

Unusual Absorption and Fluorescence Properties of p-Substituted Stilbenes in Poly(vinyl alcohol) Films

A. Kowski, B. Kukliński, and T. Nowosielski

Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland

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The behaviour of absorbance, fluorescence and emission anisotropy of linear molecules with one double bond, i.e. 4-amino-4'-nitrostilbene (ANS), 4-dimethylamino-4'-nitrostilbene (DNS) and 4,4'-diphenylstilbene (DPS), was examined in poly(vinyl alcohol) (PVA) films at different temperatures (293–423 K). The unusual behaviour of absorption and fluorescence properties of the molecules investigated, similar to those of linear polyenes in PVA, was, however, less pronounced.

1. Introduction

The unusual behaviour of the absorbance of non-polar linear polyenes, $\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$, for $n=2, 3, 4$ in poly(vinyl alcohol) (PVA) films heated to 423 K is evoked by thermal cis-trans isomerization in the ground state [1–3]. It was found that above a glassy transition temperature of 358 K in the PVA polymer, the optical density in the longwave region of the absorption band grows. For 1,4-diphenyl-1,3-butadiene (DPB) ($n=2$) the increase is five-fold, being ten-fold for 1,6-diphenyl-1,3,5-hexatriene (DPH) ($n=3$) and almost twenty-fold for 1,8-diphenyl-1,3,5,7-octatetraene (DPO) ($n=4$). It turns out that the effect observed enhances with the growing length of the chain with double bonds.

The aim of the present work is to investigate the behaviour of the absorbance and fluorescence of molecules with one double bond in PVA. To this end, three stilbene derivatives were chosen: 4-amino-4'-nitrostilbene (ANS), 4-dimethylamino-4'-nitrostilbene (DNS) and 4,4'-diphenylstilbene (DPS) (Figure 1).

Molecules ANS and DNS are strongly polar, and upon excitation their dipole moment, μ_e , grows as much as 3.2 times (for ANS: $\mu_g=21.7 \times 10^{-30}$ Cm, $\mu_e=69 \times 10^{-30}$ Cm; for DNS: $\mu_g=24.0 \times 10^{-30}$ Cm, $\mu_e=77.0 \times 10^{-30}$ Cm) [4]. Characteristic of ANS and DNS molecules are relatively short mean lifetimes, 2.3 and 2.6 ns, respectively [5]. Irrespective of short mean lifetimes, these molecules have quite high fluorescence quantum yields.

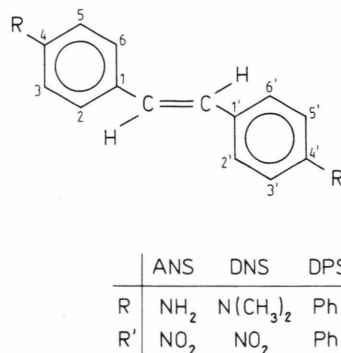


Fig. 1. Structural formulae of ANS, DNS and DPS.

2. Experimental

Isotropic poly(vinyl alcohol) (PVA) films were prepared by the method described in [6, 7]. Absorption and fluorescence as well as emission anisotropy spectra were measured by the apparatus described in [8–10].

3. Results and Discussion

3.1 Optical Density of ANS, DNS and DPS in PVA Films

As in the case of diphenylpolyenes ($n=2, 3, 4$), also for ANS, DNS and DPS in PVA the increase in the absorbance can be observed in the longwave absorption band when increasing the temperature from 293 to 428 K. Figure 2 shows an example of the absorp-

Reprint requests to Prof. Dr. Alfons Kowski.

