

# Isomerization of Diphenyl Polyenes.

## Part III. Absorption and Fluorescence Properties of 1,4-Diphenyl-1,3-butadiene in Poly(vinyl alcohol) Film

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*Dedicated to Professor Wolfgang Liptay on the occasion of his 65th birthday*

The effect of temperature on the absorption and fluorescence properties of 1,4-diphenyl-1,3-butadiene (DPB) in poly(vinyl alcohol) film (PVA) was investigated in the range from 293 to 423 K. Upon heating above 353 K, the optical density in the long wavelength region (at 339 nm) increases five times only, whereas for 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) ten and twenty times, respectively. However, the total quantum yield ( $\Phi_F = 0.68$ ) at 293 K is greater than that for the *trans-trans* form ( $\Phi_F = 0.63$ ) and decreases with growing temperature. Both this effect and broadening effect in the fluorescence band at 293 K evidence the existence of two emission centres, i.e. the *trans-trans* and *cis-trans* conformers.

### 1. Introduction

In Parts I and II of this study [1, 2] we described an unusual temperature dependence of 1,8-diphenyl-1,3,5,7-octatetraene (DPO,  $n = 4$ ) absorption and fluorescence in poly(vinyl alcohol) (PVA) film. The optical density (in the long wavelength region) and the quantum yield of the isotropic PVA film with DPO admixtures were found to increase considerably in the temperature range from 353 K to 423 K. A similar effect was observed for 1,6-diphenyl-1,3,5-hexatriene (DPH,  $n = 3$ ) in PVA film, but it was smaller than for DPO in PVA film [3]. The effect found for diphenyl polyenes,  $\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$ , for  $n = 3$  and 4 is irreversible, i.e. once the sample is heated it retains its absorbance and fluorescence quantum yield upon cooling to room temperature. It has its origin in the *cis-trans* conversion of DPH and DPO molecules in PVA film at high temperatures [1–3].

Diphenylpolyenes for  $n = 3$  and  $n = 4$  possess anomalous fluorescence properties that are not observed in 1,4-diphenyl-1,3-butadiene (DPB) for  $n = 2$ . The radia-

tive rate parameter  $k_F$  (given by  $\Phi_F/\tau$ , where  $\Phi_F$  and  $\tau$  are the fluorescence yield and decay time, respectively) is smaller than the rate parameter  $k_F^c$  calculated from the integrated absorption spectrum, with the ratio  $R = k_F^c/k_F$  increasing with the chain length [4, 5]. For DPB ( $R \approx 1.2$ ) this effect is significantly less pronounced than for DPH ( $R \approx 5.6$ ) and DPO ( $R \approx 22$ ) [5, 6]. As also shown for DPB in methylcyclohexane/isohexane and propylene glycol,  $k_F$  in a given solvent is independent of temperature and of the solvent at a given temperature [5].

In this part of the paper we have tested the absorption and fluorescence behaviour of DPB in PVA film at different temperatures.

### 2. Experimental

1,4-Diphenyl-1,3-butadiene (DPB) from Aldrich Chemical Company, Inc., Steinheim, BRD, was used without further purification. Poly(vinyl alcohol), 100% hydrolyzed, molecular weight 106,000–110,000, was from Aldrich Chemie. Methanol was spectral grade and water was bidistilled.

Isotropic PVA films were prepared at room temperature by introducing DPB into an aqueous PVA solu-

