

Isomerization of Diphenyl Polyenes.

Part VII. The effect of Daylight and Direct Irradiation on the Photoisomerization of $\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$ for $n=2, 3, 4$ in Poly(vinyl alcohol) Films

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

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

Z. Naturforsch. **48a**, 1177–1181 (1993); received September 28, 1993

Photoisomerization of 1,4-diphenyl-1,3-butadiene (DPB), 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in poly(vinyl alcohol) (PVA) films was studied under daylight and direct irradiation. The most efficient photoisomerization occurs in the DPB molecule, the smallest among the compounds investigated. For the greatest, DPO, molecule no distinct isomerization was observed in daylight and only a temperature effect was noted. Therefore, the DPO molecule in the PVA film heated to 423 K may serve as a fluorescence standard.

1. Introduction

Linear polyenes $\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$ of medium size ($n=2, 3, 4$) display an efficient photoisomerization in well defined molecular cavities [1]. Kohler and co-workers demonstrated that for very narrow bands, observed in low-temperature (4.2 K) *n*-alkane solutions of linear polyenes, the small differences in the excitation energies of *cis* and *trans* isomers are great enough compared to the band widths for the spectra of *cis* and *trans* isomers being quite independent and readily distinguishable. They also found that even in these liquid helium temperature solid solutions the *cis*, *trans*, and *trans*, *trans* isomers are interchangeable photochemically [2].

Since there is much support for the hypothesis that a viscous solution should inhibit photoisomerization, an essential question arises about the effect of daylight on polyenes in a rigid polymer of poly(vinyl alcohol) (PVA) film.

The unusual behaviour of the absorbance and quantum yield of 1,8-diphenyl-1,3,5,7-octatriene (DPO) and 1,6-diphenyl-1,3,5-hexatriene (DPH) in the PVA film in a glassy phase (above the glassy transition temperature, $T_g \approx 358$ K) of the heated polymer

reflects the occurrence of the thermal *cis-trans* isomerization in the ground state [3–7]. Above this temperature (up to 423 K), the absorbance and fluorescence quantum yield strongly grow. This phenomenon is irreversible, i.e. the sample retains high absorbance and fluorescence quantum efficiency following its cooling to room temperature. This suggests that there is also an effect of light on the above characteristics.

In the present paper we report the results of investigations on the effect of daylight and direct irradiation in the short- and longwave absorption band upon the behaviour of the absorption and fluorescence spectra of three polyenes ($n=2, 3, 4$) in PVA films.

2. Experimental

1,4-Diphenyl-1,3-butadiene (DPB, $n=2$) 1,6-diphenyl-1,3,5-hexatriene (DPH, $n=3$) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO, $n=4$), from Aldrich Chemical Company Inc., Steinheim, F.R.G., were used without further purification. Poly(vinyl alcohol), 100% hydrolyzed, molecular weight 106 000–110 000, was from Aldrich Chemie. The preparation of the PVA polymer films was described in [3, 4]. The measurement methods were described in [3–5]. For direct irradiation, a 250 W xenon lamp was used. The wavelengths required for the irradiation were selected using prismatic monochromators (Carl Zeiss, Jena).

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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3. Results and Discussion

3.1. Spectral properties of DPB in PVA films

The absorption and fluorescence spectra of DPB in nonheated PVA film (Fig. 1) were measured at different times after the preparation of the samples. The samples were exposed in a room to indirect daylight (the number of hours given in the figures embrace both day and night). A fresh sample exhibited comparable absorbances in the short- and longwave bands. After 240 hours, the absorbance of the longwave band decreased considerably and the fluorescence band markedly narrowed. In addition, the fluorescence intensity strongly dropped, thus reflecting a marked decrease in the fluorescence efficiency (Figure 2). All the above applies also to the DPB sample heated to 423 K and exposed to the daylight. A freshly prepared and heated sample shows no characteristic band corresponding to the *cis* conformer (Figure 3). However, a shortwave band appears after about 70 hours. Following further 600 and more hours, the intensity of the shortwave absorption band (265 nm) is markedly stronger than that of the longwave band (300–350 nm) with a characteristic isosbestic point corresponding to photochemical equilibrium. When this system (after a 800-hour exposition to the daylight) is subjected the ultraviolet irradiation ($\lambda = 265$ nm

corresponds to the shortwave band maximum of the *cis* conformer), the intensity of the longwave band, corresponding to the *trans* conformer, increases (Fig. 4) together with the intensity of the fluorescence band. Thus, the system is photochemically reversible.