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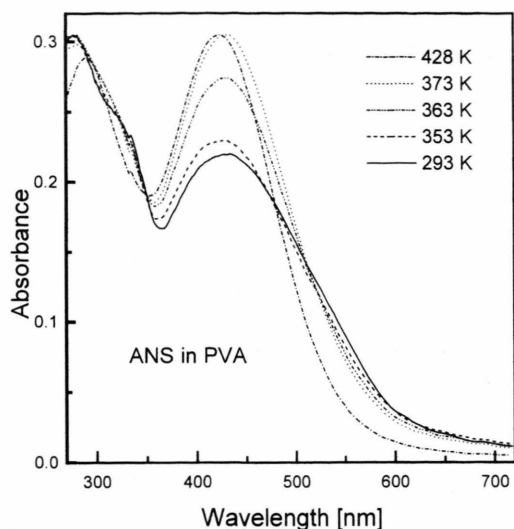


Fig. 2. Absorption spectra of ANS in PVA film at different temperatures.

tion spectrum of ANS in PVA film. The optical density at the maxima of the ANS, DNS and DPS absorption bands as a function of temperature is shown in Figure 3. For the molecules investigated in the temperature range 293–358 K, the optical density does not change. It is only above a glassy transition temperature of 358 K that the growth in the optical density is about 1.6-fold for ANS, 2.2-fold for DNS and 3-fold for DPS, which is markedly lower than that observed in diphenylpolyenes.

The above effect is irreversible, i.e. after cooling the sample down to room temperature, its high absorbance is retained. ANS, DNS and DPS molecules, insoluble in PVA, were introduced into the solution thorough methanol. As in the case of polyenes, also for the molecules examined, water is responsible for the occurrence of *cis* conformers in the ground state. As a result of heating, conformational changes and transitions from the *cis* to the luminescent *trans* forms occur, according to the energy diagram presented in Fig. 4 of [1].

3.2 Fluorescence Spectra of ANS and DNS in PVA Films

Figures 4 and 5 show the fluorescence spectra of ANS and DNS in PVA films, respectively, at different temperatures. In the temperature range 296–358 K,

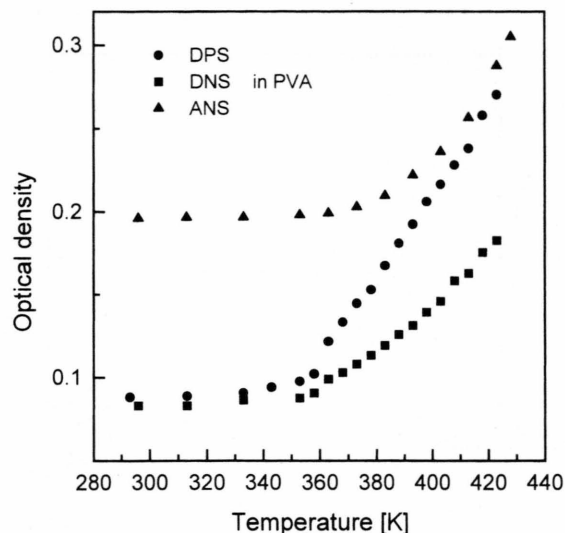


Fig. 3. Dependence of the longwave absorption maximum (optical density) of ANS, DNS and DPS in PVA film upon temperature.

when the optical density does not change (see Fig. 3), characteristic fluorescence quenching occurs (curves 1, 2 and 3 in Figs. 4 and 5). Above a glassy transition temperature of 358 K (curves 4, 5, and 6 in Figs. 4 and 5), the increase in the optical density corresponds to the growth in the fluorescence intensity which for DNS in PVA is considerably stronger than that for ANS in PVA in the temperature range examined. If the samples heated to 423 K are cooled down to room temperature and next again heated to 423 K, a characteristic quenching can be observed in the whole temperature range (Figs. 6 and 7).

3.3 Absorption, Fluorescence and Anisotropy Spectra of ANS and DNS in PVA Films

Figures 8 and 9 show absorption and fluorescence as well as emission anisotropy spectra of ANS and DNS in PVA films, measured at 296 K in films freshly prepared and heated to 423 K. In the case of ANS in PVA, the heating did not cause any marked shift of the absorption and fluorescence band maxima, and only a slight broadening of the fluorescence spectrum. For DNS in PVA, a greater fluorescence band shift relative to the shift of the absorption band maximum was observed in the sample heated to 423 K, compared to that in the unheated sample. This is due to the greater difference between the electric dipole moments.

