Isomerization of Diphenyl Polyenes. Part II. Fluorescence Properties of 1,8-Diphenyl-1,3,5,7-octatetraene in Poly(vinyl alcohol) Film

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The effect of temperature on the fluorescence properties of 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in poly(vinyl alcohol) film (PVA) was investigated in the range from 295 to 428 K. Upon heating above 353 K, the quantum yield of DPO increases rapidly. This effect is irreversible, similarly as the optical density in the long wavelength absorption band (320–440 nm). It has its origin in the cis-trans conversion of DPO molecules in PVA film at high temperatures. The behaviour of the fluorescence anisotropy in the same temperature range was also investigated. The emission anisotropy was found to be a viscosity indicator in the microenvironment of the DPO molecules in PVA film.

1. Introduction

Diphenylpolyenes, $Ph-(CH=CH)_n-Ph$, exhibit a number of anomalous fluorescence properties in various solvents [1, 2]. In part I of this paper [3] we described an unusual temperature dependence of 1,8-diphenyloctatetraene (DPO, $n=4$) absorption in poly(vinyl alcohol) (PVA) film. It was found that the absorption of isotropic PVA film with DPO admixtures increases considerably in the spectral range of 320–440 nm temperatures exceeding 353 K. The absorption at 423 K was even twenty times higher than that observed at room temperature. This effect is irreversible which means that high absorption capability of the sample is retained upon its cooling. The observed effect has its origin in the cis-trans conversion of DPO molecules in PVA films in the ground state at high temperatures.

The present paper deals with the temperature effect (from 295 to 428 K) on the fluorescence properties, in particular the quantum yield, ϕ_F, and emission anisotropy, r, of 1,8-diphenyl-1,3,5,7-octatetraene in PVA films.

2. Experimental

DPO, from Aldrich Chemical Company Inc., Steinheim, BRD, was used without further purification. Poly(vinyl alcohol), 100% hydrolized, molecular weight 106,000–110,000, was from "Aldrich Chemie".

Isotropic PVA films were prepared at room temperature by the method described previously [4–6]. Diphenylpolyenes are relatively poorly soluble in aqueous PVA and were therefore introduced to the solutions through methanol. PVA films without DPO were used as references in the absorption measurements. The fluorescence spectra were recorded by means of a fully corrected spectrofluorimeter designed and built in our laboratory [7].

Fluorescence quantum yields, ϕ_F, were determined by comparison with those of a standard substance according to the relation [8, 9]:

$$\phi_F = \phi_F^s \frac{\int_0^\infty I_F(\tilde{\nu})\,d\tilde{\nu}}{\int_0^\infty I_F^s(\tilde{\nu})\,d\tilde{\nu}} \left(\frac{1-10^{-D^s}}{1-10^{-D}}\right)\left(\frac{n}{n^s}\right)^2\left(\frac{2-r_n^s}{2-r_n}\right), \quad (1)$$

where ϕ_F^s is the fluorescence quantum yield of a standard substance, D and D^s are optical densities, n nd n^s are the refractive indices, and r_n and r_n^s are the emis-

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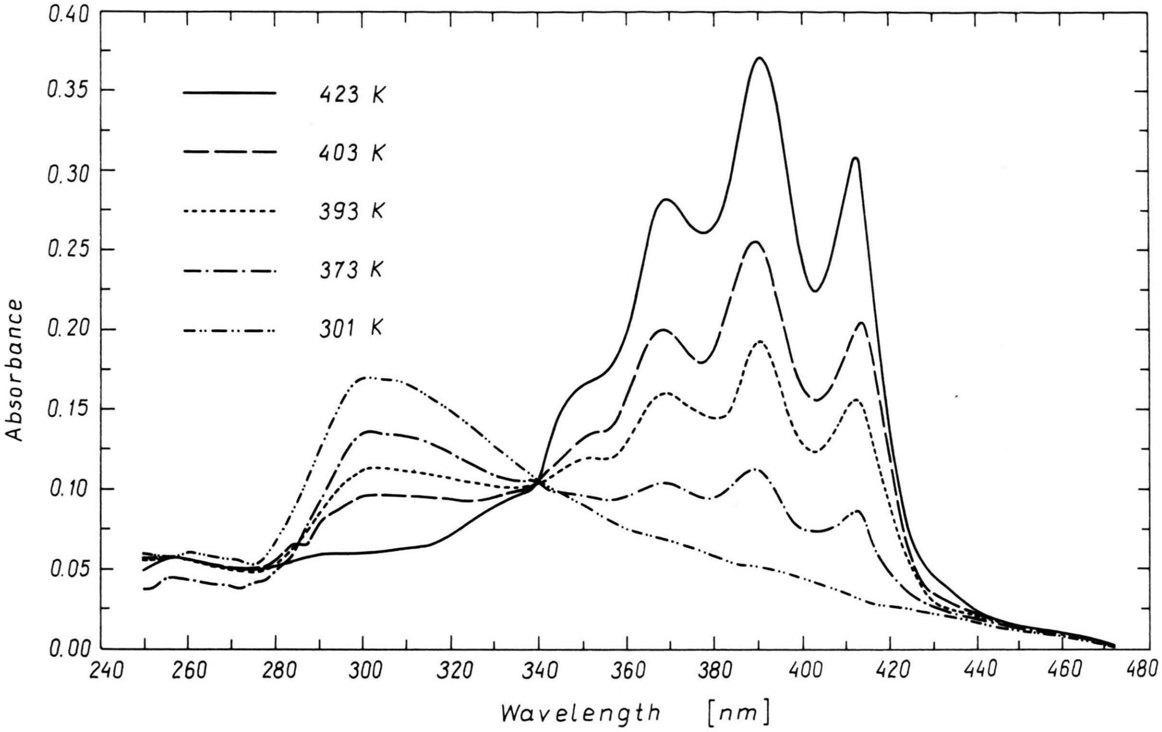

