

Photoluminescence Properties of *trans*-4,4'-Diamino-stilbene in Poly(vinyl alcohol) Films

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Experimental studies have shown that the nonpolar molecule 4,4'-diamino-stilbene (DAS) in poly(vinyl alcohol) film (PVA) at 296 K, apart from fluorescence displays phosphorescence whose intensity differs only slightly from that observed at 84 K. The overlapping of fluorescence and phosphorescence bands is the reason of the unusual behaviour of the emission anisotropy in the longwave absorption and photoluminescence bands. A distinct effect of direct irradiation on the intensity of these bands was observed.

1. Introduction

As demonstrated previously, $\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$ linear polyenes ($n = 2, 3, 4$) as well as *p*-substituted stilbenes behave differently in poly(vinyl alcohol) (PVA) and polyvinyl chloride (PVC) films, although their glassy transitions temperatures are very close (358 and 354 K, respectively) [1–4]. This unusual behaviour of the absorption and fluorescence properties of luminescent compounds containing at least one double bond can only be observed in PVA. No phosphorescence of the polyenes examined ($n = 2, 3, 4$) and of three stilbene derivatives: 4-amino-4'-nitrostilbene (ANS), 4-dimethyl-amino-4'-nitrostilbene (DNS) and 4,4'-diphenyl-stilbene (DPS), was observed at room temperature in neither PVA nor PVC films [3]. In the case of nonpolar DPS molecules in PVA, a very low anisotropy was measured, which did not vary throughout the emission band (about 0.1) at the excitation wavelength $\lambda_{\text{exc}} = 340 \text{ nm}$ [3]. The anisotropy of DPS in PVC also remained constant in the emission band; its value, however, was as high as 0.3 for $\lambda_{\text{exc}} = 355 \text{ nm}$ [4]. The very low emission anisotropy of DPS in PVA is due to the considerable mobility of DPS in the polymer.

Next, by examining the photoluminescence properties of the nonpolar molecule of *trans*-4,4'-diamino-stilbene (DAS) in PVA films, the occurrence of phosphorescence along with fluorescence was detected at room temperature (296 K). No phosphorescence was found for this molecule in PVC films.

In the present paper we report the results of studies on the fluorescence and phosphorescence properties of the DAS molecule in PVA film at room and liquid nitrogen temperature.

2. Experimental

The preparation of PVA films is described in [5, 6]. The absorption, fluorescence and phosphorescence spectra, as well as the emission anisotropy and lifetimes of the DAS molecule were measured in PVA films by the use of instruments described in [2, 7, 8]. In the experiment reported in [7], when measuring the phosphorescence anisotropy, an additional mechanical chopper was employed together with the electronic system cutting off the fluorescence, with a broad-range frequency adjustment.

3. Results and Discussion

3.1. Absorption and Emission Spectra of DAS in Methanol and in PVA Films. Lifetimes

Diphenylpolyenes, similarly as *p*-substituted stilbenes, are slightly soluble in aqueous PVA solution and can therefore be introduced into the solution through methanol [9]. Figure 1 shows the absorption and fluorescence spectra of DAS in methanol. The effect of direct irradiation with light of wavelength $\lambda_{\text{exc}} = 342 \text{ nm}$ is readily seen. As a result of light induced *trans-cis*-isomerization, the absorption and fluorescence band intensity decreases. Similar effect of direct irradiation with wavelength 340 nm can be ob-

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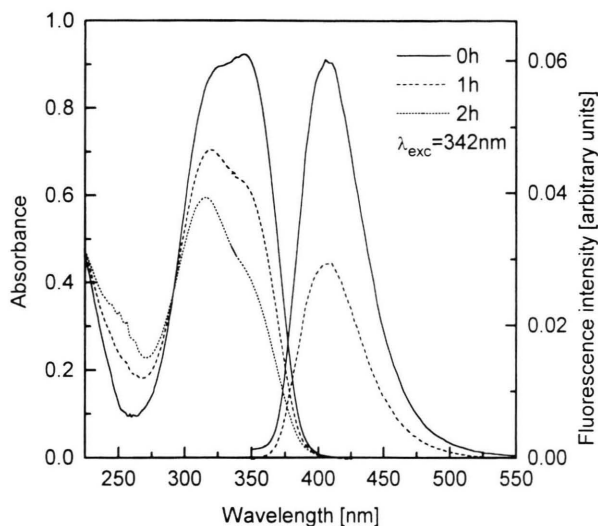


Fig. 1. Absorption and fluorescence spectra of DAS in methanol exposed to direct irradiation at $\lambda = 342$ nm for 1 hour and 2 hours (measured at 296 K and $\lambda_{\text{exc}} = 342$ nm).