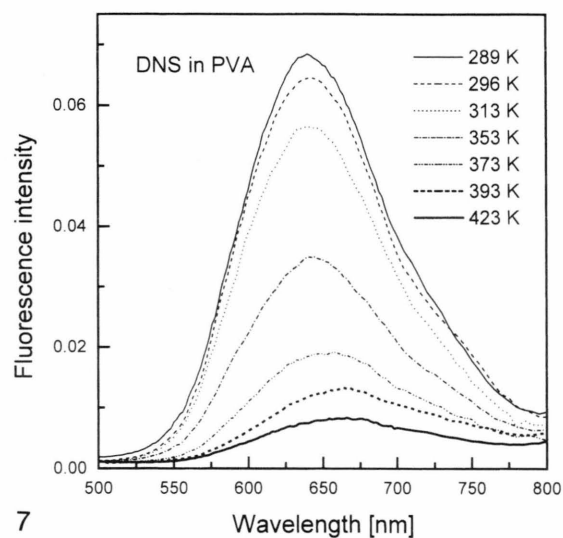
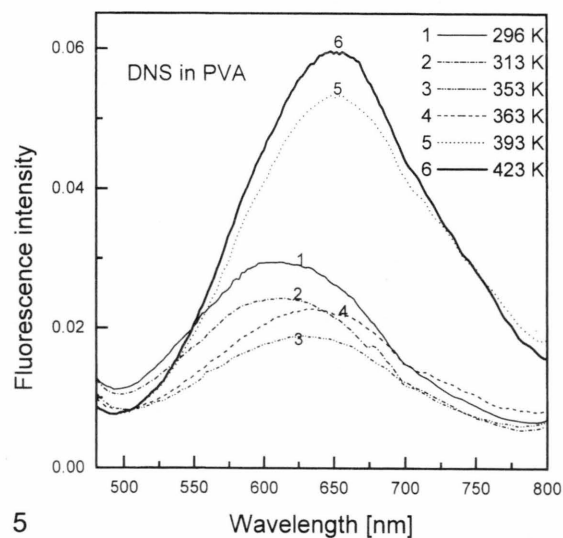
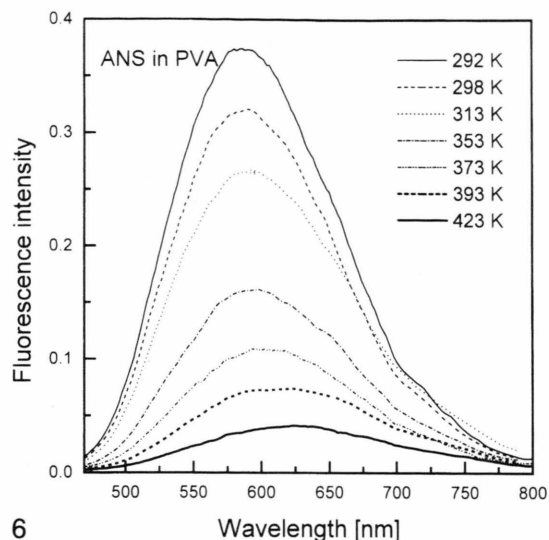
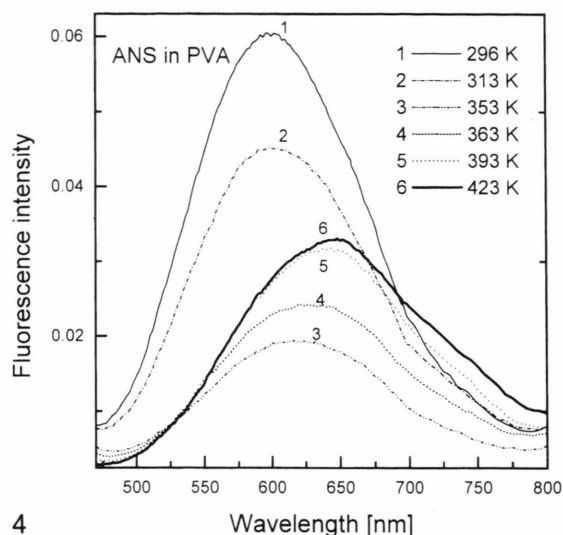
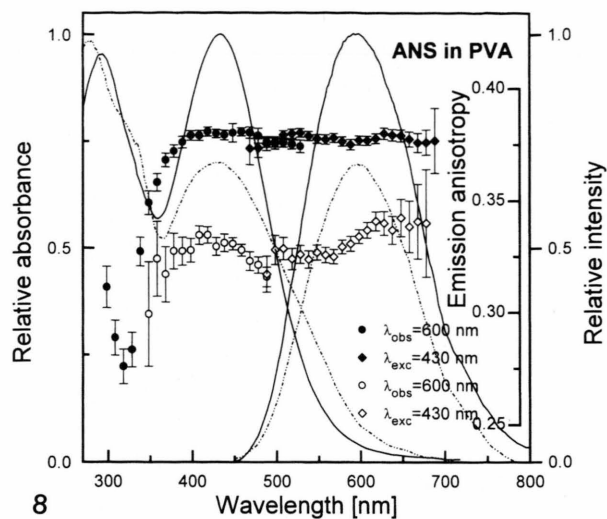


