Isomerization of Diphenyl Polyenes. Part V. The Origin of Fluorescence of 1,6-Diphenyl-1,3,5-hexatriene in Poly(vinyl alcohol) Films

A. Kawski, A. Kubicki, B. Kukliński, and G. Piszczek

Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland

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The effect of temperature on the absorption and fluorescence spectra of 1,6-diphenyl-1,3,5-hexatriene (DPH) was investigated in three different polymer films: poly(vinyl chloride) (PVCh), poly(vinyl formal) (PVF) and poly(vinyl alcohol) (PVA) in the temperature range 296–423 K. Anomalous behaviour of the fluorescence intensity was observed only for DPH in non-heated PVA film. The intensity distribution in the fluorescence band of DPH in both non-heated and heated PVCh and PVF films was found to be independent of the excitation light wavelength, λ_{exc}. The behaviour of DPH is similar in the PVA film heated to 423 K. For these samples, single exponential fluorescence decay was observed. The behaviour of non-heated DPH samples in PVA is quite different, the intensity distribution and the fluorescence band position depending strongly on λ_{exc} and the fluorescence decay being double exponential. It can be inferred that the fluorescence of DPH in a non-heated PVA sample consists of two components, the first originating from the all-*trans* conformer and the second from the ground-state s-*cis* conformer.

1. Introduction

As reported in previous papers [1–4], three diphenyl polyenes, Ph–(CH=CH)$_n$–Ph ($n=2$–4), behave quite differently in poly(vinyl alcohol) films (PVA). It was observed that above the glass transition temperature of 358 K, the optical density in the longwave absorption band of 1,4-diphenyl-1,3-butadiene (DPB) ($n=2$) increases about five-fold, whereas for 1,6-diphenyl-1,3,5-hexatriene (DPH) ($n=3$) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) ($n=4$) the increase is ten- and twenty-fold, respectively. In addition, it was found for DPH and DPO that above 358 K the fluorescence quantum yield strongly increases and that this effect is irreversible, i.e. after having been cooled the sample retains its high absorption and fluorescence quantum yield at room temperature. DPB differs from DPH and DPO as to the behaviour of the fluorescence spectra and quantum yields in the temperature range from 296 to 423 K. When increasing the temperature above 358 K, the fluorescence spectra of DPH and DPO broaden whereas that of DPB narrows. The investigations of quantum yields, fluorescence decay times and fluorescence anisotropy spectra have shown that the fluorescence emission of DPB in PVA is due to the presence of *trans-trans* and *cis-trans* conformers [4, 5].

Experimental and theoretical investigations have confirmed the assignment of Hudson and Kohler [6–8] that the dipole-forbidden 2^1A_g state (S_1) lies below the allowed 1^1B_u state (S_2) for DPH and DPO, while in DPB these states are so close to each other that their ordering is affected by the solvent environment [9, 10].

The energy gap between the states 2^1A_g and 1^1B_u strongly depends on the length of polyene chain. When increasing n, the energy gap broadens [11]. The $2^1A_g \leftarrow 1^1A_g$ transition is symmetry forbidden in the single-photon absorption spectrum and allowed in the two-photon absorption spectrum. For the $1^1B_u \leftarrow 1^1A_g$ transition the converse applies. Since the $1^1B_u - 2^1A_g$ energy gap in DPH is sufficiently small for thermal repopulation to occur to the 1^1B_u state, which is reflected by the delayed fluorescence from the 1^1B_u state observed by Alford and Palmer [12, 13] and others [14, 15] in the form of a shoulder at the onset of DPH fluorescence spectra, the fluorescence can be emitted from both the lower 2^1A_g state (S_1) and 1^1B_u state (S_2) with a slightly higher energy. The investigations of Felder et al. [16] of the transient behaviour of DPH and DPO carried out using picosecond time-resolved fluorescence spectroscopy have shown that, contrary to DPO, the prompt fluorescence of DPH from the

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Reprint requests to Prof. Dr. Alfons Kawski, University of Gdańsk, Institute of Experimental Physics, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

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1^1B_u state is weak, exhibiting an abormally long decay time (> 30 ps).