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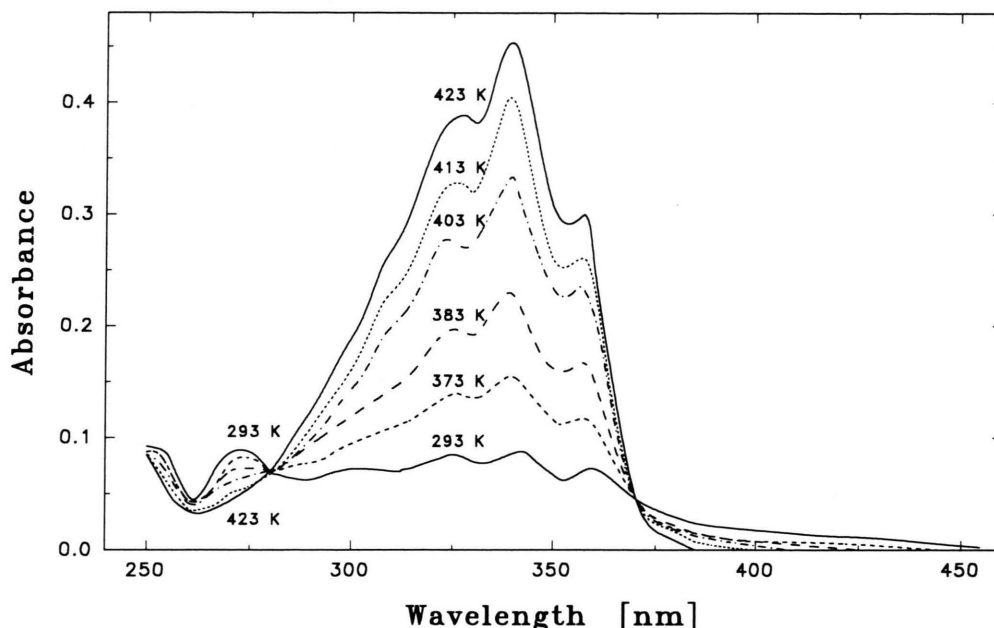


Fig. 1. Absorption spectra of 1,4-diphenyl-1,3-butadiene (DPB) in Poly(vinyl alcohol) (PVA) film at different temperatures.

tion through methanol using the method described in previous papers [7, 8]. PVA films without DPB were used as references in the absorption measurements.

Absorption and fluorescence spectra, quantum yields and emission anisotropy were measured in a special thermostatic cell enabling the temperature of the sample to be maintained with an accuracy of  $\pm 0.5$  K in the temperature range from 293 K to 423 K. The measuring systems were described in the previous papers [1, 2, 9].

### 3. Results

#### 3.1. Temperature Induces Changes in DPB Absorption in PVA Film

The absorbances of DPB measured in PVA film at different temperatures behave similarly as those demonstrated in [1] for DPO and in [3] for DPH (Figure 1). The DPB absorption spectrum in PVA film does not change up to 353 K. Above 353 K an increase in the long wavelength (285 nm–370 nm) absorption of the sample was observed. A slight absorption band shift toward short waves (blue shift) is observed (by up to 2.8 nm) when changing the temperature from 293 K to 423 K. At 423 K, the optical density of the sample is only five times higher than

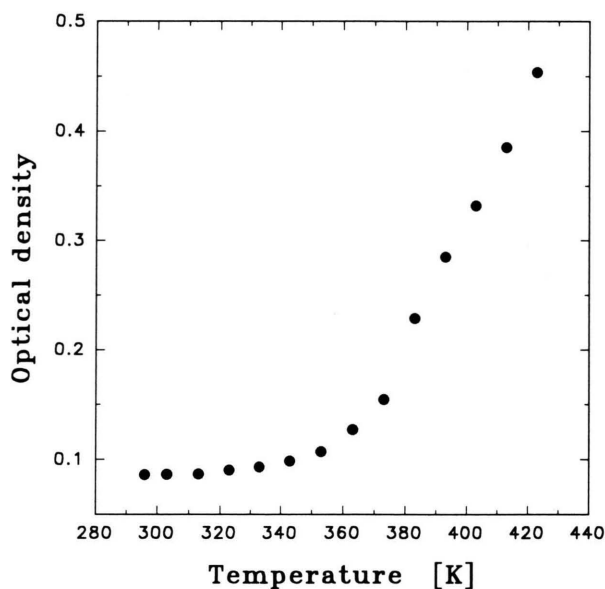


Fig. 2. Dependence of the long wavelength absorption maximum (optical density) of DPB in PVA film on temperature.

