

# Isomerization of Diphenyl Polyenes.

## Part IV. Evidence for Two Luminescent Conformers of 1,4-Diphenyl-1,3-butadiene in Poly(vinyl alcohol) Films

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Investigations of the effect of the excitation light wavelength on the intensity distribution in the fluorescence band of 1,4-diphenyl-1,3-butadiene (DPB) in poly(vinyl alcohol) films (PVA) at 296 and 87 K for samples before and after heating to 423 K, and fluorescence lifetime measurements have shown that *trans-trans* and *cis-trans* conformers are responsible for the emission of fluorescence. The fluorescence properties of the DPB sample in PVA heated to 423 K were found to be similar to those of DBP in polyvinyl chloride and polyvinyl formal at 296 K.

### 1. Introduction

From among three diphenylpolyenes,  $\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$  with  $n = 2, 3, 4$ , investigated in poly(vinyl alcohol) films (PVA), 1,4-diphenyl-1,3-butadiene (DPB) with  $n = 2$  distinctly differs from 1,6-diphenyl-1,3,5-hexatriene (DPH) with  $n = 3$  and diphenyl-1,3,5,7-octatetraene (DPO) with  $n = 4$  as regards the behaviour of both fluorescence spectra and quantum yields in the temperature range from 293 to 423 K [1–3]. When increasing the temperature from 293 to 423 K, the fluorescence spectrum of DPB in PVA film strongly narrows instead of broadening, the latter being the case for the DPH and DPO molecules in PVA. The overall fluorescence quantum yield at 293 K ( $\Phi_F = 0.68$ ) is higher than that of the DPB sample at the same temperature but previously heated to 423 K ( $\Phi_F = 0.63$ ). Both these findings clearly indicate the occurrence of two emission centres, i.e. two different conformers [1]. DPB can exist in three steric forms: *trans-trans*, *cis-trans*, and *cis-cis* [4–6] (Figure 1).

Absorption spectra and photoisomerization of DPB in hexane and benzene were investigated by Zechmeister et al. [6, 7], who showed that *trans-trans* DPB irradiated with ultraviolet (UV) light isomerizes to the *cis-trans* isomer, the same being true for the *cis-cis* form. According to Hirshberg et al. [8], the *trans-trans* form of DPB in benzene under the UV

irradiation displays a more intense fluorescence than that of the *cis-trans* isomer in which resonance is partly inhibited by steric hindrances. In [1] the fluorescence of DPB in PVA film was assumed to be due to the *trans-trans* and *cis-trans* conformers.

In this paper further experimental evidence is given for the occurrence of two DPB conformers in PVA films which are capable of emitting fluorescence.

### 2. Experimental

The method of preparing the DPB samples in PVA and the measurements of the absorption and fluorescence spectra and the quantum yields and emission anisotropies at different temperatures were described in [1–3, 9].

Fluorescence decays were measured on a pulse FL 900 spectrofluorimeter from Analytical Instruments (Scotland), using a standard time-correlated single photon counting method. A nitrogen or hydrogen nF 900 nanosecond lamp with a pulse time halfwidth of about 800 ps was used as an excitation source. The time interval between the points was about 50 to

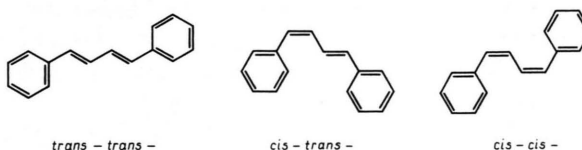


Fig. 1. Structure of the 1,4-diphenyl-1,3-butadiene (DPB) conformers.

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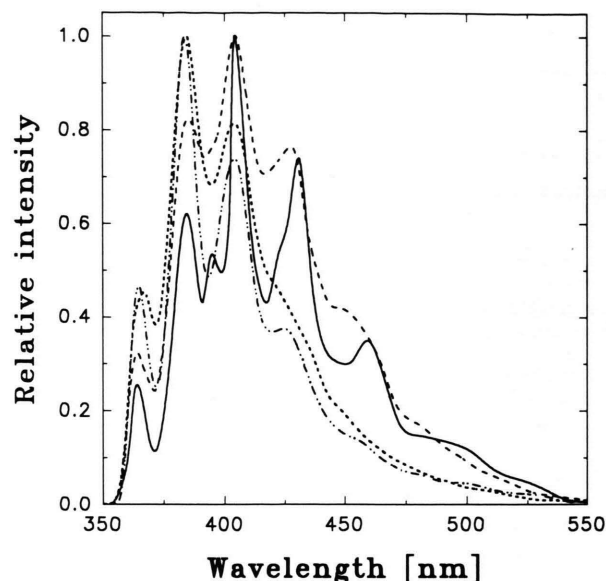


Fig. 2. Normalized fluorescence spectra of DPB in PVA film measured at 296 K — before heating and ···· after heating to 423 K, and at 87 K — before heating and - - - after heating to 423 K.

