-bis[4-(phenylamino)-6-(methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid as dichroic dye, which has intense blue fluorescence, were investigated by polarized luminescence and absorptionspectroscopy in the IR and UV regions. With fourfold uniaxial stretching of the film the orientation parameter of the dye amounts to 0.82–0.86, the maximum polarizing ability of the film is 96% (at the maximum of the absorption band at 375 nm), and the degree of polarization and quantum yield of fluorescence at the optimum concentration of the dye amount to 0.90 and 0.91. The degree of orientation of the dye molecules depends weakly on the concentration (0.01–0.50 wt.%) and increases with increase of the uniaxial stretching of the film. The insertion of the dye molecules between the PVA chains leads to a reduction of the crystallinity of the polymeric matrix.

Keywords: IR and UV spectroscopy, fluorescence, polyvinyl alcohol films, bistriazinylaminostilbene dye, optical anisotropy.

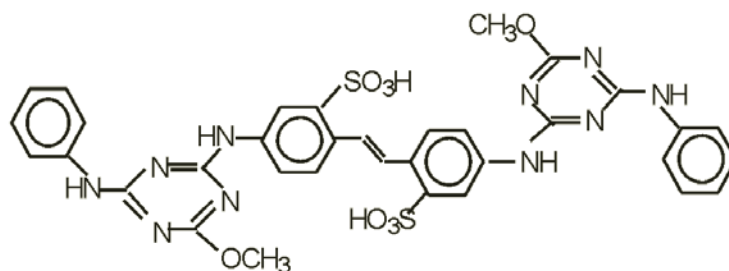
Polymeric matrices with inserted dyes are of interest both basically during investigation of the mechanisms of intermolecular interaction in a polymer–dye system [1, 2] and in the solution of various practical tasks, including the creation of devices for conversion of solar energy into electrical energy [3], materials for optical recording of information [4], laser media [5], and holography [6]. Such materials have widespread use in the manufacture of signs, license plates of motor vehicles, and road signs, and also in the production of liquid crystalline devices for the display of information (electronic calculators and clocks, displays and indicators, and various measuring instruments) [7, 8]. Polyvinyl alcohol (PVA) occupies a special position among polymeric materials thanks to the relatively low cost of the raw material, the high optical transparency of PVC film, the ease of stretching of the film to produce a high degree of anisotropy, and the ecologically clean production technology [9]. No less important is the choice of dye, which must be synthesized from cheap components, be highly compatible with the polymeric matrix, and have high probability of radiative processes in the polymeric medium, photochemical stability (a long working life), and a broad spectral range. At the present time an active search is being made for polymeric materials that would meet the requirements set out above.

In the present work the spectral polarization characteristics of isotropic and anisotropic extended films of PVA doped with the well-known optical whitener 4,4-bis[4-(phenylamino)-6-(methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2-disulfonic acid [10] were investigated. Greatest attention was paid to measurement and interpretation of the polarization and luminescence characteristics of dye molecules in PVA films using polarized luminescence and absorption in the IR and UV regions. The dependence of the optical dichroism and crystallinity on the degree of stretching and the concentration of the dye was also investigated.

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The procedure for preparation of the films based on PVA was described in [11]. The dye 4,4'-bis[4-(phenylamino)-6-(methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid was used:



The consistency of the structure and molecular mass of the compound was monitored on a Thermo Scientific LTQ chromatomass spectrometer (USA).

The IR transmission spectra of the dye and the PVA films were recorded on a Nicolet Nexus-670 FT-IR Fourier spectrometer with a resolution of 2 cm^{-1} , and the absorption spectra in the UV and visible regions were recorded on a Cary 500 UV-Vis-NIR spectrophotometer. A Glan prism was used to generate the polarized light. The spectral polarization and kinetic fluorescence characteristics were measured on a Solar (Belarus) fluorometer and a PRA-300 pulse fluorometer operating in a time-correlated photon counting regime. The fluorescence quantum yield of the dye in ethanol was measured with reference to coumarin 1 in ethanol, for which $\Phi_{\text{fl}} = 0.73$ [12].

From the absorption spectra of the fourfold stretched film of PVA with the dye (Fig. 1) it is seen that the optical density of the films depends on the angle between the vector of the linearly polarized absorbed light and the orientation axis of the film. The electronic transition of the dye molecule corresponding to the longwave absorption band with $\lambda_{\text{a}}^{\text{max}} = 375\text{ nm}$ is directed along the long molecular axis. During stretching of the film the long molecular axes of the dye are set out along the orientation axis of the film. With the dichroic ratio $R_d = D_{\parallel}/D_{\perp}$ it is possible to calculate the orientation parameter of the dye $S_{\text{dy}} = (R_d - 1)/(R_d + 2)$ [13]. The high value of $S_{\text{dy}} = 0.86$ for the longwave transition and $S_{\text{dy}} = 0.6$ for the electronic transition with $\lambda_{\text{a}}^{\text{max}} = 268\text{ nm}$ indicates a substantial difference in dichroism between the longwave and shortwave moments of the electronic transitions in the molecule since the shortwave moment of the electronic transition arises from the aromatic ring with the triazine substituent while the longwave transition arises from the conjugated chain of double bonds in the central fragment of the molecule.