that at room temperature (Fig. 2), whereas for DPH and DPO it is ten and nearly twenty times [1, 3] higher, respectively. Note that in a freshly prepared DPB sample in PVA at 293 K a marked maximum (at 272 nm) appears at the short-wavelength side of the

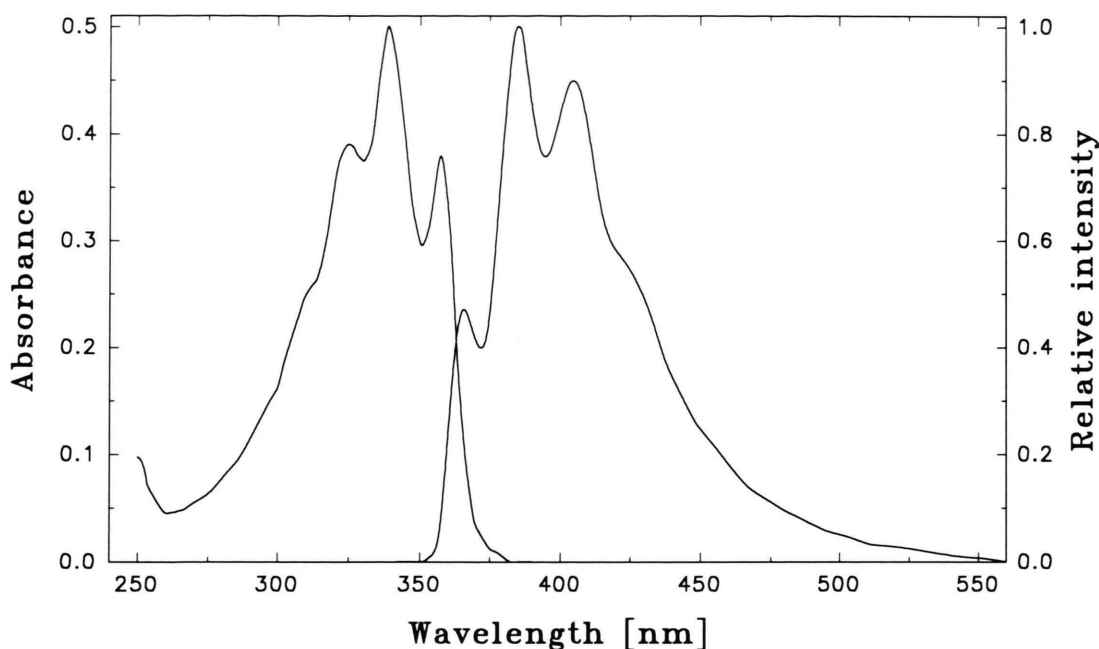


Fig. 3. Absorption and fluorescence spectra of DPB in PVA film measured at 293 K after previous heating to 423 K and cooling to room temperature.

absorption spectrum, which corresponds the *cis*-form, and that the absorbance of this band is comparable with the absorbance of the long-wave maximum band (at 339 nm) of the *trans*-form. When a dilute methanol solution of all-*trans*-DPB was kept in diffuse daylight, a rearrangement to a hindered *cis*-form took place with a characteristic continuous band at 250 nm. Figure 3 shows the absorption spectrum of DPB in PVA film measured at 293 K following previous heating to 423 K and cooling to room temperature. At the short-wavelength side of the absorption spectrum the band at 272 nm disappears. This spectrum (Fig. 3) possesses a distinct structure. On account of a marked drop in microviscosity of the surrounding medium, the DPB molecule in PVA film at 423 K interacts with its closest environment and provokes a partial effacement of the vibrational structure of the absorption spectrum.