100 ps. The idea of the measurement was to record the curves of the excitation light pulse decay together with the response fluorescence decay of the sample. The deconvolution was performed by means of a commercial programme based on the nonlinear least squares method using the Marquardt algorithm.

### 3. Results and Discussion

#### 3.1. Fluorescence Spectra

Supplementing our previous investigations, Fig. 2 shows the fluorescence spectra of DPB in PVA measured at room temperature (293–296 K) prior to and after heating the sample to 423 K and the respective spectra at 87 K. The structure of the low temperature fluorescence spectra has clearly improved. The spectra of samples before heating are very broad compared to those recorded after heating. The substantial change in the spectral shape and the quantum yield occurs above the PVA vitrification temperature,  $T_g \approx 358$  K, at which the PVA polymer undergoes the transition from an elastic to a rigid solid phase. Although a more distinct structure of the fluorescence spectra is observed at 87 K, the *rigid solid state* has not yet been fully achieved after the heating. In such a

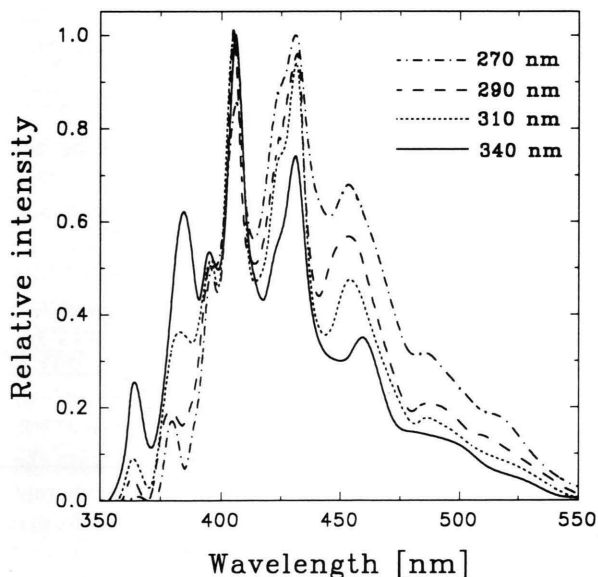
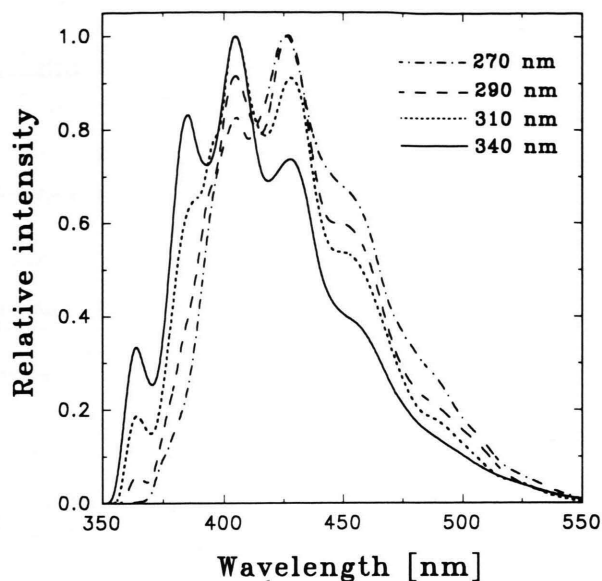


Fig. 3 and 4. Normalized fluorescence spectra of DPB in PVA film at different excitation wavelengths: 270, 290, 310 and 340 nm, measured at 296 K (Fig. 3) and 87 K (Figure 4).

polymer there is considerable local disorder, as a result of which molecular-sized cavities occur. This is also confirmed by the value of the fluorescence anisotropy,  $r_0 = 0.33$ , which is markedly lower than the fundamental emission anisotropy of 0.4. In the case of DPB in PVA, the change in the fluorescence anisotropy does not exceed 2% when passing from room temperature to 87 K.