The orientation parameter S_{dy} depends little on the concentration of the substance in the films containing between 0.01 and 0.5 wt.% of the dye. This indicates the absence of substantial association between the dye molecules in the investigated range of concentrations. It is possible that interaction of the dye with the polymer prevents aggregation of its molecules. It should be noted that the ratio of optical densities D_{375}/D_{268} depends on the degree of stretching of the PVA films: it increases in the parallel orientation and decreases in the perpendicular orientation of the electric vector of the probing radiation in relation to the direction of stretching of the film. This is due to the fact that the longwave electronic transition passes along the long molecular axis of the dye, which has a higher degree of orientation than the other axes of the molecule in relation to the stretching axis of the film. This is indicated by the dependence of the dichroic ratio (R_d) of the film on the degree of stretching (R_S): with increase of R_S from 1 to 4–5 the R_d value increases from 1 to ~ 19 along the 375 nm band and from 1 to ~ 6 along the 268-nm band.

We note also the high radiative efficiency of the dye in the polymeric PVA matrix, which shows up in the form of intense blue fluorescence with $\lambda_{\text{fl}}^{\text{max}} = 432\text{ nm}$ (see Fig. 1). The results of the spectral kinetic measurements show that the fluorescence quantum yield of the dye in the 3–4 times stretched film is $\Phi_{\text{fl}} = 0.91 \pm 0.05$, i.e., practically all the absorbed energy is transformed into radiation in the blue-green region of the spectrum (400–500 nm). From the measured duration of fluorescence $\tau_{\text{fl}} = 0.97\text{ ns}$ it is possible to estimate the rate constant of fluorescence from the equation $k_{\text{fl}} = \Phi_{\text{fl}}/\tau_{\text{fl}} = 9.4 \cdot 10^8\text{ s}^{-1}$. Thus, the dye in the anisotropic PVA film, having maximum possible fluorescence parameters $k_{\text{fl}} = 9.4 \cdot 10^8\text{ s}^{-1}$ and $\Phi_{\text{fl}} = 91\%$, can be used as source of polarized radiation in the region of 400–500 nm.

In order to assess quantitatively the polarization characteristics of the dye we measured the degree of polarization of the fluorescence $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$ (I_{\parallel} and I_{\perp} are the intensity of fluorescence polarized parallel with and perpendicular to the electric vector of the exciting polarized light) for the unoriented and oriented ($R_S = 3.5$) films: $P = 0.45 \pm 0.05$ (Fig. 1, curve 5) and 0.90 ± 0.05 (curve 6). These data also demonstrate the high polarizing ability of the dye in the PVA film