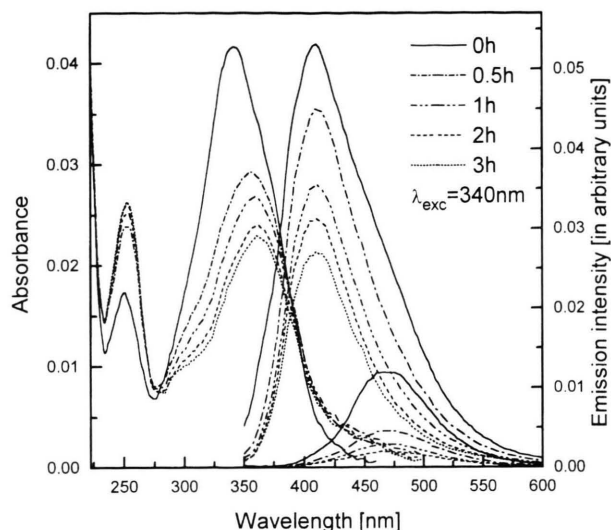


Fig. 2. Absorption, global emission (fluorescence + phosphorescence) and phosphorescence spectra of DAS in PVA film exposed to direct irradiation at $\lambda = 340$ nm for 0 to 3 hours (non-heated sample, measured at 296 K and $\lambda_{\text{exc}} = 340$ nm).

served for DAS placed in PVA film (Figure 2). The total emission (fluorescence + phosphorescence) and phosphorescence spectra were observed for $\lambda_{\text{exc}} = 340$ nm at 296 K for the sample when non-heated and heated above the glassy transition temperature. Since the phosphorescence band (400–550 nm) lies within the fluorescence band, we do not deal with pure fluorescence but with a global emission. Similar results were obtained for DAS in a film preheated to 423 K. Lowering of the temperature to 84 K did not essentially affect the phosphorescence band intensity (cf. Figs. 2 and 3). Figure 3 shows the measured global emission (solid line) and phosphorescence (dotted line), and the spectrum of pure fluorescence obtained by subtracting the two lines.

In order to obtain the mean fluorescence lifetime, τ_F , of DAS in PVA, the excitation was in the longwave absorption band, $\lambda_{\text{exc}} = 340$ nm, and the observation at $\lambda_{\text{obs}} = 380$ nm enabled the possible contribution from phosphorescence to be eliminated. The values of τ_F obtained at room temperature for the sample non-heated and heated to 423 K were 1.583 and 1.577 ns, respectively. The phosphorescence lifetimes, τ_P , for the same sample at $\lambda_{\text{exc}} = 340$ nm and $\lambda_{\text{obs}} = 470$ nm for the non-heated and heated sample were 75.5 and 78.8 ms, respectively. The heating above the glassy transition temperature had in this case no essential effect upon mean lifetimes, τ_F and τ_P .

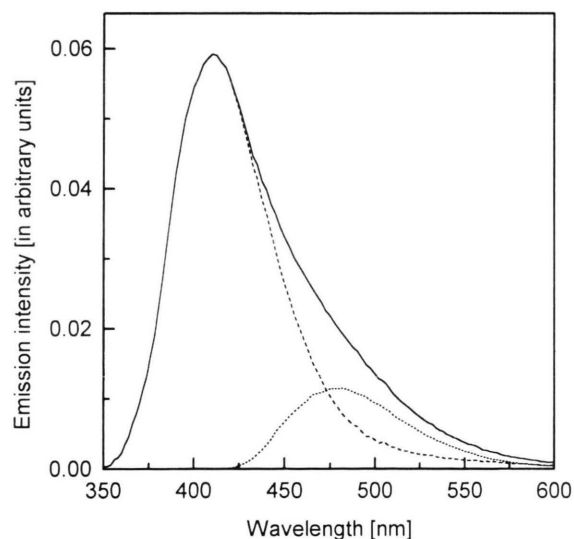


Fig. 3. Global emission (fluorescence + phosphorescence) (solid line), phosphorescence (dotted line) and fluorescence (dashed line) spectra of DAS in non-heated PVA film measured at 84 K and $\lambda_{\text{exc}} = 340$ nm.