As shown recently by Saltiel and coworkers [17], the fluorescence of DPH in liquid solvents has two components, one of which is the combined mixture of the $2^1A_g/1^1B_u$ fluorescence from the all-*trans* conformer and the other the emission from the *cis* conformers.

One cannot exclude the possibility that also in the case of the DPH fluorescence in different polymers such as poly(vinyl chloride) (PVCh), poly(vinyl formal) (PVF) and, in particular, poly(vinyl alcohol) (PVA), a combined $2^1A_g/1^1B_u$ fluorescence from all-*trans* and *cis* conformers may occur. Having this in mind, the investigations of the fluorescence spectra, quantum yields, emission anisotropy and decay times were taken up for DPH in PVA, PVCh and PVF films at room temperature (samples non-heated and heated to above 358 K) and at 87 K.

2. Experimental

1,6-Diphenyl-1,3,5-hexatriene (DPH) (for scintillation measurements) from Aldrich Chemical Co. was used without further purification. PVCh films were prepared using poly(vinyl chloride) from BDH Chemicals Ltd., Poole England (high molecular weight, MW approximately 200,000), PVF film was prepared using poly(vinyl formal) from SERVA, Heidelberg (molecular weight unknown), and PVA films were obtained from poly(vinyl alcohol) (100% hydrolyzed, MW 106,000 ÷ 110,000, Aldrich-Chemie).

To a 5% solution of PVCh in tetrahydrofuran, 10^{-5} M of DPH was added. Next, the solution was stirred and poured on a levelled Petri dish. During free evaporation of tetrahydrofuran at room temperature, lasting for about 5 days, a layer of PVCh film was formed from DPH. The same procedure was applied to PVF film obtained from DPH. PVA films were prepared by introducing DPH through methanol into 5% water solution of poly(vinyl alcohol) and evaporating on the Petri dish for 10 days. All the films were prepared under laboratory conditions with access to daylight. Detailed description of the film preparation is given in [18, 19].

The methods of measuring the fluorescence spectra and quantum yields, the emission anisotropies and fluorescence decay times were described in the preceding papers [2–5].

3. Results

3.1. Absorption, Fluorescence and Emission Anisotropy Spectra

Figures 1 and 2 show absorbance and fluorescence spectra of DPH in PVA film measured at 296 and 87 K prior to and after heating the sample to 423 K, respectively. In the spectrum of the non-heated sample (Fig. 1), the absorption band, corresponding to the all-*trans* conformers, is partly covered in the shortwave region by a stronger band from stereoisomers. The absorption spectrum of the sample heated to 423 K (Fig. 2) distinctly differs from that shown in Fig. 1: in the 280–300 nm region the band disappears and the absorbance of the longwave band (310–400 nm) strongly increases. The fluorescence spectrum of DPH in PVA film heated to 423 K is broader compared to that of the non-heated sample at 296 K. Lowering of the temperature to 87 K, both for heated and non-heated samples, results in more structure of the absorption and fluorescence spectra. At the shortwave side of the fluorescence spectrum of the non-heated and heated (to 423 K) samples, the band broadening is observed at 296 K, which can be attributed to the fluorescence emission from the 1^1B_u state (S_2) overlapping with the emission from 2^1A_g. Cooling the samples below room temperature (down to 87 K) prevents thermal repopulation from the 2^1A_g to the 1^1B_u state. In order to verify whether the absorbance of DPH in other polymers at 296 K is similar to that in PVA (Fig. 1), the absorbance of DPH in PVCh and PVF was investigated, as described in the previous paper [3]. The spectra obtained are similar to that of DPH in the PVA film heated to 423 K. Thus, the unusual behaviour of the DPH absorbance is characteristic only of the nonheated PVA film. The measurements of DPH fluorescence in PVA, PVCh and PVF films as functions of temperature confirm this finding (Figure 3). For DPH in PVA film (Fig. 3 A), the fluorescence band intensity increases with temperature (from 296 to 423 K), whereas in the other polymers the fluorescence intensity decreases (see Figs. 3 B and 3 C). Figures 4 and 5 show the fluorescence and emission anisotropy spectra of DPH in PVA, PVCh and PVF films depending on the excitation light wavelength for non-heated and heated samples, respectively. It is characteristic that for DPH in PVCh and PVF no distinct dependence of the intensity distribution in the fluorescence band upon the excitation light wavelength is observed for both the non-heated and heated