### 3.2. Fluorescence Spectra and Quantum Yields

Figure 4 shows the normalized fluorescence spectra of DPB in PVA film after preparation measured at three different temperatures from 293 K to 423 K at  $\lambda_{\text{exc}} = 339$  nm. The intensity distribution strongly depends on temperature. Band narrowing on the long-

wave side of the spectrum band is observed with increasing temperature. Figure 5 shows the fluorescence spectra of DPB in PVA film at different temperatures, measured under the same conditions at  $\lambda_{\text{exc}} = 339$  nm. As clearly seen, the fluorescence intensity behaviour is normal and different from that observed for DPO and DPH in PVA film [2, 3]. For a freshly prepared sample of DPB in PVA film the intensity distribution at room temperature (296 K) depends distinctly on the exciting wavelength, which means that two forms (*trans-trans* and *cis-trans*) are responsible for the emission.

In addition to absorption, Fig. 3 shows the fluorescence spectra of DPB in PVA film measured from 293 K to 423 K after the previous heating of the sample to 423 K and cooling to room temperature. In this case, the fluorescence spectra are identical and independent of temperature and the excitation wavelength. Similar fluorescence spectra were observed for DPB in other polymer films without water. Figure 6 shows the DPB fluorescence spectra in ethyl acetate (EtA), polyvinyl chloride (PVCh) and polyvinyl formal (PVF) at 293 K. DPB was introduced into these polymers through tetrahydrofuran. In the above named polymers, similar to the heated PVA film (to 423 K), DPB appears in the *trans*-form. Water-induced *trans-cis* isomerisation of diphenyl polyenes

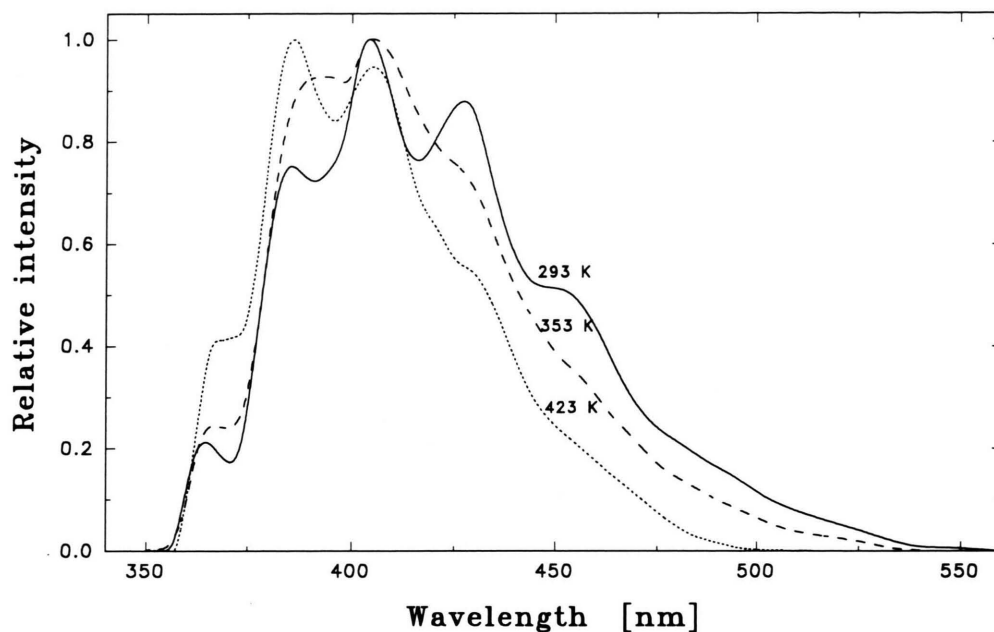


Fig. 4. Normalized fluorescence spectra of DPB in PVA film at three different temperatures ( $\lambda_{\text{exc}} = 339$  nm,  $\lambda_{\text{obs}} = 430$  nm).