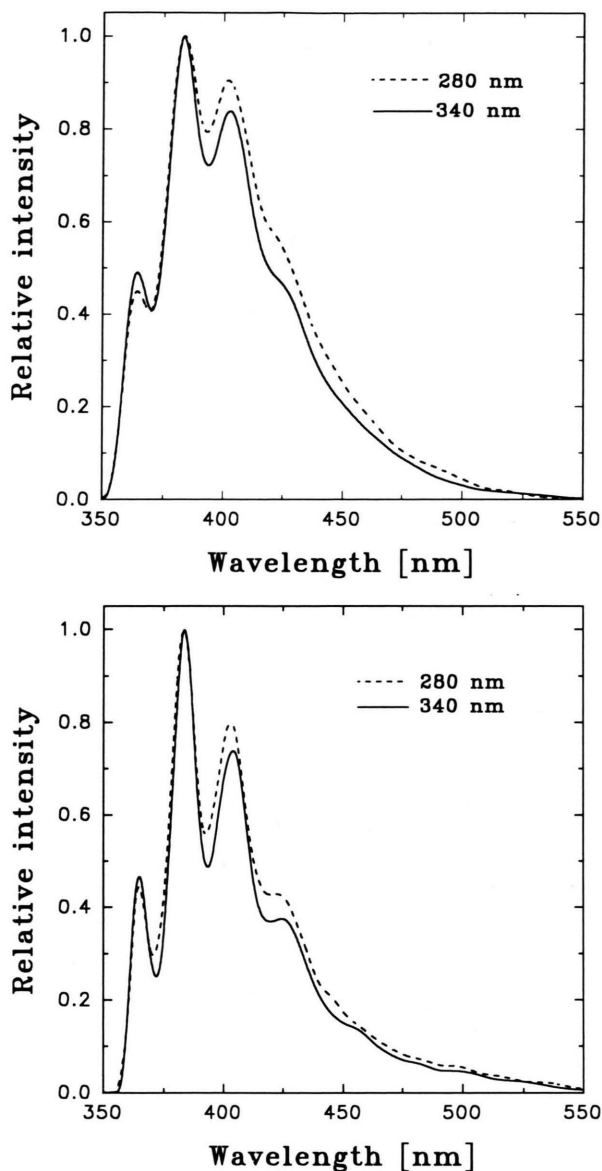


Fig. 5 and 6. Normalized fluorescence spectra of DPB in PVA film at two different excitation wavelengths: 280 and 340 nm, measured at 296 K (Fig. 5) and 87 K (Figure 6). In both cases the samples were previously heated to 423 K.

The fluorescence spectrum of the DPB sample in PVA before heating to 423 K is very broad, and its intensity distribution strongly depends on the excitation light wavelength at both 296 and 87 K (Figs. 3 and 4). Upon excitation at the maximum of the longwave absorption spectrum (340 nm), vibrational bands with a marked intensity are observed within the

shortwave fluorescence spectrum. On the other hand, when shortening the excitation wavelength down to 270 nm the intensities of these bands strongly decrease. A reverse effect is observed in the longwave part of the fluorescence spectrum. Such a behaviour of the intensity distribution in the fluorescence band results from overlapping of (at least) two bands that can be attributed to the *trans-trans* and *cis-trans* fluorescing forms.

When the DPB sample in PVA is heated to 423 K and then cooled, its fluorescence spectrum at 296 K is similar to that of DPB in polyvinyl chloride (PVCh) and polyvinyl formal (PVF) (cf. Fig. 6 in [1]). The heating of the PVA film with DPB results in the *cis-trans* conversion of the DPB molecules. In [1] it was assumed that in the PVA film heated to 423 K the *trans-trans* form of DPB only occurs. In order to verify this assumption, the dependence of the intensity distribution upon the excitation light wavelength was measured at 296 K for a sample previously heated to 423 K. A slight dependence was found in the intensity distribution, particularly at the longwave side of the fluorescence spectrum. Figures 5 and 6 show the effect of  $\lambda_{\text{exc}}$  for DPB in the PVA film (the previously heated sample) at 296 and 87 K, respectively. Whether or not only one form exists can be verified by measuring the emission anisotropy and observing its behaviour in the fluorescence band and by the fluorescence decay measurements.