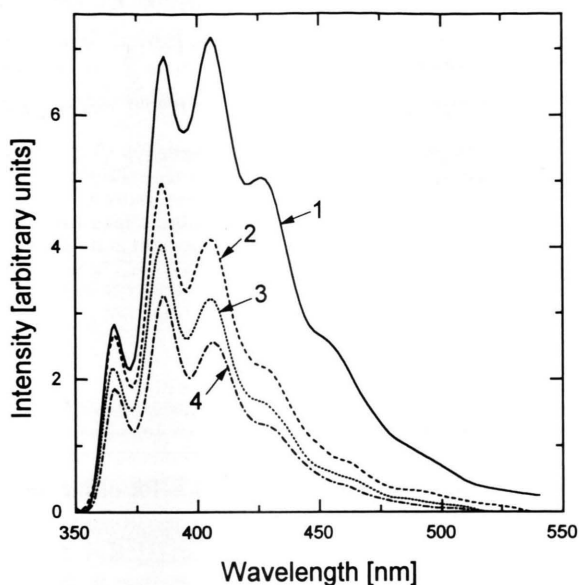


Fig. 2. Fluorescence spectra (in arbitrary units) of DPB in PVA film (before heating) exposed to the daylight for: (1) 0 hours, (2) 24 hours, (3) 96 hours and (4) 240 hours (measured at 293 K, $\lambda_{\text{exc}} = 340$ nm).

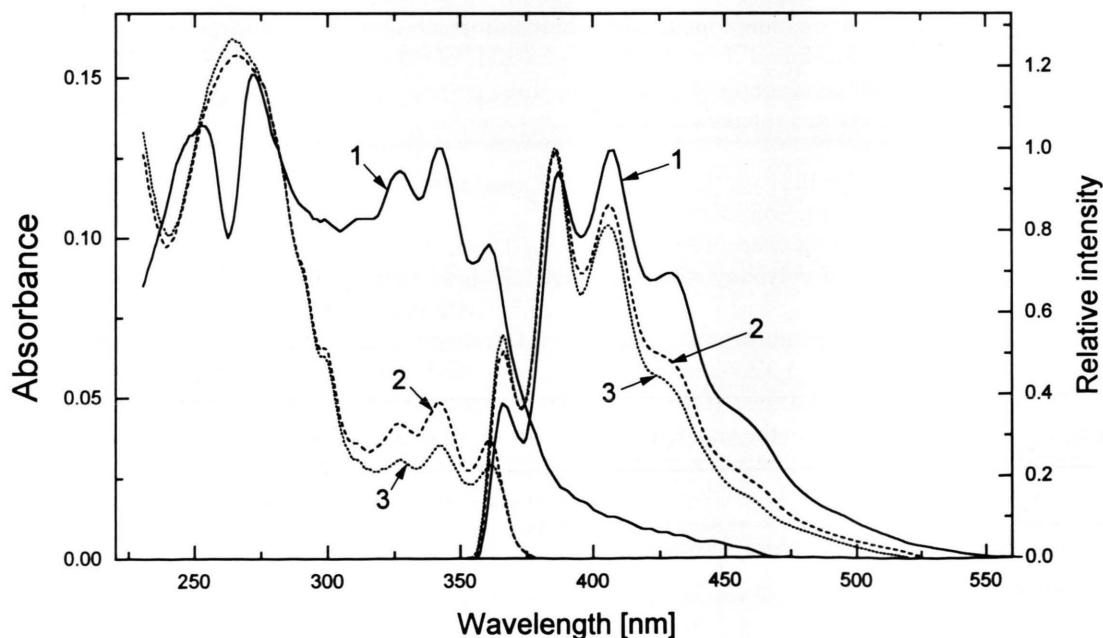


Fig. 1. Absorption and fluorescence spectra of DPB in PVA film (before heating) exposed to the daylight for: (1) 0 hours, (2) 24 hours, (3) 240 hours, (measured at 293 K, $\lambda_{\text{exc}} = 340$ nm).