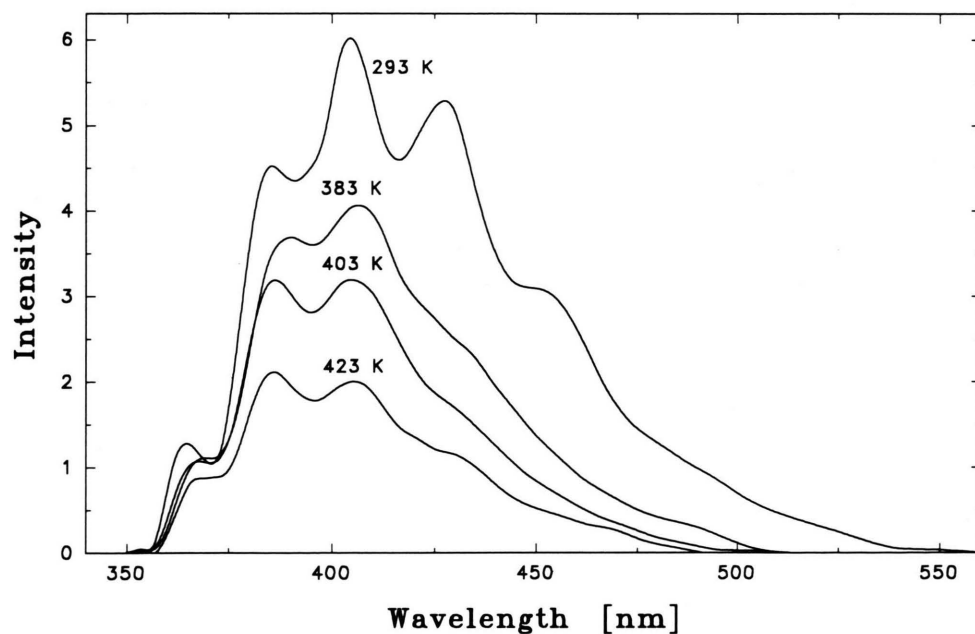


Fig. 5. Fluorescence spectra (arbitrary units) of DPB in PVA film at different temperatures, excited ( $\lambda_{\text{exc}} = 339$  nm) under the same conditions.