### 3.2. Emission Anisotropy Spectra

Figure 7 shows the emission anisotropy spectra of DPB in the PVA film prior to heating, measured at 296 K for two excitation light wavelengths. A strong drop in the emission anisotropy is distinct in the fluorescence band, which is due to the overlap of two fluorescence bands with different emission anisotropies. DPB molecules which are in *trans-trans* and *cis-trans* forms have differently directed transition moments. For DPB in PVA heated to 423 K, for which a slight dependence of the intensity distribution is observed in the fluorescence spectrum, no distinct change (as was the case for the non-heated film) in the emission anisotropy was found (Figure 7).

### 3.3. Fluorescence Lifetimes

Different fluorescent conformers should exhibit different fluorescence decay times,  $\tau$ . In order to

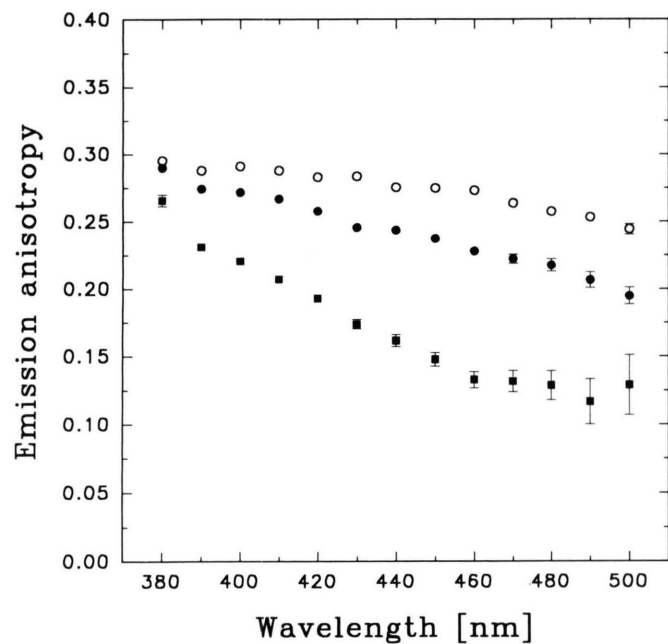


Fig. 7. Fluorescence emission anisotropy spectra of DPB in PVA film measured at 296 K for two samples: before heating ( $\lambda_{\text{exc}} = 310$  nm, ■ and  $\lambda_{\text{exc}} = 340$  nm, ●) and after heating to 423 K ( $\lambda_{\text{exc}} = 340$  nm, ○).

