Absorption and Fluorescence Properties of p-Substituted Stilbenes in Poly(vinyl chloride) Film

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Experimental studies have demonstrated that the absorption and fluorescence spectra of linear molecules with one double bond, i.e. 4-amino-4′-nitrostilbene (ANS), 4-dimethylamino-4′-nitrostilbene (DNS) and 4,4′-diphenylstilbene (DPS), contained in preheated to 393 K or nonheated poly(vinyl chloride) (PVC) films are identical in shape and position, unlike those observed for ANS, DNS and DPS in poly(vinyl alcohol) (PVA) films. For polar ANS and DNS molecules in PVC film a decrease in the emission anisotropy with growing wavelength of the fluorescence band was observed. This unusual behaviour of the emission anisotropy is accounted for by the overlap of two close emission bands from different luminescent centres, resulting from different microenvironments of the ANS and DNS molecules in PVC film. The emission anisotropy of nonpolar DPS molecule in PVC does not change within the fluorescence spectrum.

1. Introduction

In [1] an unusual behaviour of the absorbance and fluorescence of 4-amino-4′-nitrostilbene (ANS), 4-dimethylamino-4′-nitrostilbene (DNS) and 4,4-diphenylstilbene (DPS) was observed in poly(vinyl alcohol) (PVA) films in the temperature range 296–423 K. The optical density increase in the longwave region of the absorption band of the above luminescent compounds at temperatures growing above the glassy transition temperature (358 K) of the PVA polymer is due to thermal cis-trans isomerization in the ground state [2–4]. The presence of water was found to be favourable for the occurrence of the cis conformer in the ground state.

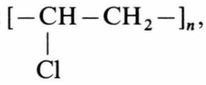
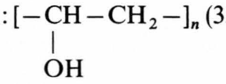
In the present study, poly(vinyl chloride) (PVC), which is insoluble in water, served as a matrix. Compared to PVA, PVC has almost the same glassy transition temperature (354 K) and is more polar.

2. Experimental

Isotropic PVC films were prepared by the method described in [5]. The luminescent compounds investigated, ANS, DNS, and DPS, were introduced into powdered PVC through tetrahydrofuran. Absorption, fluorescence and emission anisotropy spectra were measured by means of an experimental setup described in [6–8]. Fluorescence decays were measured on a pulse FL 900 spectrofluorimeter from Analytical Instruments (Scotland), using a standard time-correlated single photon counting method [9].

3. Results and Discussion

3.1. *Absorption and Fluorescence Spectra of ANS, DNS and DPS in PVC and PVA films*

Although PVC matrix:  $[-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH}_2-]_n$, insoluble in water, has almost the same glassy transition temperature (354 K) as PVA matrix:  $[-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH}_2-]_n$ (358 K), no unusual behaviour of its absorbance and fluorescence can be observed. Figures 1–3 show for comparison the absorbance and fluorescence spectra of ANS, DNS and DPS in freshly prepared PVC and PVA films, measured at 296 K. For the strongly polar ANS and DNS molecules (as a result of excitation to the singlet state S_1, the electric dipole moment increases 3.2-fold), markedly greater fluorescence band shifts relative to absorption bands are observed in PVA than in the more polar PVC. Both absorption and fluorescence spectra of these molecules are diffused and in PVC are markedly narrower. In the case of the nonpolar DPS molecule, the fluorescence bands are structured in both matrices. At room temperature, the absorption and flu-