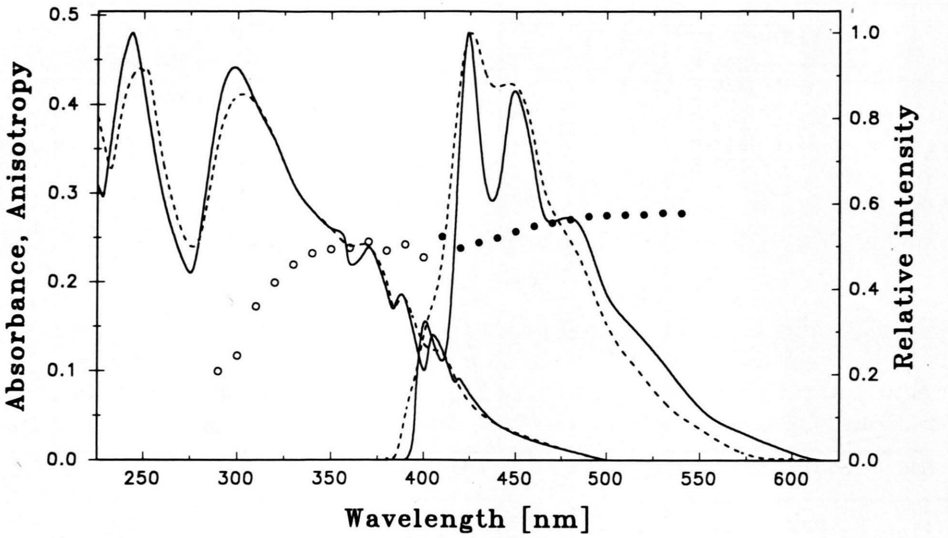

Fig. 1. Absorption, fluorescence and emission anisotropy spectra of DPH in PVA film measured at 296 K (– – – –) and 87 K (———) before heating. The fluorescence and emission anisotropy spectra (●) were obtained for $\lambda_{exc} = 365$ nm. ○ denote the values of emission anisotropy at different λ_{exc} and by $\lambda_{obs} = 430$ nm.