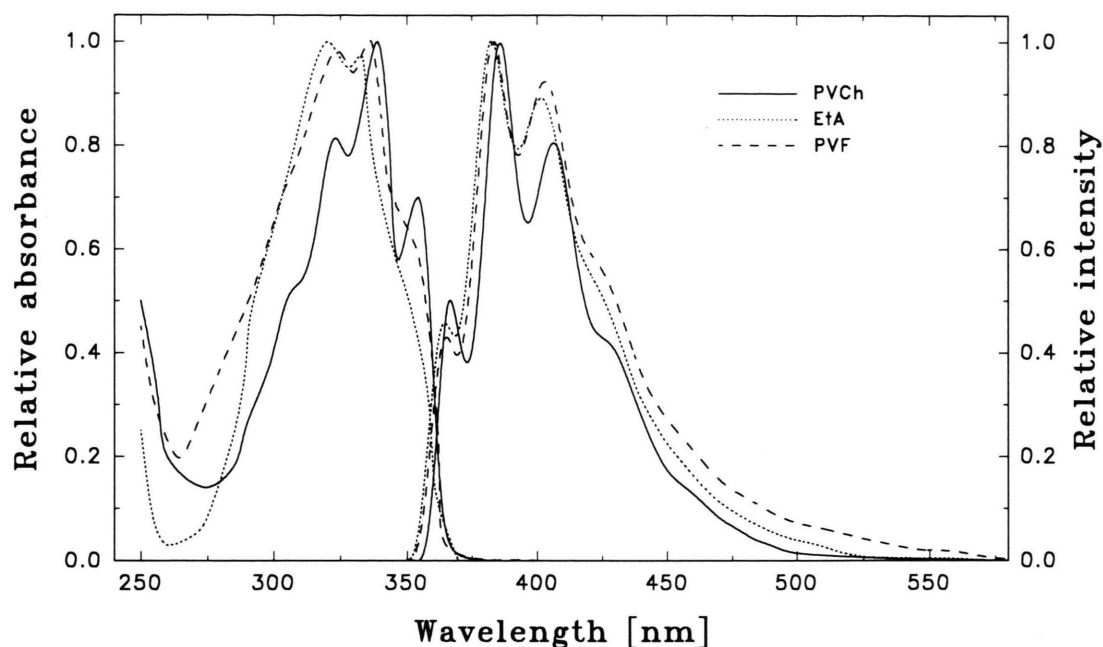


Fig. 6. Normalized fluorescence spectra of DPB in ethyl acetate (EtA), polyvinyl chloride (PVCh) and polyvinyl formal (PVF) at 295 K.

( $n=2, 3, 4$ ) is monitored by absorption and fluorescence change.

As seen in Fig. 5, the fluorescence intensity considerably decreases upon heating from 293 to 423 K. The measured quantum yields  $\Phi_F$  (relative to quinine sulfate) of DPB in PVA film shown in Fig. 7 refer to two directions of the temperature change, from 293 to 423 (circles) and from 423 to 293 K (squares). This is in clear contrast to the behaviour of the DPH and DPO quantum yields in PVA film.

### 3.3. Emission Anisotropy

DPB has an all-*trans*-polyene structure with absorption and fluorescence transition moments directed along the major axis of the molecule [10, 11]. The angle  $\beta$  between the absorption and fluorescence transition moments in DPB is  $7^\circ$  [12], while the absorption transition moment makes the angle  $\varphi \approx 7^\circ$  with the long molecular axis [11]. For DPH and DPO, the corresponding angles  $\beta$  and  $\varphi$  are slightly smaller as the length of the molecules affects considerably the effectiveness of their orientation in the stretched PVA film.

Figure 8 shows the emission anisotropy behaviour of DPB in PVA film as a function of temperature.

Each time the samples were excited with  $\lambda_{\text{exc}} = 340$  nm ( $\lambda_{\text{obs}} = 430$  nm) and continuously heated during the emission anisotropy measurement so as to keep a constant temperature by means of a thermostating unit in successive measurement points every 10 K. At temperatures above 353 K, the DPB molecules, similarly as for DPO and DPH molecules [2, 3], undergo a transition from *cis* to *trans* form. Irrespective of the fact that above 353 K the PVA polymer becomes more and more soft (the microviscosity around the DPB molecules decreases) the emission anisotropy grows due to photoselection, finally attaining the maximum value. Figure 9 shows the behaviour of the DPB emission anisotropy in PVA films as a function of the excitation light wavelength at 293 K before (black circles) and after (hollow circles) heating.

## 4. Discussion

The fluorescence transition in all-*trans*-DPB ( $n=2$ ) is not  $^1A_g^* \rightarrow ^1A_g$  as observed in longer polyenes ( $n=3, 4$ ) but  $^1B_u^* \rightarrow ^1A_g$  as in *trans*-stilbene ( $n=1$ ) [5]. The fact that the  $^1B_u^*$  state lies below the  $^1A_g^*$  state of DPB in condensed media is consistent with spectroscopic observations for these molecules in supersonic