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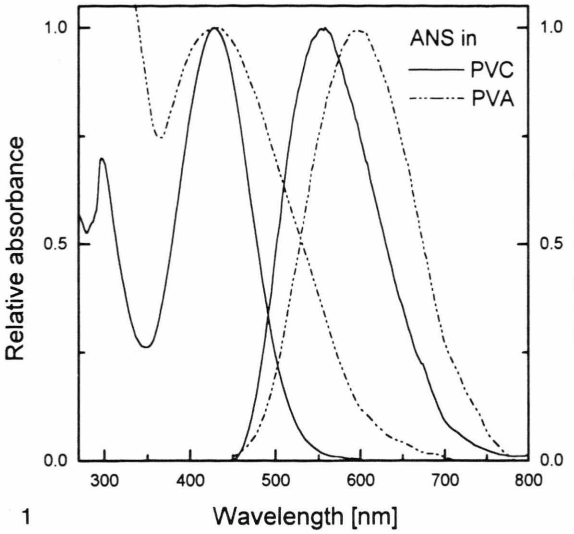
orescence spectra of ANS, DNS and DPS in PVC films, both nonheated and preheated to 393 K *, do not differ in position and intensity, contrary to the results obtained for these molecules in PVA film.

3.2. Emission Anisotropy Spectra of ANS, DNS and DPS in PVC Films

In the fluorescence band of ANS and DNS in PVC films, the emission anisotropy decreases when increasing the wavelength (Figures 4 and 5). A similar behaviour of the anisotropy in the fluorescence band was already observed for phthalimide derivatives [10, 11], and was explained in [11] by the marked overlapping of the two fluorescence bands [12, 13], resulting from two different luminescent centres displaying different emission anisotropies.

Being strongly polar, the ANS and DNS molecules are capable of forming luminescent centres depending on the composition of the close environment which is the PVC polymer. Empty cavities can also be formed in the polymer, in which the interaction of polar ANS and DNS with the surrounding polymer molecules is weak (insignificant). The behaviour of the emission anisotropy of ANS and DNS in PVC, measured at 296 K as a function of the wavelength in the absorption and fluorescence bands for fresh and preheated (to 393 K) films, differs completely from that observed for ANS and DNS in the PVA polymer [1]. In the preheated PVC films lower emission anisotropy values are noted than in the nonheated films (Figs. 4 and 5), whereas for the nonpolar DPS molecule in PVC (Fig. 6) no effect of heating is observed and the emission anisotropy is equal in the whole emission band. This agrees with results obtained for DPS in methyl polymetacrylate and polystyrene [14, 15]. The emission anisotropy of DPS in PVC film is distinctly lower than that of ANS and DNS in the same polymer, which is due to a greater rotational freedom in the polymer cavities.



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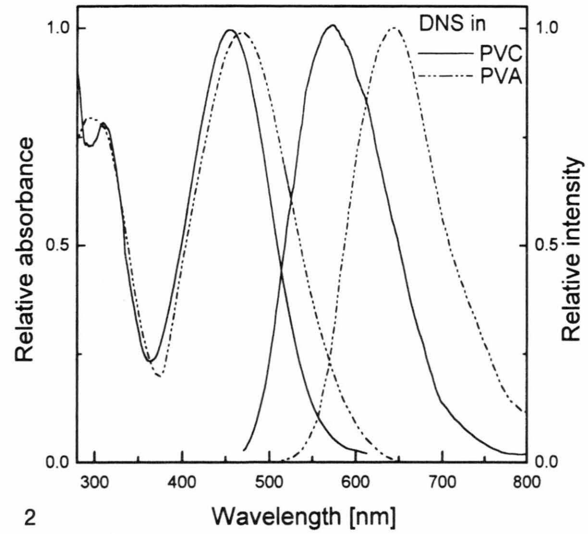

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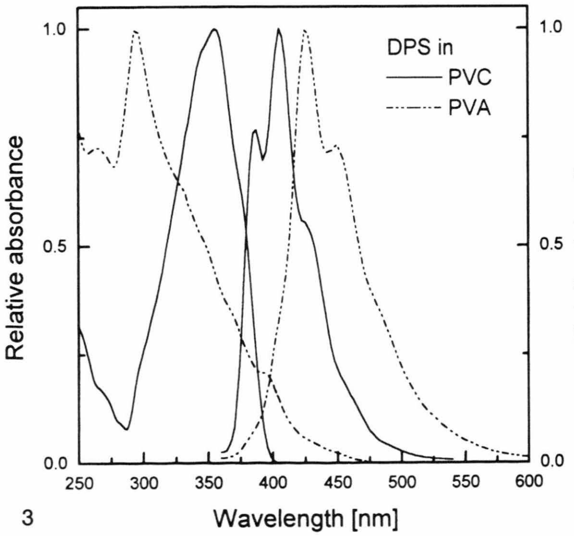

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Figs. 1–3. Comparison of absorption and fluorescence spectra of ANS ($\lambda_{exc} = 420$ nm), DNS ($\lambda_{exc} = 450$ nm) and DPS ($\lambda_{exc} = 355$ nm) in freshly prepared isotropic PVC and PVA films, measured at 296 K.

