Isomerization of Diphenyl Polyenes. Part VI. Properties of 1,8-Diphenyl-1,3,5,7-octatetraene Fluorescence in Poly(vinyl alcohol) and other Polymer Films

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

Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Poland

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Absorption, fluorescence and emission anisotropy spectra of 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in non-heated and heated poly(vinyl alcohol) (PVA) films were measured at 296 and 87 K. Similar spectra to those of DPO in PVA heated to 423 K were observed for DPO in polymer films: poly(vinyl chloride) (PVCh), poly(vinyl formal) (PVF) and ethylacetate (EtA). Unusual photophysical properties of DPO fluorescence occur only in non-heated PVA. These are the increase in the absorbance and quantum yield at temperatures above 358 K and the change in the emission anisotropy, r, due to softening or stiffening of the PVA film. For DPO in PVCh and EtA, high values of r, close to 0.4, are observed (0.391 and 0.389, respectively), thus manifesting the stiffening of the microenvironment around the DPO molecule in these polymers. In the case of DPO in non-heated PVA film, strong temperature dependence of the intensity distribution in the fluorescence band and double exponential emission decay are observed. This proves that the fluorescence originates from two conformers: all-trans and s-cis.

2. Experimental

DPO from Aldrich Chemical Company Inc., Steinheim, Germany, was used without further purification.

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

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Figs. 1–3. Absorption and fluorescence spectra of DPO in PVA film before heating (Fig. 1), after heating to 373 K (Fig. 2) and after heating to 423 K (Fig. 3), measured at 296 K (solid line) and 85 K (dashed line). The fluorescence and emission anisotropy (○) spectra were obtained for $\lambda_{\text{exc}} = 390$ nm. ○ denote the emission anisotropy at $\lambda_{\text{obs}} = 430$ nm for various $\lambda_{\text{exc}}$. 
The preparation of the polymer films (PVCh, PVF, EtA, and PVA) was described [18].

The methods of measuring the absorption and fluorescence spectra, and the quantum yields and emission anisotropies were described in [15–17]. Fluorescence decays were measured on a K2 multifrequency cross-correlation phase and modulation fluorometer at the Biochemistry Department of the University of Ancona, Italy.

3. Results

3.1. Absorption, Fluorescence and Emission Anisotropy Spectra

Figures 1–3 show the absorption, fluorescence and emission anisotropy spectra of DPO in PVA films, measured at 296 and 87 K prior to heating (Fig. 1) and after heating to 373 K (Fig. 2) and 423 K (Figure 3). In the non-heated sample (Fig. 1), on the short-wave side of the absorption band of the all-trans conformer a very strong band with a maximum at 300 nm occurs, corresponding to the ground-state cis conformer. As a result of heating to 373 K the structured long-wave (350–440 nm) absorption band intensifies (Figure 2). Finally, upon heating to 423 K (Fig. 3), the long-wave band becomes fully developed while the short-wave band almost completely disappears. The spectrum of the emission anisotropy is very interesting. The emission anisotropy of the non-heated sample is close to 0.3, whereas after heating to 373 K it drops to 0.150 due to the softening of the PVA polymer. In the sample heated to 423 K the value of the emission anisotropy reaches 0.354, which, however, differs markedly from the fundamental value of 0.4.

Similar as with DPH in PVA heated to 423 K, no distinct dependence of the intensity distribution upon the excitation light wavelength is observed for the DPO sample in PVA heated to 423 K.

Figures 4–6 show the absorption, fluorescence and emission anisotropy spectra of DPO in PVCh (Fig. 4), PVF (Fig. 5) and EtA (Fig. 6) for non-heated samples and samples heated to 423 K. Unlike the non-heated samples of DPO in PVA, no effect of the excitation light wavelength on the intensity distribution in the fluorescence band can be observed. The absorption and fluorescence spectra of DPO in PVCh, PVF and EtA heated to 423 K are the same as those of the non-heated samples. Thus, the temperature effect on the absorption and emission properties of DPO in PVA films does not occur in other polymers such as PVCh, PVF and EtA, in which a high fluorescence anisotropy, close to the fundamental value $r_0 = 0.4$, is observed: 0.391 and 0.389 for DPO in PVCh and EtA, respectively.

It should be pointed out that the polymers used have their own absorption in the short-wave region.
Figs. 4–6. Absorption and fluorescence spectra of DPO in PVCh (Fig. 4), PVF (Fig. 5), and EtA (Fig. 6) films measured at 296 K before (solid line) and after heating (dashed line). The fluorescence and emission anisotropy (●) spectra were obtained for \( \lambda_{\text{exc}} = 390 \text{ nm} \). ○ denote the emission anisotropy at \( \lambda_{\text{obs}} = 483 \text{ nm} \) for various \( \lambda_{\text{exc}} \).
and emit weak fluorescence. For example, Fig. 7 shows the global fluorescence spectrum of DPO in PVA heated to 423 K, the spectrum of PVA alone and the corrected spectrum. On the short-wave side of the main fluorescence band, a weak band can be observed. A similar band was recorded for DPO in non-heated PVCh films (solid line in Fig. 8) and EtA (dashed line). In all the three cases the excitation light wavelength, \( \lambda_{\text{exc}} \), was 320 nm.