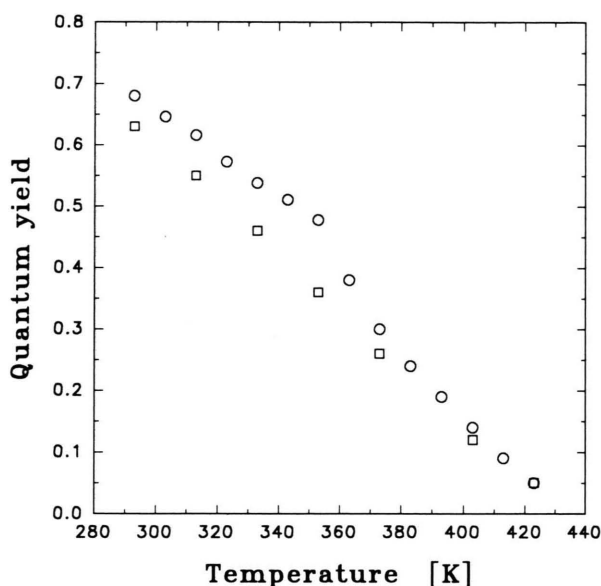


Fig. 7. Dependence of the quantum yields of DPB in PVA film on temperature: ○ the sample heated from room temperature to 423 K, and □ the sample cooled from 423 K to room temperature.

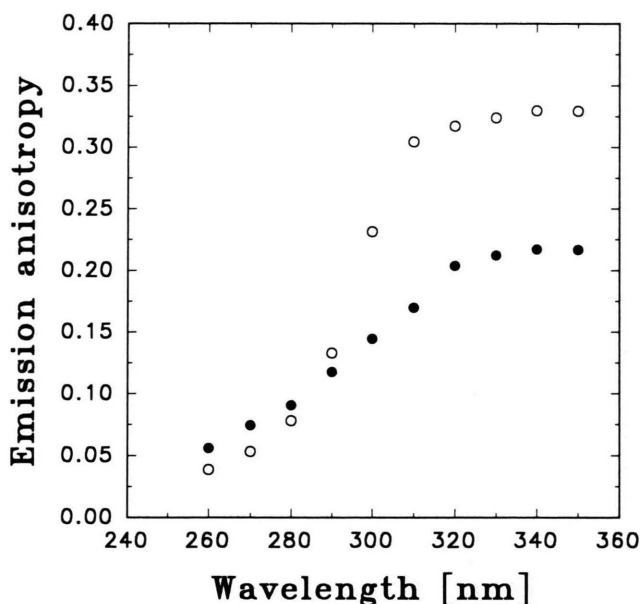


Fig. 9. Dependence of the emission anisotropy of DPB in PVA in film on the excitation wavelength. The black circles denote the measured points for a not heated sample at room temperature; the hollow circles denote the sample heated to 423 K, cooled to room temperature and measured at 293 K.

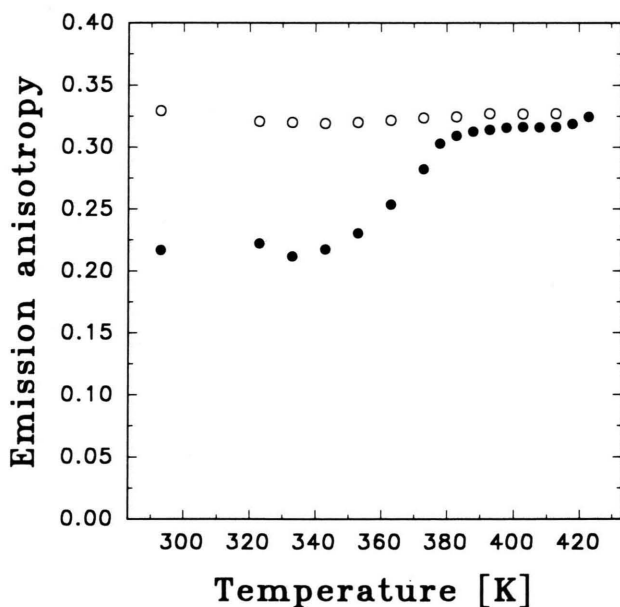


Fig. 8. Dependence of the emission anisotropy of DPB in PVA film on temperature ( $\lambda_{\text{exc}} = 340$  nm,  $\lambda_{\text{obs}} = 430$  nm): The filled and the hollow circles denote heating and cooling, respectively.