Fig. 1. Absorption spectra of 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in poly(vinyl alcohol) (PVA) film at different temperatures.

sion anisotropies of the sample and the standard, respectively, upon excitation by unpolarized light. As a fluorescence standard, a 5×10^{-3} M solution of quinine sulphate in 1 N sulphuric acid was used [10, 11]. The fluorescence anisotropy of the quinine sulfate standard is $r_n^s \cong 0$. The integrals represent the areas under the spectra of the sample and of the standard compound.

The emission anisotropy was measured by a photon apparatus designed and constructed in our laboratory [12].

Absorption and emission spectra, quantum yields and emission anisotropies were measured in a special thermostatic cell enabling the temperature of the sample to be maintained with an accuracy of ± 0.5 K in the temperature range from 295 to 428 K. The PVA film samples, placed between two quartz plates, were inserted into an aluminium thermostatic unit. The temperature was stabilized by a TC 650 temperature controller with a 100 W electric heater coiled on the outer surface of the aluminium unit, and a platinum sensor placed about 3 mm from the fluorescence light observation panel.

A thermoelement was used for additional temperature read-out on a digital meter. The temperature changes are limited to 428 K by the parameters of thermoconducting adhesive, THERMOCON, used to fasten the heater and termperature sensors to the aluminium unit of the thermostat ($T_{\max} = 432$ K).

3. Results and Discussion

3.1. Emission Spectra and Fluorescence Quantum Yields

In the preceding investigations [3] we used PVA from Austranal-Präparate, Loba-Chemie (Austria), the molecular weight of which was not known precisely. Now we used PVA with a molecular weight between 106,000 and 110,000 g/mole, and all absorption, fluorescence and emission anisotropy measurements for DPO were done in PVA with the molecular weight given above. The absorbances of DPO measured in PVA from "Aldrich Chemie" at different temperatures (Fig 1) behave similarly as those demonstrated in [3]. No changes in the absorption spectrum