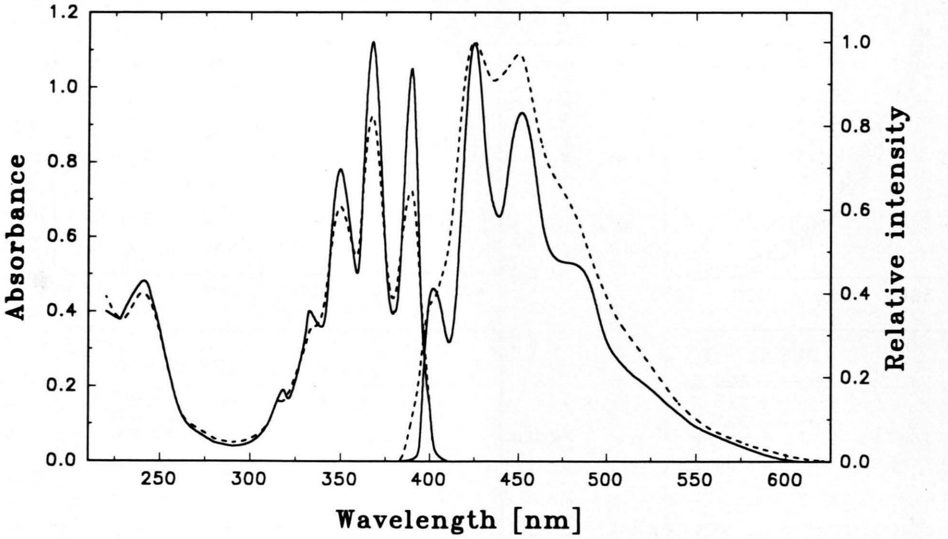

Fig. 2. Absorption and fluorescence spectra of DPH in PVA film measured at 296 K (– – – –) and 87 K (———) after heating to 423 K. The fluorescence spectra were obtained for $\lambda_{exc} = 365$ nm.

samples. The emission anisotropy of these samples in the fluorescence band is high and does not change significantly. Similar behaviour can be observed for DPH in the heated PVA film. A strong dependence of the intensity distribution in the fluorescence band upon the excitation light wavelength and a marked change in the emission anisotropy in the absorption and fluorescence band is observed for DPH in non-heated PVA film (Figs. 1 and 4A).

3.2. Fluorescence Lifetimes

The fluorescence decay times, τ, measured for DPH in several solvents and in PVA polymers are summa-

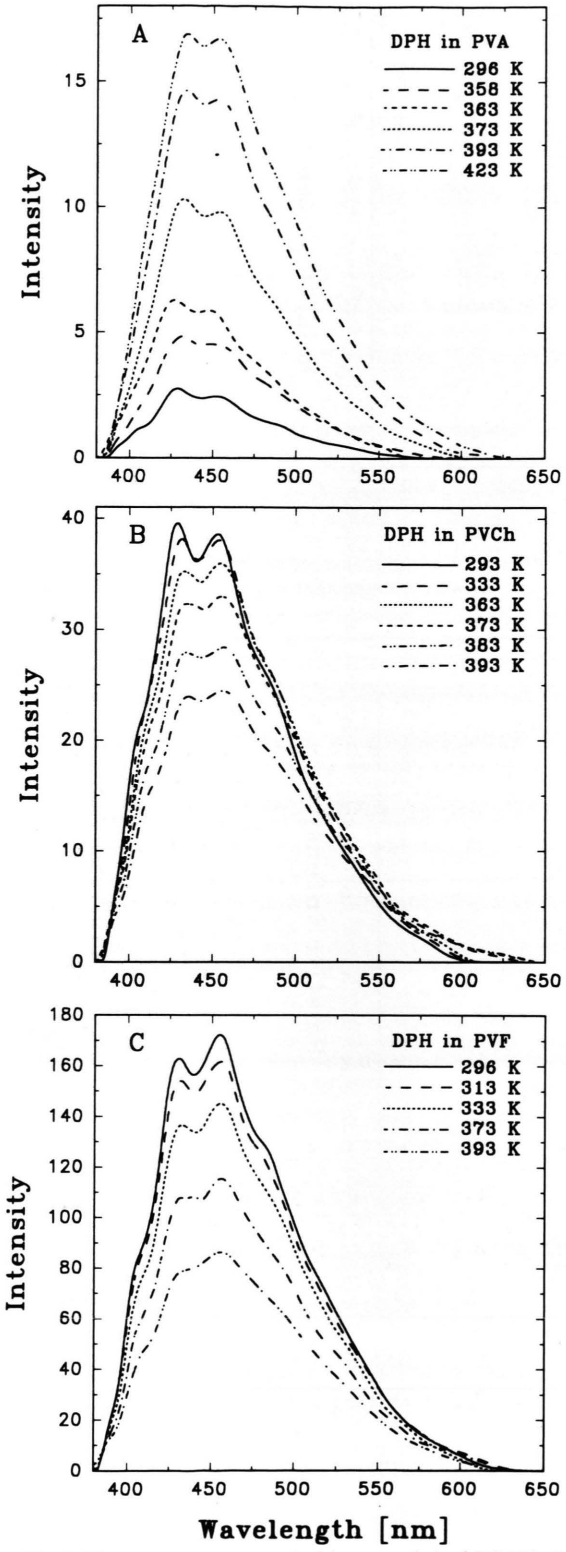

Fig. 3. Fluorescence spectra (arbitrary units) of DPH in PVA (A), PVCh (B) and PVF (C) films at different temperatures excited ($\lambda_{exc} = 365$ nm) under the same conditions.