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* Since PVC turns yellow above 393 K, no measurements were carried out at higher temperatures.

Table 1. Fluorescence decay times of ANS, DNS and DPS in PVC films before and after heating to 393 K and measured at 296 K.

Molecule	λ_{exc} [nm]	λ_{obs} [nm]	τ_1 [ns]	A_1[a]	τ_2 [ns]	A_2[a]	χ^2[b]
ANS							
before	420	550	2.81	0.789	1.69	0.211	0.932
after	420	550	2.68	0.832	1.15	0.168	0.833
DNS							
before	420	550	2.89	0.836	1.05	0.164	1.003
after	420	550	2.84	0.882	0.85	0.118	0.998
DPS							
before	350	405	1.06	1.00	–	–	0.997
after	350	405	1.08	1.00	–	–	1.280

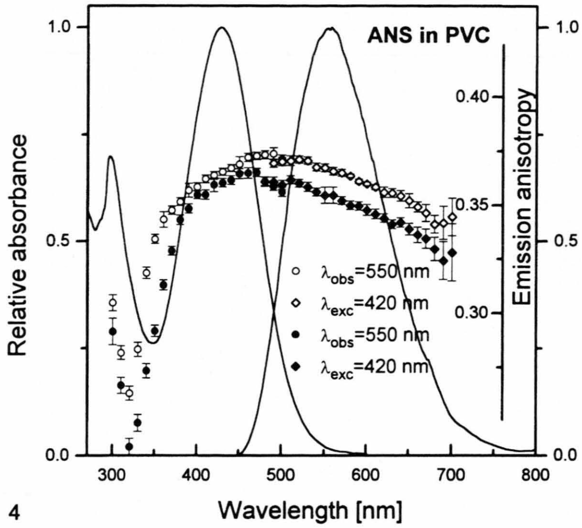
[a] A_1 and A_2 are the preexponential factors (normalized relative fluorescence intensities, $A_1 + A_2 = 1$) representing the time-resolved decay of the components with a lifetime τ_1 and τ_2.

[b] From least-squares analysis of time-resolved decays.

3.3. *Influence of the Excitation Light Wavelength on the Fluorescence Band Position. Fluorescence Lifetimes*

Whether or not one or two emission fluorescence centres are present, can independently be verified by investigating the effect of the excitation light wavelength on the position of the emission band of molecules in PVC and by measuring fluorescence decay times. For both ANS and DNS in PVC film, a slight dependence of the fluorescence band maximum position upon the excitation light wavelength is observed. Figure 7 shows results obtained for DNS in PVC. No such dependence was observed for the nonpolar DPS in PVC.

The results of fluorescence decay time measurements given in Table 1 for the three molecules investigated confirm the existence of two types of luminescent centres in the case of ANS and DNS in PVC films, which can account for the unusual behaviour of the emission anisotropy in the fluorescence band (see Figures 4 and 5). On the other hand, only one mean lifetime was obtained for DPS in PVC film (Table 1), with the fluorescence band position being independent of the excitation light wavelength. This is in full agreement with the behaviour of the emission anisotropy in the fluorescence band (see Figure 6). It should be mentioned that