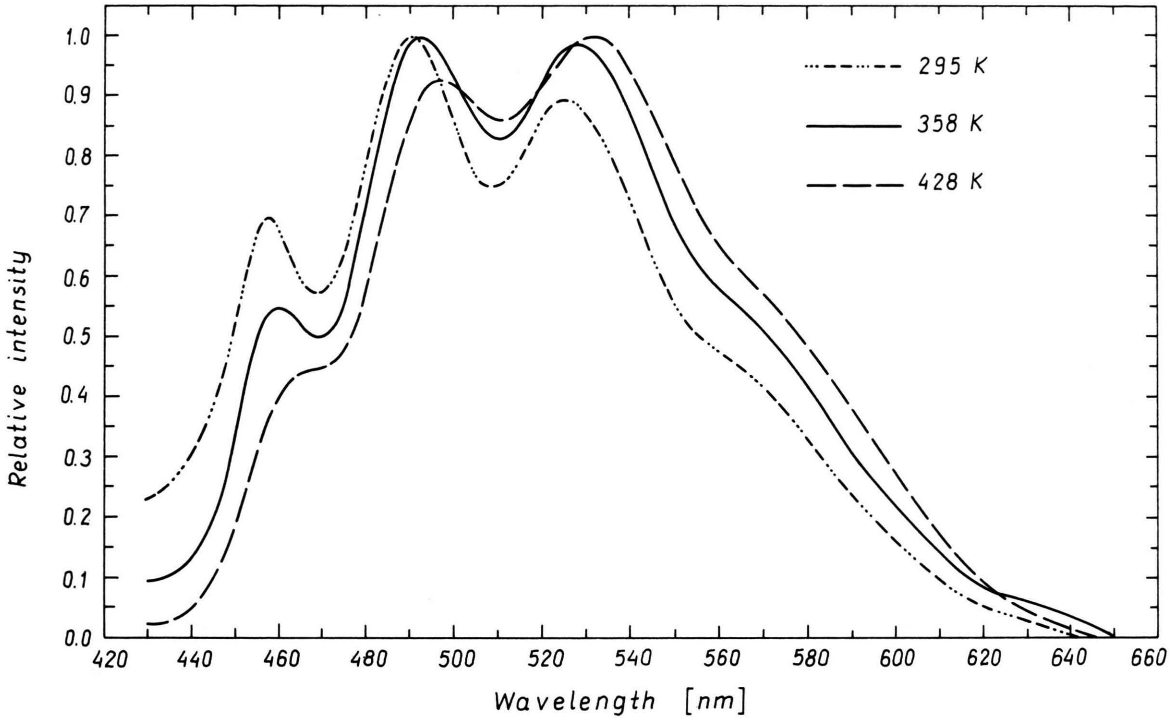

Fig. 2. Normalized fluorescence spectra of DPO in PVA film at different temperatures by $\lambda_{exc} = 390$ nm.

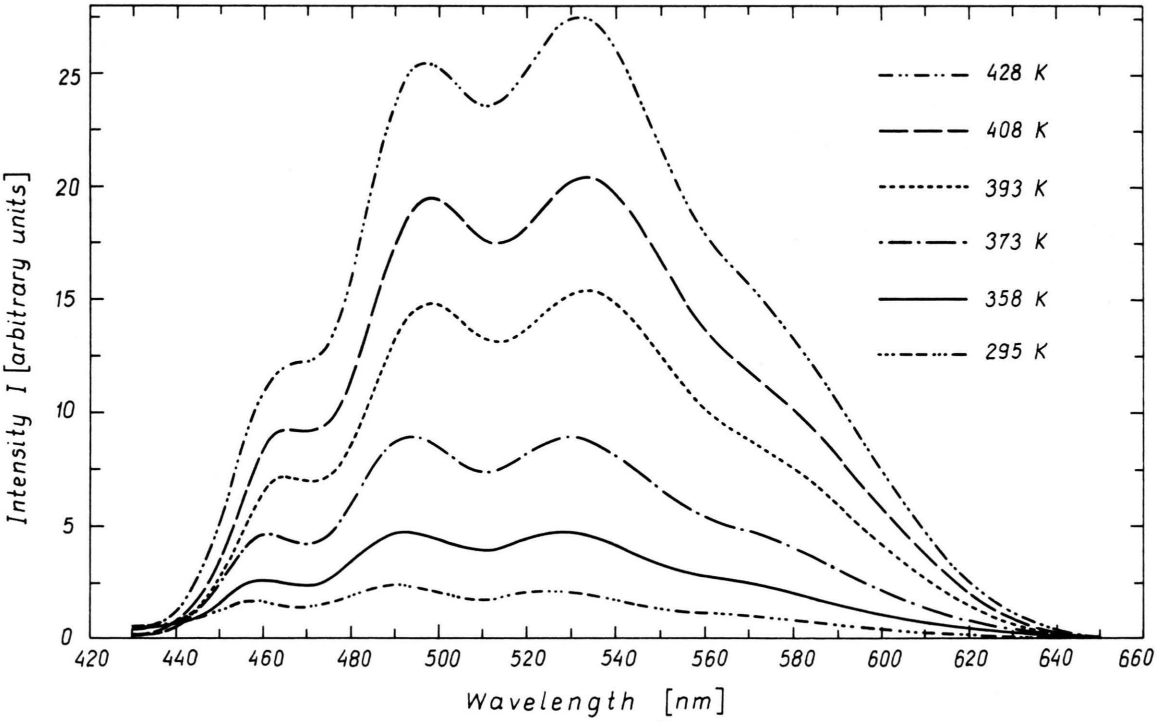

Fig. 3. Fluorescence spectra (arbitrary units) of DPO in PVA film at different temperatures excited ($\lambda_{exc} = 390$ nm) at the same conditions.

of DPO in PVA film were observed at temperatures from 293 to 353 K. It was only at higher temperatures that the absorption of DPO in PVA film increased progressively in the spectral range 320–440 nm, similarly as shown in Fig. 2 of [3]. In the short wavelength region (270–330 nm) the absorption decreased considerably. No absorption band shift was observed with growing temperature.