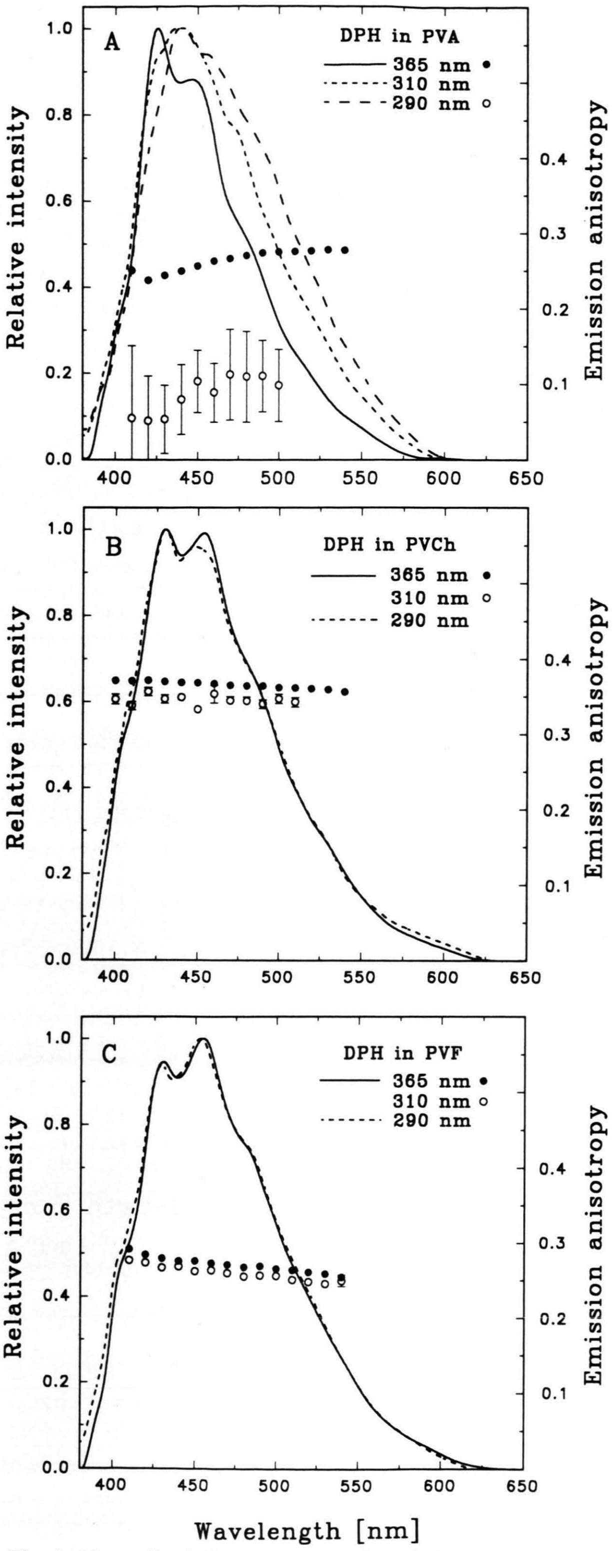

Fig. 4. Normalized fluorescence and emission anisotropy spectra of DPH in PVA (A), PVCh (B) and PVF (C) films for different excitation wavelengths. The samples were measured at 296 K before heating.