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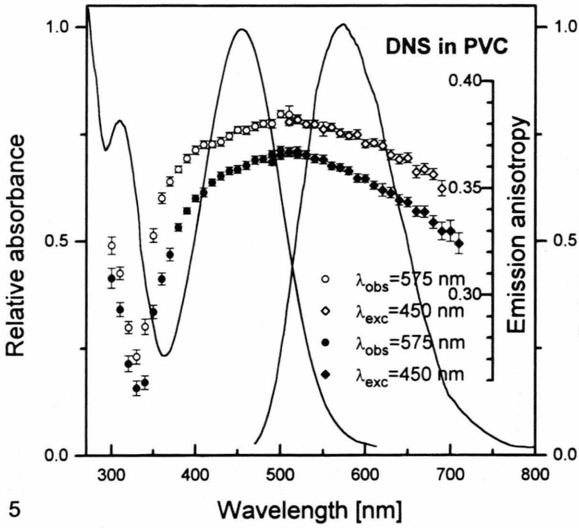

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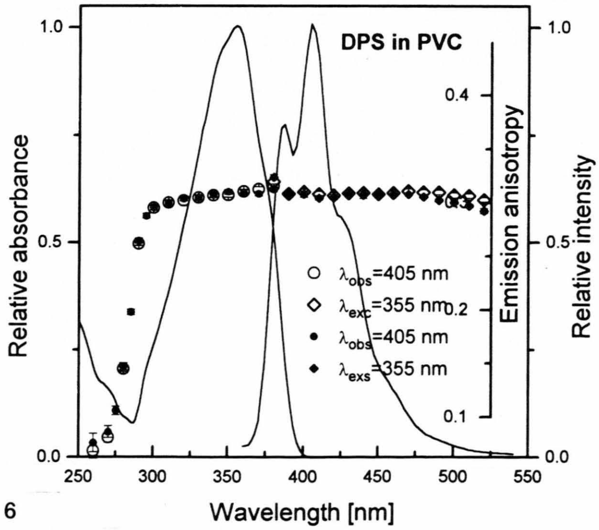

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Figs. 4–6. Absorption, fluorescence and emission anisotropy spectra of ANS, DNS and DPS in PVC film measured at 296 K. Empty circles correspond to the freshly prepared films, and black circles to the samples preheated to 393 K.

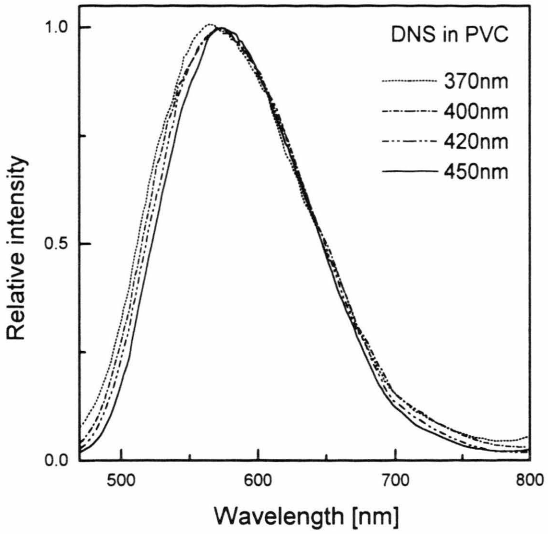

Fig. 7. Normalized fluorescence spectra of DNS in PVC film at different excitation wavelengths: 370, 400, 420, and 450 nm, measured at 296 K.

for DPS in PVA film, a distinct strong dependence of the intensity distribution and fluorescence band position upon the excitation light wavelength was obtained [1]. This unusual behaviour is typical of the PVA matrix and requires further studies to be undertaken.

4. Conclusions

a) Although PVC and PVA polymers have almost the same glassy transition temperatures, p-substituted stilbenes behave differently as regards their absorption and fluorescence properties.

b) The unusual behaviour of the emission anisotropy in the fluorescence band of ANS and DNS in PVC film can be accounted for by the overlapping of two close emission bands originating from different luminescent centres.

c) The preheating of PVC films with ANS, DNS and DPS does affect the emission anisotropy but not the absorption and fluorescence properties. Upon increasing the temperature, the emission anisotropy of ANS and DNS in PVC decreased but did not change for DPS in PVC.

Acknowledgements

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