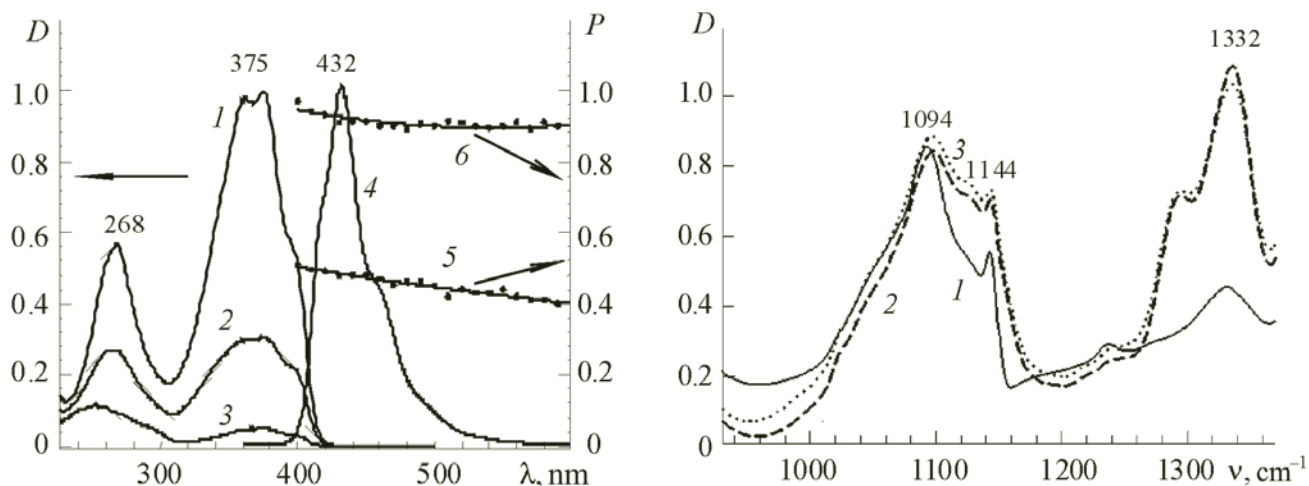


Fig. 1. The absorption (1–3), fluorescence (4), and fluorescence polarization (5, 6) spectra of PVA film containing 0.2 wt.% of dye and stretched four times: 1), 3) exciting light polarized parallel with and perpendicular to the stretching axis; 2) unpolarized light; 5) isotropic film: 6) anisotropic film with $R_S = 4$.

Fig. 2. IR absorption spectra in the region of $930\text{--}1370\text{ cm}^{-1}$ for isotropic films of PVA without the dye (1) and with the dye (2 wt.%) (2), the anisotropic film with the dye (2 wt.%) stretched three time (3); the exciting light was not polarized.

emitting linearly polarized fluorescence. It should be noted that the maximum values for the degree of polarization are already achieved at a dye concentration of 0.05 wt.%.

In order to ascertain the effect of the dye on such an important parameter of the supermolecular structure of PVA as crystallinity we chose the intensities of the two bands at 1332 and 1144 cm^{-1} in the absorption spectra of PVA in the isotropic and anisotropic films (Fig. 2). These bands were used in [14] to determine the degree of crystallinity α . The band at 1144 cm^{-1} characterizes the degree of crystallinity of the polymer [15]. Its intensity was normalized to the band at 1332 cm^{-1} , which made it possible to exclude the effect of the thickness of the film. The band at 1332 cm^{-1} , corresponding to the deformation vibrations of the CH and OH bonds, is not sensitive to the crystallinity and tacticity of the polymer. The values of D were determined in relation to a base line drawn in the form of a tangent to the wings of the complex spectral contour. Comparison of the D_{1144}/D_{1332} values for the dyed and undyed films shows that the crystallinity of the PVA is lower in the presence of the dye: in the isotropic undyed film $D_{1144}/D_{1332} = 1.47$, in the dyed film (concentration of dye 2 wt.%) it is 0.68. In the anisotropic ($R_S = 3.0$) dyed film D_{1144}/D_{1332} increases to 0.78. Thus, the introduction of the dye into the PVA polymeric matrix greatly reduces the crystallinity of the polymer, while subsequent stretching of the film leads to a gradual increase of this structural parameter.

The structural differences in the isotropic and anisotropic dyed films show up clearly during investigation of their spectral kinetic characteristics in the electronically excited states by femtosecond spectroscopy. In uniaxially stretched films the kinetics of induced absorption consists of two components: short-lived with decay time ≤ 10 ns and long-lived (~ 1.0 ns). The life time of the short component decreases with increase of R_S . The short-lived component is practically absent in the isotropic films. A long-lived excited state of 0.97 ± 0.05 ns was detected by nanosecond fluorometry.

Thus, the uniaxially oriented films of polyvinyl alcohol containing 4,4'-bis[4-(phenylamino)-6-(methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid have polarizing character. The positive dichroism indicates that under the influence of an external deforming force (uniaxial stretching) the long molecular axis of the molecule is oriented along the direction of stretching of the film. The degree of orientation of the dye molecules depends little on its concentration (up to 0.5 wt.%) and increases with increase in the degree of uniaxial stretching of the film. In the fourfold stretched film containing 0.2–0.3 wt.% of the dye the orientation parameter $S_{dy} = 0.82\text{--}0.86$, while the maximum polarizing ability at the maximum of the absorption band at 375 nm amounts to 96%. The luminescence spectral investigations showed that the dye

in the anisotropic polyvinyl alcohol films has strong emission ($\Phi_{fl} = 91\%$) and polarization ($P = 0.90$) characteristics, which makes it possible to regard it as an effective source of polarization emission in the region of 400–500 nm. The introduction of the bistriazinylaminostilbene dye into the polymeric matrix of the PVA film leads to a change in the D_{1144}/D_{1330} ratio characterizing the crystallinity of the PVA, and this indicates that the dye has an effect on the supermolecular structure of the polymer. The decrease in the crystallinity of the PVA under the influence of the dye assists in the accumulation of its molecules in the regions of the polymeric matrix where uniaxial orientation of the polymer chains and subsequent involvement of the dye molecules in this process are facilitated.

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