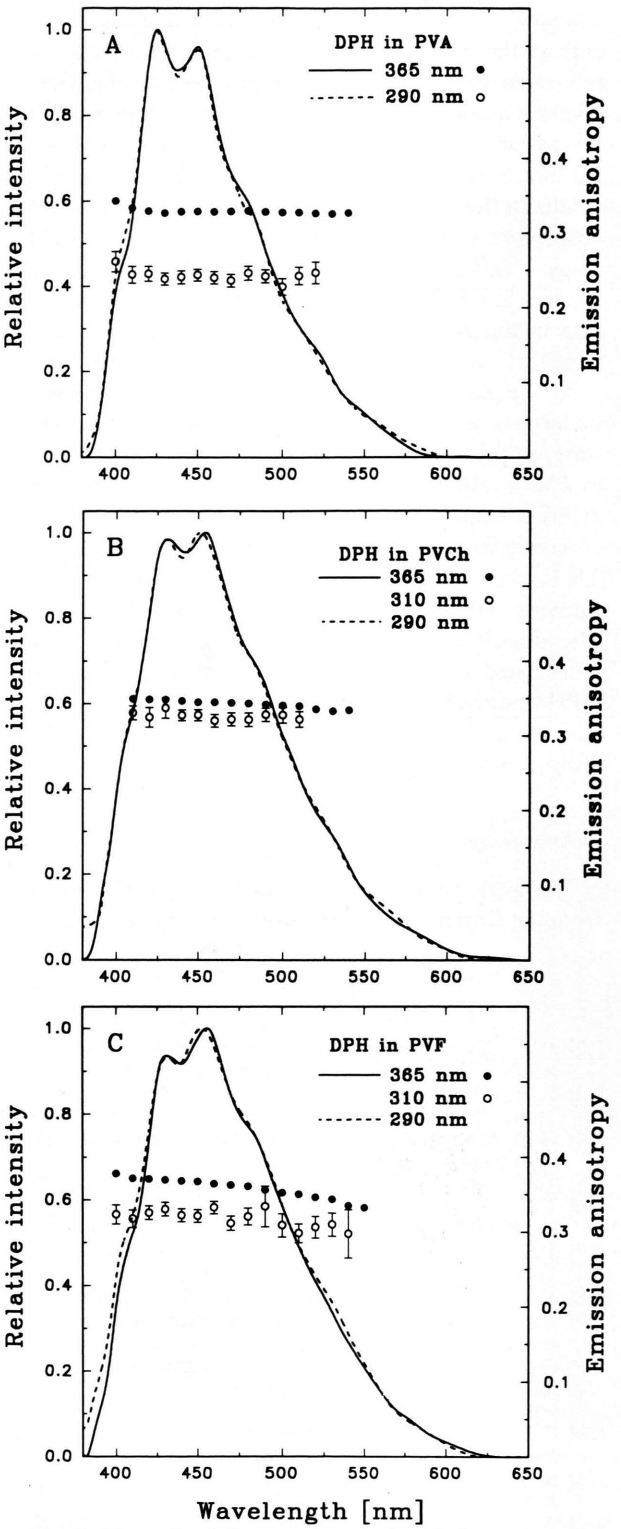

Fig. 5. Normalized fluorescence and emission anisotropy spectra of DPH in PVA (A), PVCh (B) and PVF (C) films for different excitation wavelengths. The samples were measured at 296 K after heating to 423 K (A), 393 K (B) and 393 K (C).

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

Medium	λ_{exc} [nm]	τ_1 [ns]	A_1 [a]	τ_2 [ns]	A_2 [a]
Benzene	360	5.4	1.00	–	–
Cyclohexane	354	8.1	1.00	–	–
Methanol	350	3.9	1.00	–	–
PVA (before heating)	375 320	4.0 5.0	0.67 0.18	0.02 0.02	0.33 0.82
PVA (weak heated)	375	5.0	0.73	2.4	0.27
PVA (after heating to 423 K)	362 320	3.9 4.0	1.00 1.00	– –	– –

[a] $A_{1,2}$ 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 $\tau_{1,2}$.