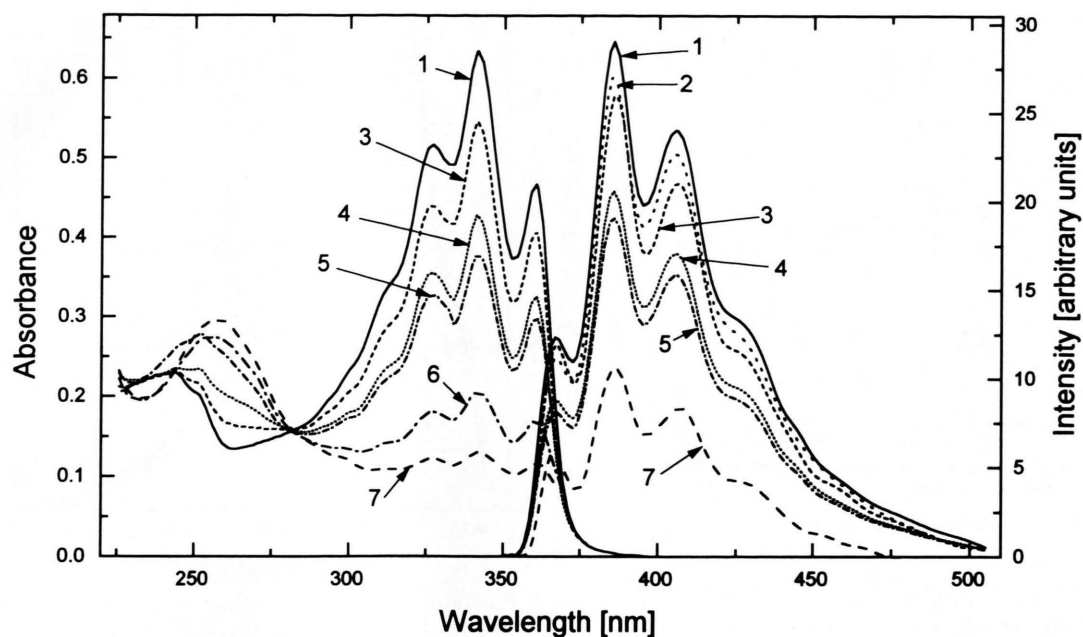


Fig. 3. Absorption and fluorescence spectra of DPB in PVA film (after previous heating to 423 K) exposed to the daylight for: (1) 0 hours, (2) 24 hours, (3) 72 hours, (4) 240 hours, (5) 288 hours, (6) 672 hours, (7) 800 hours (measured at 293 K, $\lambda_{\text{exc}} = 340$ nm).