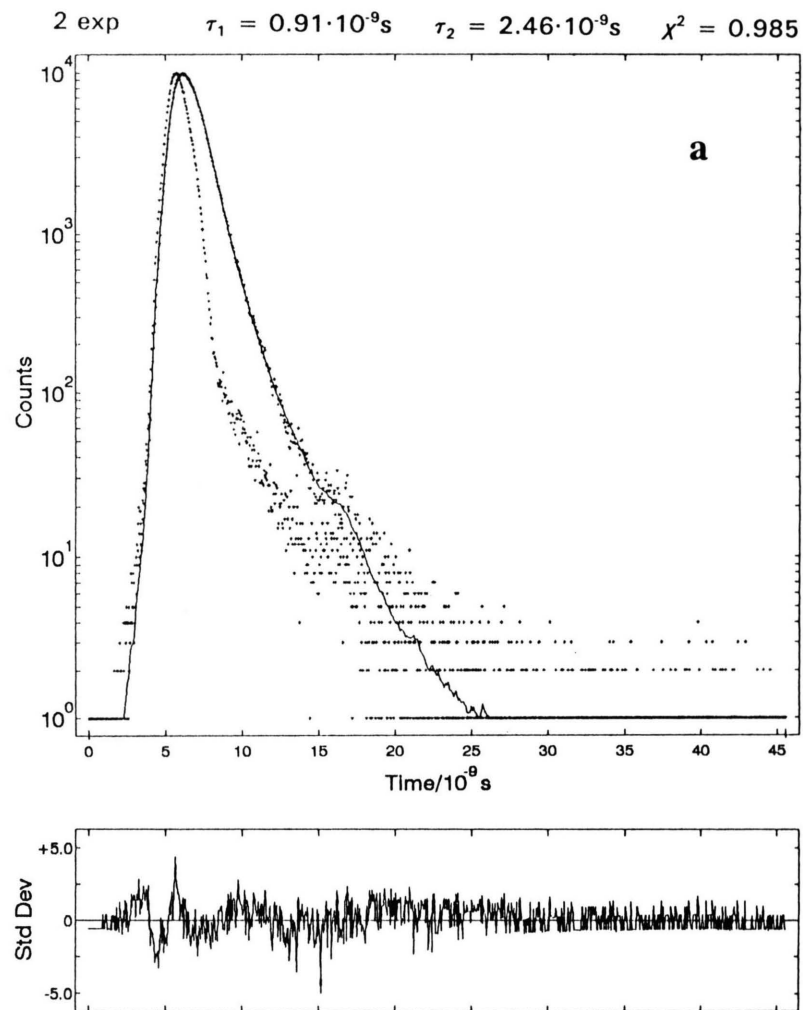


Fig. 8 a

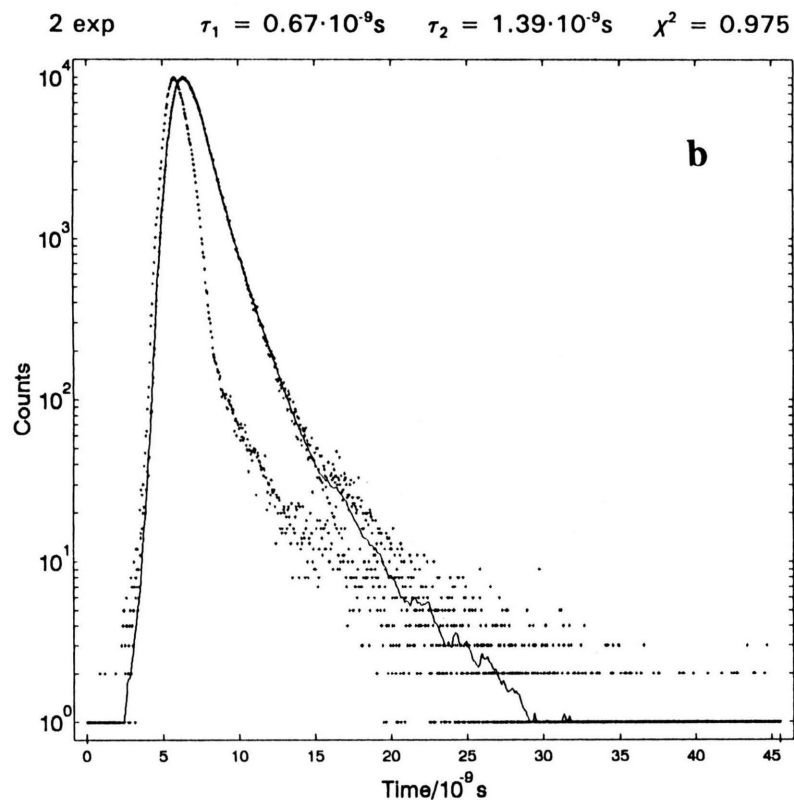


Fig. 8 b

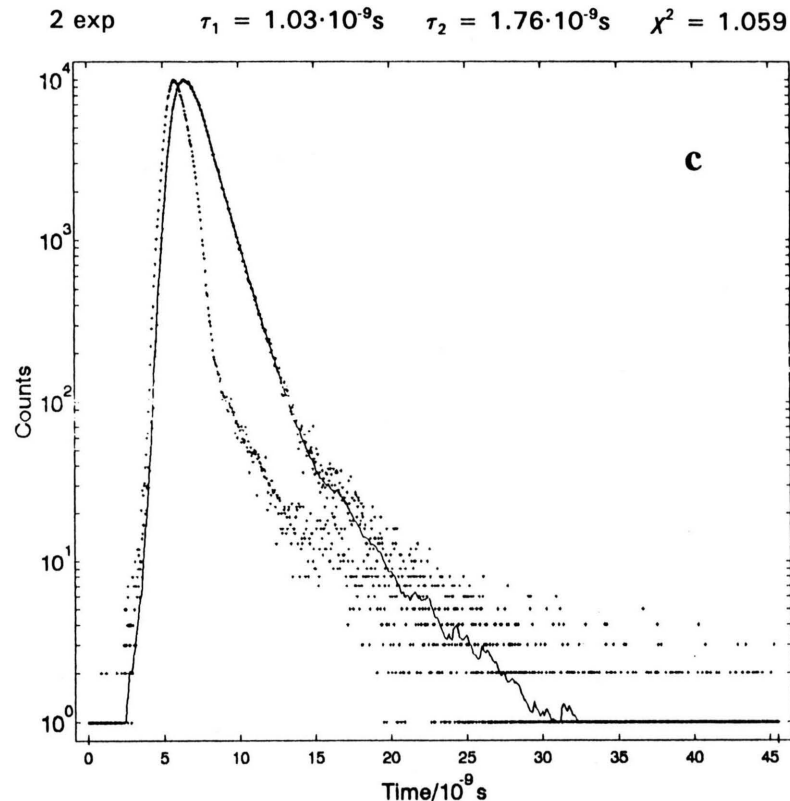


Fig. 8 c

Fig. 8. Fluorescence decay of DPB in PVF (Fig. 8 a), PVA (Fig. 8 b) and PVA after previous heating to 423 K (Fig. 8 c), calculated for a double exponential decay. The same figures show also the plots of weighted residuals resulting from two component fit.

Table 1. Values of fluorescence decay times of DPB in different media at 296 K.

Medium	$\lambda_{\text{exc}}$ [nm]	$\tau_1$ [ns]	$A_1^a$	$\tau_2$ [ns]	$A_2^a$	$\chi^2^b$
Benzene	335	0.30	1.00			0.890
Cyclohexane	330	0.58	1.00			0.812
PVCh	338	0.97	0.99	5.63	0.01	0.863
PVF	335	0.91	0.96	2.46	0.04	0.985
PVA	340	0.67	0.51	1.39	0.49	0.975
PVA (after previous heating)	340	1.03	0.89	1.76	0.11	1.059

<sup>a</sup>  $A_{1,2}$  are the preexponential factors (normalized relative fluorescence intensities,  $A_1 + A_2 = 1$ ) representing the fractional contributions to the time-resolved decay of the components with a lifetime  $\tau_{1,2}$ .

<sup>b</sup> From least-squares analysis of time-resolved decays.

demonstrate this, fluorescence lifetimes were first measured for DPB in benzene and cyclohexane and next different polymers (see Table 1). In liquid solvents, single exponential fluorescence decay, corresponding to a single *trans-trans* form, was observed. Since the liquid solutions were not degassed, the values of  $\tau$  are slightly lower due to oxygen quenching. For example, Birks and Dyson [10] obtained  $\tau = 0.8$  ns and Chattopadhyay *et al.