rized in Table 1. In benzene, cyclohexane and methanol, single exponential fluorescence decay was observed, definitely corresponding to a single all-*trans* conformer. In the case considered, the liquid solution was not degassed and the values of τ are therefore slightly lower due to oxygen quenching. Cehelnik et al. [20] obtained 6.1 ns for DPH in benzene, the respective value reported by Chattopadhyay et al. [21] being 7.2 ns. In cyclohexane and methanol 12,9 ns and 5.2 ns were obtained, respectively [21]. It is worth mentioning that double exponential fluorescence decay with lifetimes τ_1 and τ_2 is observed for DPH in non-heated and weakly heated PVA film (see Table 1). For a sample strongly heated to 423 K, single exponential decay was obtained, similar to DPH in non-heated PVCh and PVF films.

4. Discussion

There are six theoretically possible stereoisomers of DPH [22, 23]. The considerations of Pauling [24, 25] regarding spatial conditions have led to the opinion that in the case of the existence of normal localized double bonds the number of isomers is lower due to steric conditions. Experimental investigations enabled the conclusion to be drawn of the existence of polyenes with a *forbidden* system of double *cis*-bonds [26, 27]. These are more stable thermally and differ from the *allowed cis* polyenes in the characteristic flattened absorption spectrum shifted towards the ultraviolet region. This may be the case for DPH (and for DPO) in the non-heated PVA film (Figure 1). Heating the sample to 423 K leads to the *cis-trans* isomerization (see Fig. 4 in [1]), which is evidenced by the disappearance of the shortwave structureless absorption band at 280–300 nm (see Figure 2).

The intensity distribution in the DPH fluorescence spectra in PVCh and PVF films, both non-heated and heated to 423 K, does not depend on the excitation light wavelength (Figs. 4 B, C and 5). The same can be observed for DPH in PVA heated to 423 K. In all the cases named, high emission anisotropy is observed in spite of using markedly differing excitation wavelengths, 365 and 290 nm (in the maximum and minimum of the longwave absorption band) (see Fig. 2 and Fig. 9 in [3]). The single exponential fluorescence decay and spectral measurements clearly indicate the existence of one fluorescing all-*trans* conformer. At higher temperatures (above room temperature) the fluorescence may be the combined $2^1A_g/1^1B_u$ emission from the *trans* conformer.

However, the behaviour of the non-heated DPH sample in PVA film (Figs. 1 and 4 A) is quite different. The intensity distribution and the positions of the fluorescence band and emission anisotropy in the fluorescence band strongly depends on the excitation light wavelength. Such a strong effect may be due to the presence of a ground-state conformer (continuous absorption band on the shortwave side of the structured longwave absorption band of the all-*trans* conformer) exhibiting certain fluorescent properties. By comparing Figs. 4 A and 5 A one find a distinct difference in the behaviour of the emission anisotropy in the fluorescence band. The heated sample (Fig. 5 A) displays markedly higher emission anisotropy, which is also the case for DPH in PVCh and PVF films (Figs. 5 B and 5 C). The heating of DPH in PVA to 423 K results in the increase in absorbance in the longwave absorption spectrum and in the quantum yield (Figs. 2 and 3), which is due to the conformational changes in DPH molecules (*cis-trans* transition) occurring in the glassy phase (above the glass transition temperature, $T > 358$ K) of the heated polymer.

At the glass transition temperature, PVA polymer undergoes a transition from the elastic to the solid state. In the case of polymers insoluble in water such as PVCh and PVF, contrary to PVA, no shortwave diffused band responsible for the absorption of the *cis*-conformer can be observed at 296 K. Thus, at 296 K the occurrence of the ground-state *cis* conformer of DPH in PVA is due to the presence of water. The double exponential fluorescence decay in the non-heated DPH sample in PVA confirms that the DPH fluorescence has two components, the first from all-*trans* and the second from s-*cis* conformers in the ground state.

Acknowledgements

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