Fig. 4 and 5. Fluorescence spectra (arbitrary units) of ANS ($\lambda_{\text{exc}} = 420$ nm) and DNS ($\lambda_{\text{exc}} = 430$ nm) in PVA film at different temperatures excited under the same conditions.

Fig. 6 and 7. Fluorescence spectra (arbitrary units) of ANS and DNS in PVA film measured at different temperatures after previous heating the samples to 423 K and cooled to room temperature.

The emission anisotropy of ANS in PVA of both the unheated and heated sample is distinctly higher than the emission anisotropy of DNS in PVA, which is due to the shorter lifetime of the ANS molecules. For ANS and DNS, a considerable scatter of the experimental points is observed in the fluorescence band of the unheated samples. This is evidence that in a

freshly prepared PVA film there are areas with different degrees of polymerization, and such a film constitutes a non-homogeneous environment. In spite of heating the sample to 423 K, the maximum value of the emission anisotropy, i.e. 0.4 (Fig. 8), is not attained. This results from restricted rotations of the molecules.



3.4 Absorption, Fluorescence and Anisotropy Spectra of DPS in PVA Films

The nonpolar DPS molecule in PVA film displays a structured fluorescence spectrum at room temperature and at 423 K. A marked fluorescence band shift is observed in the case of the sample heated to 423 K (Figure 10). The effect of temperature on the fluorescence band intensity is similar to that reported for ANS and DNS (Figure 11). Although the DPS molecule is nonpolar, a quite distinct fluorescence band shift can be observed towards short waves when increasing the temperature. For a sample heated to 423 K, a strong dependence of the fluorescence band position on the excitation light wavelength was found (Fig. 12), which may be the reason for the emission from at least two kinds of luminescent centres. For nonpolar DPS molecules surprisingly low emission anisotropy is observed for samples unheated and heated to 423 K (Figure 10). Such an effect is due to the rotational motions inside empty polymer cavities.

A necessity emerges to investigate the absorption and fluorescence properties in other polymers such as poly(vinyl chloride) (PVC), insoluble in water. Such studies are in progress.

4. Conclusions

a) Above the glassy transition temperature (358 K) of the PVA polymer, the optical density of linear luminescent molecules having double bonds in their structure, grows in the longwave region of their absorption band with increasing number, n , of the double bonds.

b) The unusual behaviour of the absorbance and fluorescence of p-substituted stilbenes in PVA is evoked by the presence of water. Heating of the samples leads to thermal cis-trans isomerization in the ground state.

c) In the case of polyenes, ANS, DNS and DPS in PVA films at room temperature no phosphorescence was observed, unlike 4-cyano-2,6,N,N-dimethylaniline and 4-cyano-2,6,N,N-tetramethylaniline in PVA films [9].