* [11]  $\tau = 0.6$  ns for DPB in cyclohexane at 293 K. However, for DPB in different polymer matrices (PVCh, PVF and PVA) double exponential decay is observed with decay lifetimes  $\tau_1$  and  $\tau_2$  (Figure 8). In the case of DPB in PVCh and PVF the *trans-trans* form is predominant (about 99% and 96%, respectively), with almost the same fluorescence decay times of 0.97 and 0.91 ns, respectively (see Table 1). The amount of the *cis-trans* form is minimal (1.0% and 4%, respectively) and the fluorescence decay times are longer, i.e. 5.6 and 2.5 ns, respectively. The behaviour of DPB in PVA is completely different. Both *trans-trans* and *cis-trans* forms occur in PVA

(before heating to 423 K) in comparable amounts. When measuring the fluorescence decay times after heating DPB in PVA to 423 K and then cooling it to 296 K, the behaviour of the sample is similar to that of DPB in PVCh and PVF films at 296 K. In the PVA film heated to 423 K, the majority of the DPB molecules convert to the *trans-trans* form (about 89%) with the fluorescence lifetime  $\tau_1 = 1.03$  ns, which is nearly the same as for DPB in PVCh and PVF at 296 K. This is consistent with the behaviour of the fluorescence spectra in these polymer matrices (*cf.* the DPB fluorescence spectra shown in Figs. 3 and 6 of [1]). The small amount of the *cis-trans* form (about 11%), characteristic of which is its own fluorescence band superimposed on the fluorescence band of the *trans-trans* form, is the reason for the observed slight dependence of the intensity distribution on the excitation light wavelength (Figs. 5 and 6). This has also been confirmed by measuring the emission anisotropies in the fluorescence bands (Figure 7).

#### 4. Conclusions

The fluorescence of DPB in PVCh, PVF and PVA films comes from *trans-trans* and *cis-trans* conformers. Fluorescent properties of the DPB sample in PVA heated to 423 K are similar to those observed in PVCh and PVF at room temperature.

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