### 3.2. Fluorescence Quantum Yields and Lifetimes

As already shown in [16], the fluorescence quantum yield, \( \Phi_F \), grows dramatically upon heating the DPO sample in PVA to above 358 K. Table 1 summarizes the quantum yield values determined for DPO in different polymers either non-heated or heated to 423 K. In the case of DPO in PVCh, PVF and EtA (non-heated samples), \( \Phi_F \) amounts to about 0.22, being very low for the non-heated DPO sample in PVA (0.03) and even lower than for DPO in cyclohexane and methanol. The values of \( \Phi_F \) for DPO in PVCh, PVF and EtA heated to 423 K are almost the same as for the non-heated samples, while for the heated DPO in PVA a strong increase in \( \Phi_F \) is observed, even to 0.32, which is markedly higher than the quantum yield in the remaining polymers.

Table 2 summarizes the fluorescence decay times, \( \tau \), of DPO measured at 296 K in methanol, in a methanol-water mixture and in different polymers. In methanol and non-heated PVCh and EtA films, a single exponential fluorescence decay, \( \tau_1 \), was observed, corresponding to the all-trans conformer,
Table 1. Fluorescence quantum yields $\Phi_F$ of DPO in different polymers measured at 296 K.

<table>
<thead>
<tr>
<th>DPO</th>
<th>Polymer</th>
<th>PVA</th>
<th>PVCh</th>
<th>PVF</th>
<th>EtA</th>
</tr>
</thead>
<tbody>
<tr>
<td>before heating</td>
<td>0.03</td>
<td>0.22</td>
<td>0.20</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>after heating</td>
<td>0.32</td>
<td>0.25</td>
<td>0.19</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Values of fluorescence decay times of DPO in different media at 296 K.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$\lambda_{\text{exc}}$ [nm]</th>
<th>$\lambda_{\text{obs}}$ [nm]</th>
<th>$\tau_1$ [ns]</th>
<th>$A_1^*$</th>
<th>$\tau_2$ [ns]</th>
<th>$A_2^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>350</td>
<td>&gt;420</td>
<td>5.35</td>
<td>1.00</td>
<td>4.50</td>
<td>0.90</td>
</tr>
<tr>
<td>Mixture of 50% methanol and 50% water</td>
<td>350</td>
<td>&gt;420</td>
<td>0.001</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVCh</td>
<td>386</td>
<td>534</td>
<td>7.79</td>
<td>1.00</td>
<td>6.83</td>
<td>0.35</td>
</tr>
<tr>
<td>EtA</td>
<td>386</td>
<td>534</td>
<td>7.21</td>
<td>1.00</td>
<td>6.83</td>
<td>0.35</td>
</tr>
<tr>
<td>PVA (before heating)</td>
<td>375</td>
<td>&gt;420</td>
<td>0.001</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA (after heating)</td>
<td>375</td>
<td>&gt;420</td>
<td>0.96</td>
<td>0.265</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

$A_1^*$ and $A_2^*$ 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 $\tau_{1,2}$.

Fig. 9. Double exponential analysis of the emission of DPO in PVA film before heating. (●) and ○ denote experimental points for the phase angle and modulation, respectively.

while for the non-heated PVA a double exponential fluorescence decay was obtained with decay times $\tau_1$ and $\tau_2$ (Table 2), which evidences the emission of both forms. Figures 9 and 10 show the results of the decay time, $\tau$, measurements carried out for DPO in non-heated and heated PVA film, respectively. The all-trans conformer with its longer decay time $\tau_1$, in the non-heated film is less abundant (35%) than the cis conformer with its shorter lifetime $\tau_2$ (65%). In the PVA film heated to 423 K, as many as 96% of the DPO molecules occur as all-trans conformers, with the lifetime $\tau_1$ being the same as for the PVCh film. Stronger heating (to above 423 K), which might have transformed all the DPO molecules from the cis to the trans configuration, was not possible due to yellowing of the PVA film.

4. Discussion

The results obtained for DPO in different polymer films (PVCh, PVF and EtA) either non-heated or
heated to 423 K indicate, similar as for DPH [18], the occurrence of all trans conformers only. Unlike PVA, in polymers insoluble in water, no short-wave diffused band responsible for the absorption of the s-cis conformer can be observed at 296 K. In water-methanol mixture (Table 2), upon the 350 nm excitation and observation above 420 nm, a double exponential fluorescence decay occurs, whereas for methanol alone, a single exponential decay is found. Similar behaviour is observed for the PVA film either non-heated or heated. Heating to 423 K causes that as many as 96% of the molecules undergo transition to the all-trans configuration and only 4% remain as s-cis conformers. This problem was discussed in more detail in [18] for DPH in PVA and other polymers. Nonetheless, the following issues deserve attention.

As shown in Figs. 7 and 8, on the short-wave side of the strong fluorescence band a weak fluorescence band appears which probably corresponds to the transition from the 1^1B_u(S_2) level with a very short decay time. The very short emission decay time observed for DPO in water-methanol mixture and in the non-heated PVA film, amounting to 1 ps, cannot be attributed to the transition from the 1^1B_u level since the observation wavelengths were above 420 nm. Thus, also this fact supports the conclusion that the fluorescence of DPO in the PVA film, either non-heated or heated to 423 K, originates from all-trans and groundstate s-cis conformers, similar as observed for DPH [19].

The second problem is that the behaviour of the emission anisotropy varies in different polymers. In PVC and EtA a value close to 0.4 is obtained, reflecting the enhanced rigidity of the microenvironment around the DPO molecules in these polymers. In PVA heated to 423 K, the emission anisotropy of DPO is distinctly different, amounting to 0.354. This results from a certain degree of orientational freedom of this molecule. Therefore also in this case isomerization can occur in the solid phase (PVA polymer), like e.g. in low-temperature n-alkane solutions of DPO [2]. In part VII of this series photoisomerization of diphenylpolyenes in PVA polymers will be dealt with.

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