At the same time, the measured fluorescence spectra slightly shift (by up to 10 nm) when increasing the temperature with simultaneous changes in the relative intensities of the individual maxima in the structured fluorescence spectrum (Figure 2).

Figure 3 shows the fluorescence spectra of DPO in PVA films at different temperatures, measured under the same conditions at $\lambda_{exc} = 390$ nm. As clearly seen, the fluorescence intensity at room temperature ($T = 295$ K) is about 15 times lower than that at 428 K. The measured quantum yields (relative to quinine sulfate) of the same DPO sample in PVA film are shown in Figure 4. Thus, the temperature increase to above 353 K results in a strong enhancement in the quantum yield of DPO in PVA film. After cooling, the sample retains its properties evoked by temperature. This effect is irreversible, similarly as with the behaviour of the optical density (see Fig. 3 in [3]).

As already noted in the first section of [3], the described increase in absorption results from conformational changes in the DPO molecules occurring in the glassy phase of the heated PVA polymer. While preparing PVA films, the DPO molecules are fixed in the drying polymer in the conformational state in which they were in liquid aqueous-methanol PVA solution. The exsiccated PVA film exhibits different environmental properties. Nevertheless, the DPO molecules cannot attain their lowest trans energy state in view of the high viscosity of the medium in room temperature (see the energy diagram illustrating cis-trans isomerization of DPO in PVA film in the ground state, Fig. 4 in [3]). Due to the alternation of the medium, the DPO molecules were artificially transferred to a nonequilibrated state. In other words, the system was pumped to attain the inversion of conformational states. While heating the sample and the following the attainment of the glassy phase by the polymer, the DPO molecules pass to the lowest energy state in the mdium, i.e. to the trans-configuration that is responsible for the fluorescence., This was confirmed by a marked increase in the quantum yield of DPO in PVA film at temperatures above 353 K.

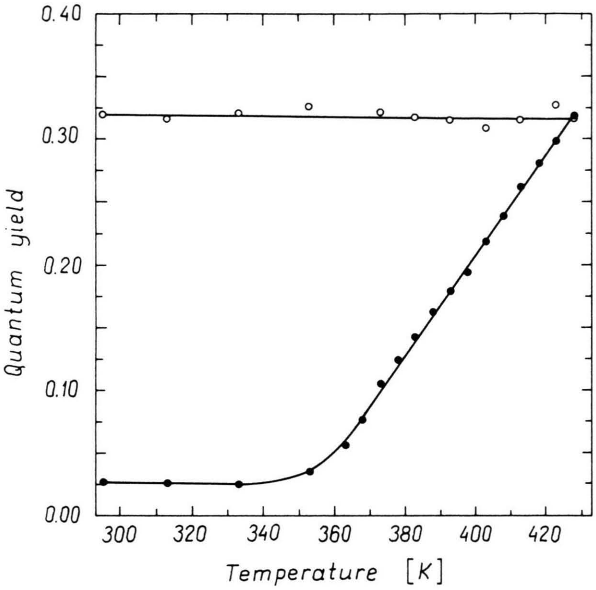

Fig. 4. Dependence of the quantum yields of DPO in PVA film on temperature; (●) the sample was heated from room temperature up to 428 K; (○) the sample was heated to 428 K then cooled to room temperature and next heated to a given temperature before measuring the quantum yields.

3.2. *Emission Anisotropy*

The transition moment directions in the long-wavelength absorption and in the fluorescence of DPO molecule are known to be coincident and lie along the long molecular axis of DPO [5, 6]. The angle β between the absorption and fluorescence transition moments in DPO is 4° [13], while the absorption transition moment makes an angle of $\varphi \approx 4.5°$ with the long molecular axis [14].