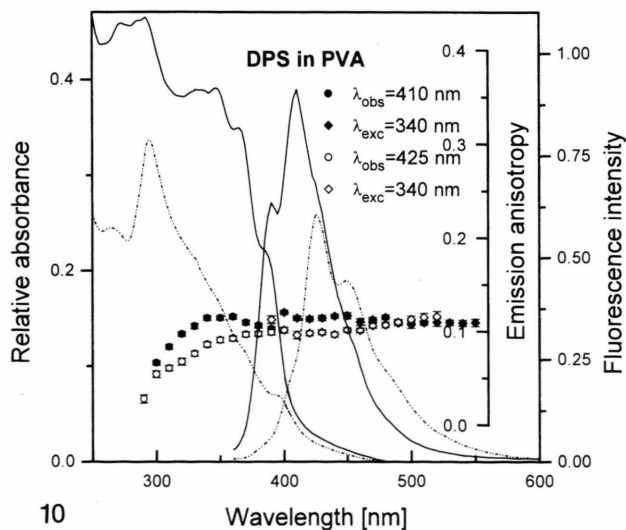
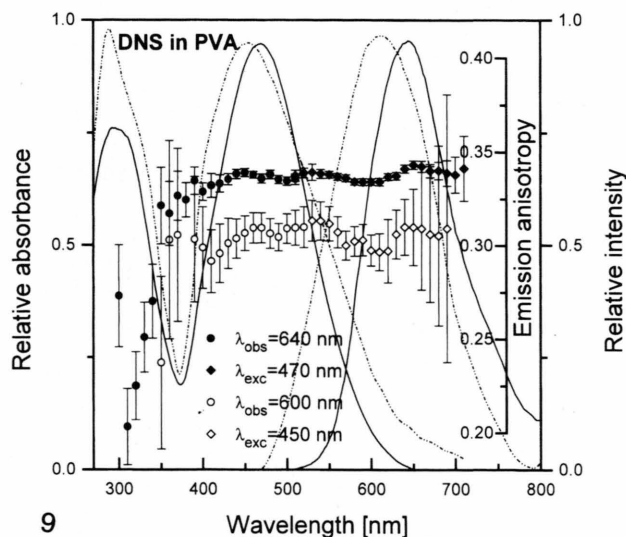


Fig. 8–10. Absorption, fluorescence and emission anisotropy spectra of ANS, DNS and DPS in PVA film measured at room temperature. The black points and solid lines concern the samples preheated to 423 K and then cooled to room temperature before the measurement.

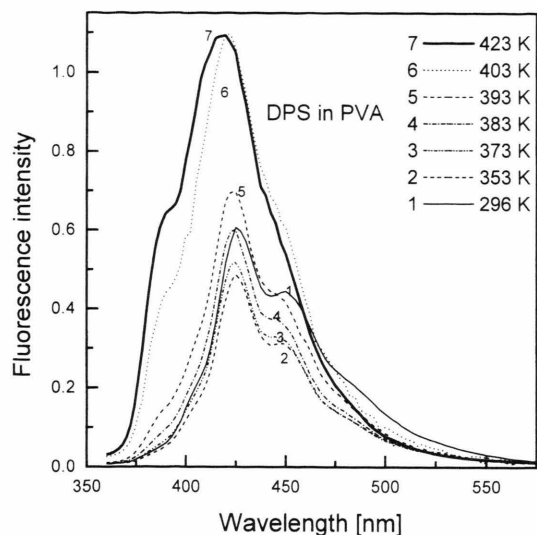


Fig. 11. Fluorescence spectra (arbitrary units) of DPS in PVA film ($\lambda_{\text{exc}} = 340$ nm) at different temperatures excited under the same conditions.

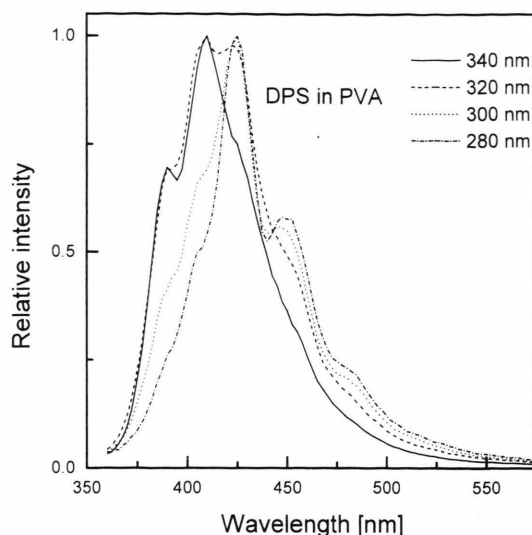


Fig. 12. Normalized fluorescence spectra of DPS in PVA film at different excitation wavelengths measured at 296 K. The sample was previously heated to 423 K.

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