jets [13–16]. Straus [17, 18] obtained the following three expected steric forms of DPB: *trans-trans*, *cis-trans* and *cis-cis*. Within a given stereoisomeric set, the all-*trans* compound occupies a privileged position, which means that its spectral band shows a longer wavelength maximum and a higher extinction value than the band of any *cis* isomer [19]. The infrared studies carried out by Zechmeister *et al.* [19] show that between 10.0  $\mu$  and 10.6  $\mu$  a typical “*trans*-peak” is observed that decreases and disappears during the stepwise *trans-trans*  $\rightarrow$  *cis-trans*  $\rightarrow$  *cis-cis* rearrangement. The two *cis* isomers in carbon tetrachloride solution exhibit a band around 7.25  $\mu$  and two “*cis*-peaks” in the region 12.5  $\mu$ –15  $\mu$  in cyclohexane solution, which do not appear in the *trans-trans* curve [19].

The electronic absorption spectrum of DPB in PVA film obtained at 293 K distinctly differs from the spectra shown in Fig. 6 for this molecule in polyvinyl chloride, polyvinyl formal and ethyl acetate. In the case of those latter three polymers, DPB was introduced through tetrahydrofuran. Contrary to the other polymers, PVA is soluble in water. Thus, water accounts for the occurrence of the *cis*-form in the ground



state in PVA (see Fig. 1 and the discussion of the results in Section 3.1). Let us note that the absorbance maximum in the shortwave region of the absorption spectrum (at 272 nm) is comparable to the absorbance maximum at 339 nm at 293 K. It is only when the PVA film is heated to 423 K that the shortwave part (at 272 nm) of the absorption band disappears, i.e. *cis-trans* transition occurs (cf. Fig. 4 in paper [1]). The comparison of the DPB fluorescence spectra in PVA (Figs. 4 and 5) at 293 K with those in the other polymers which are insoluble in water (Fig. 6) reveals a distinct broadening of the longwave part of the DPB fluorescence spectrum in PVA. This is the manifestation of the existence of an additional luminescence centre, i.e. of the capability of emitting light by the *cis-trans* form. When increasing the temperature from 293 to 423 K, the DPB fluorescence spectrum in PVA strongly narrows (see Fig. 4) instead of broadening, which was the case for the DPH and DPO molecules. This distinctly indicates that at 423 K the *trans-trans* form of DPB only occurs. Clearly, the spectrum of *trans-trans* DPB at this temperature incorporates the temperature broadening effect.

The existence of two forms, *trans-trans* and *cis-trans*, of DPB which are capable of emitting radiation is also confirmed by the dependence of the fluorescence quantum yield in PVA upon temperature (Figure 7). In the temperature range from 293 to 360 K, the overall quantum yield is markedly higher than the quantum yield of from *trans-trans*. When increasing

the temperature above 360 K, the difference between both quantum yields becomes smaller and, finally, a value corresponding to the all-*trans* form is achieved. The cooling of the sample from 423 to 293 K results in the quantum yield of all-*trans* form.

The DPB emission anisotropy observed in PVA as a function of temperature (Fig. 8) behaves similarly as for DPO and DPH in PVA and upon heating to 423 K attains the maximum limiting value  $r_0 = 0.33$ , markedly differing from the fundamental emission anisotropy of 0.4. Such a lowered value is due to limited rotational motions of DPB in PVA film. This evidences that in isotropic PVA films the DPB molecule has a greater freedom of limited rotational motions than the DPO and DPH molecules (for DPO and DPH  $r_0$  are 0.354 and 0.369, respectively) in the same PVA film, because of the smaller molecular length of DPB.

The emission anisotropy of DPB in PVA film strongly depends on the excitation light wavelength (Fig. 9) at 293 K both before and after heating. For the sample heated to 423 K, one all-*trans* form is dealt with. Otherwise two forms, *trans-trans* and *cis-trans*, with differently directed transition moments contribute to the emission anisotropy.

#### Acknowledgements

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