3.2. Emission Anisotropy Spectra of DAS in PVA Films

Figures 4 and 5 show normalized absorption, fluorescence and phosphorescence spectra at 296 K for DAS in PVA films non-heated and preheated to

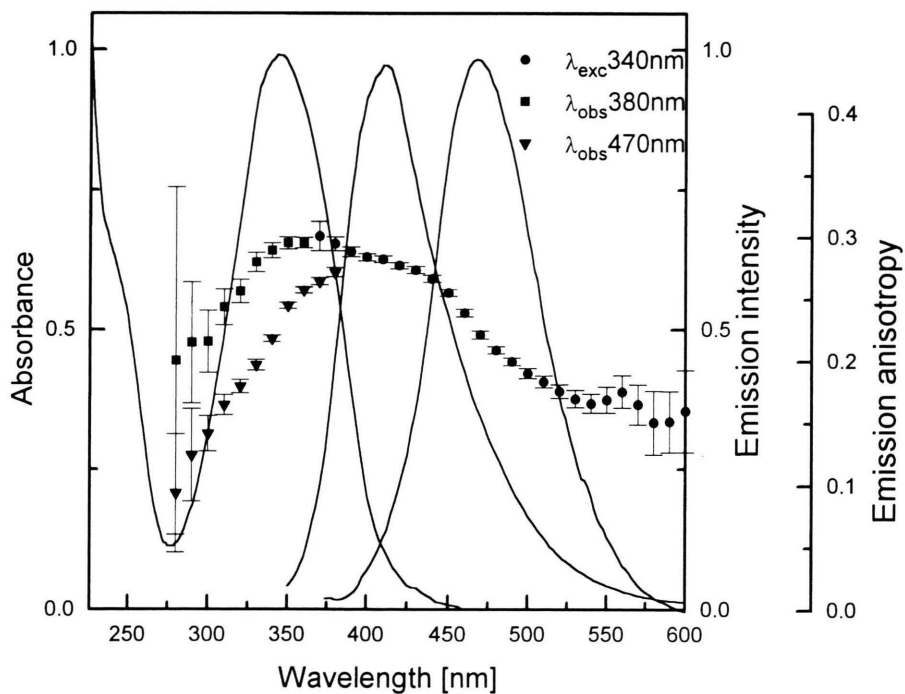
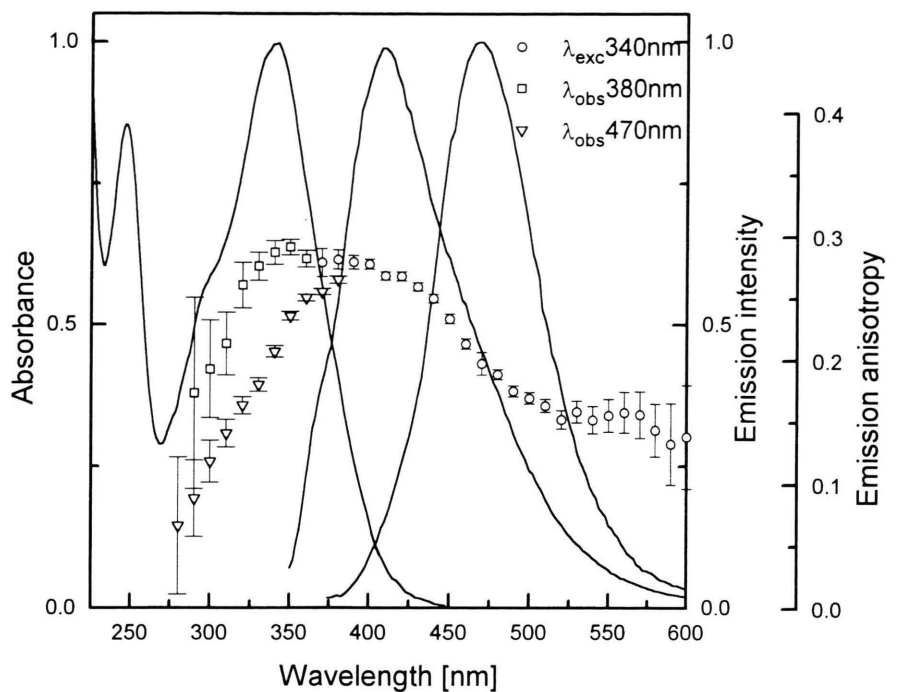