For a highly dried PVA film (prepared in 1987 and stored in dark), a limiting fluorescence anisotropy of 0.354 was measured immediately following its preparation and also recently, which differs considerably from a fundamental value of 0.4. Such a lowered value is due to limited rotational motions of DPO in PVA film. This evidences that in isotropic PVA films the DPO molecule has a certain freedom of limited rotational motions. Such motions in PVA films may be eliminated by mechanical stretching of the film at high temperature. As a result of the deformation of the polymer caused by stretching, the DPO molecules are compressed mechanically inside the polymer cavities, which causes a restriction of their thermal rotations but does not affect the character of the intramolecular

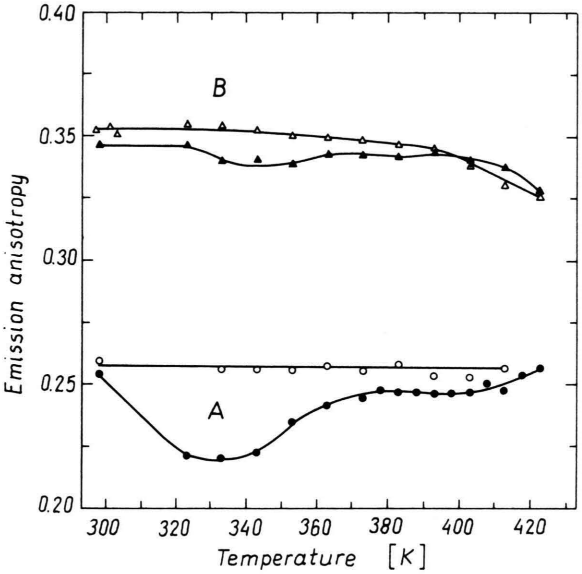

Fig. 5. Dependence of the emission anisotropy of DPO in PVA film on the temperature for two samples. A: after desiccation for two weeks, B: after desiccation for more than two weeks. $\lambda_{exc} = 390$ nm and $\lambda_{obs} = 500$ nm. The filled and hollow points designate heating and cooling, respectively.

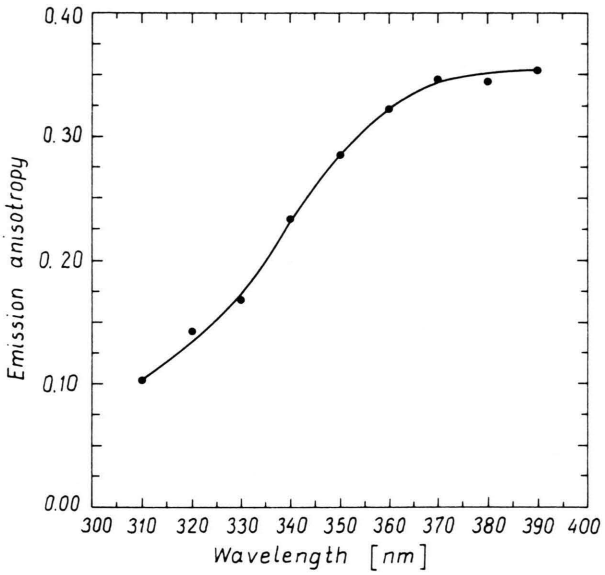

Fig. 6. Dependence of the emission anisotropy of DPO in PVA film on the excitation wavelength. The sample B was preheated to 428 K and then cooled to room temperature before measuring its emission anisotropy.

processes [13]. Upon the elimination of such restricted rotational motions, the value of the limiting anisotropy, r_0, of the DPO molecule is 0.397, thus being very close to the fundamental emission anisotropy, $r_f = 0.4$.

Thus, the value of the limiting emission anisotropy of a luminescent molecule (the DPO molecule in the case considered) in an isotropic PVA film is a measure of the rotational freedom of this molecule, i.e. of the microviscosity of its closest environment. In freshly prepared isotropic PVA films, various limiting emission anisotropy values are commonly observed in spite of the same time of drying (about 2 weeks). Figure 5 shows the emission anisotropy behaviour as a function of temperature for two samples: one dried for no longer than 2 weeks (curves A) and the other for more than 2 weeks (curves B – after 5 years). The effect of temperature on the emission anisotropy is clearly different. In the case of curve A, the PVA polymer strongly softens while increasing temperature, resulting in a marked decrease in the emission anisotropy due to the rotational depolarization. The sample was each time excited with $\lambda_{exc} = 390$ nm and continuously heated during the emission anisotropy measurement so as to keep the temperature constant by means of a thermostating unit in successive measurement points every 10 K. At temperatures above 353 K, the DPO molecules undergo transition from cis to the fluorescent trans form. Irrespective of the fact that above 353 K the polymer becomes softer and softer (the microviscosity around the DPO molecules decreases), the emission anisotropy grows due to photoselection, attaining finally the initial value. A similar, yet less temperature sensitive behaviour of the emission anisotropy is observed for PVA film subject to much longer drying (curves B). Figure 6 shows the behaviour of the DPO emission anisotropy in PVA film as a function of the excitation light wavelength for a well dried film (B). The emission anisotropy above $\lambda_{exc} \approx 370$ nm remains constant and corresponds to the trans-configuration.

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