Fig. 4 and 5. Normalized absorption, global emission and phosphorescence spectra of DAS measured at 296 K in non-heated PVA film (Fig. 4) and after pre-heating to 423 K and cooling to room temperature (Fig. 5). Different points correspond to the emission anisotropy spectra.

423 K. The spectra are accompanied by the plot of the emission anisotropy versus excitation wavelength, λ_{exc} , for two fixed observation wavelengths λ_{obs} and the runs of anisotropy in the emission band at fixed excitation wavelength ($\lambda_{\text{exc}} = 340$ nm). When carrying out the observation at $\lambda_{\text{obs}} = 380$ nm, i.e. within the fluorescence band where no phosphorescence occurs, a high emission anisotropy close to 0.3 is obtained in heated or non-heated PVA film. In turn, at $\lambda_{\text{obs}} = 470$ nm (at the maximum of the phosphorescence band), the anisotropy is markedly underrated in the longwave absorption band since the global emission (fluorescence + phosphorescence) contributes to the quantity observed. The complex anisotropy run in the emission band results also from the overlapping of the fluorescence and phosphorescence bands.

4. Conclusions

- a) 4,4'-Diaminostilbene (DAS) in poly(vinyl alcohol) film at 296 K displays phosphorescence which only slightly differs in the intensity from the phosphorescence emitted at 84 K.
- b) The unusual behaviour of the emission anisotropy in the absorption and photoluminescence bands is due to the overlapping of two fluorescence and phosphorescence bands.
- c) The mean lifetime of the DAS phosphorescence observed in PVA films at 296 K is short and amounts to 75.5 and 78.8 ms for non-heated and heated film, respectively. The respective mean fluorescence lifetimes for this sample are 1.583 and 1.577 ns.
- d) A distinct effect of direct light irradiation upon the intensity of the absorption, global emission and phosphorescence bands was observed for DAS in PVA film.

- [1] A. Kawski, A. Kubicki, B. Kukliński, and G. Piszczek, *Z. Naturforsch.* **48a**, 947 (1993).
- [2] A. Kawski, G. Piszczek, B. Kukliński, and T. Nowosielski, *Z. Naturforsch.* **49a**, 824 (1994).
- [3] A. Kawski, B. Kukliński, and T. Nowosielski, *Z. Naturforsch.* **50a**, 1170 (1995).
- [4] A. Kawski, B. Kukliński, and T. Nowosielski, *Z. Naturforsch.* **50a**, 1175 (1995).
- [5] A. Kawski and Z. Gryczyński, *Z. Naturforsch.* **41a**, 1195 (1986).
- [6] A. Kawski, *Developments in Polarized Fluorescence Spectroscopy of Ordered Systems*, in: *Optical Spectroscopy in Chemistry and Biology – Progress and Trends* (D. Fassler, ed.), VEB Deutscher Verlag der Wissenschaften, Berlin 1989.
- [7] A. Kubicki, *Exp. Tech. Phys.* **37**, 329 (1989).
- [8] A. Kawski, B. Kukliński, A. Kubicki, and G. Piszczek, *Z. Naturforsch.* **48a**, 759 (1993).
- [9] A. Kawski, Z. Gryczyński, I. Gryczyński, W. Wiczak, and H. Malak, *Z. Naturforsch.* **46a**, 621 (1991).