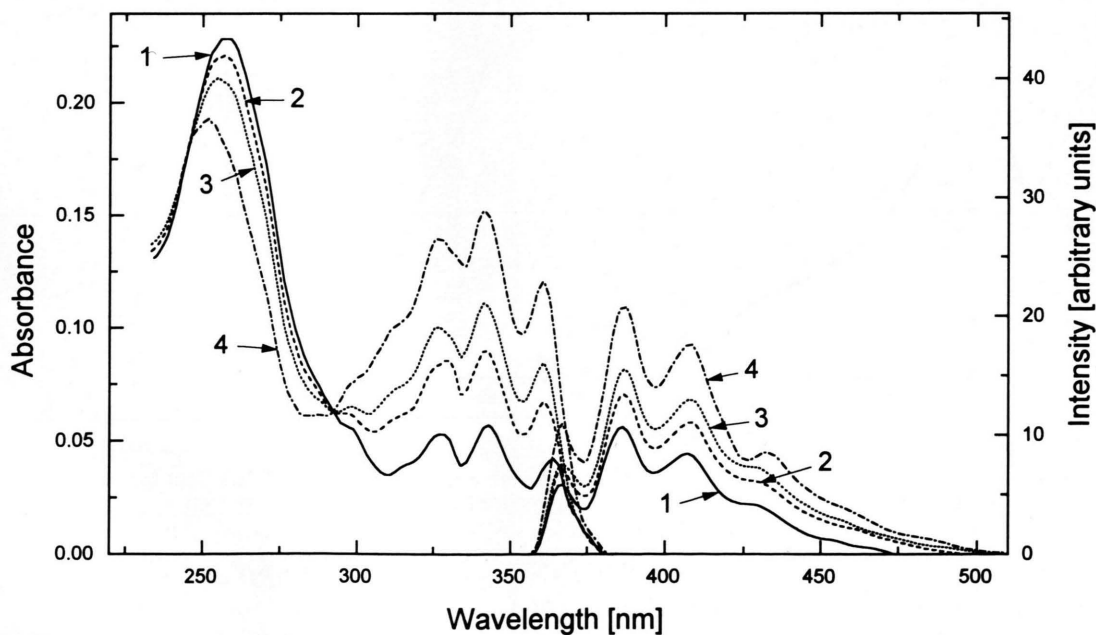


Fig. 4. Absorption and fluorescence spectra of DPB in PVA film (after previous heating to 423 K) exposed to direct UV irradiation at $\lambda = 265$ nm (measured at 293 K, $\lambda_{\text{exc}} = 340$ nm). The sample exposed to daylight for 800 hours was chosen as an initial sample. (1) 0 hours, (2) 3 hours, (3) 12 hours and (4) 36 hours of UV irradiation.

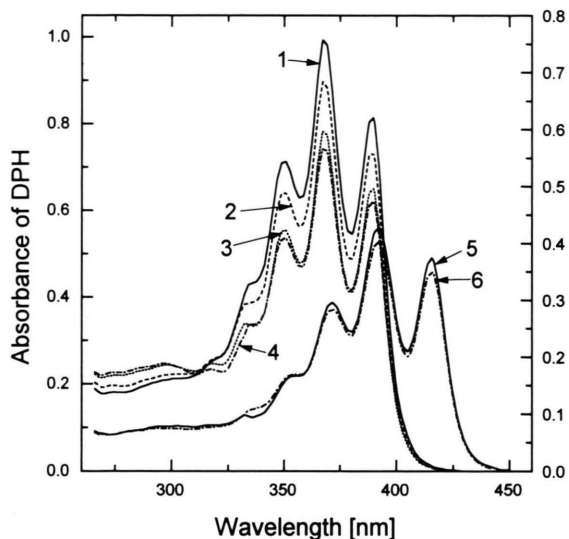


Fig. 5. Absorption spectra of DPH (curves 1, 2, 3, 4) and DPO (curves 5, 6) in PVA film measured at 293 K after previous heating to 423 K and exposed to the daylight for: (1 and 5) 0 hours, (2) 24 hours, (3) 240 hours, (4 and 6) 460 hours.

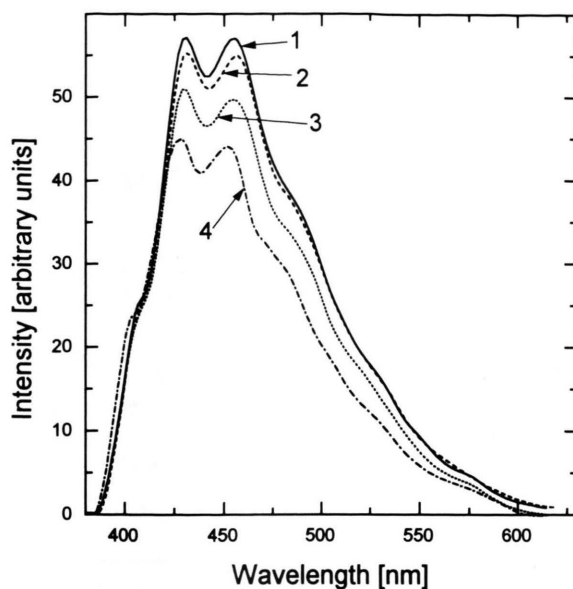


Fig. 7. Fluorescence spectra (in arbitrary units) of DPH in PVA film after previous heating to 423 K exposed to the daylight for: (1) 0 hours, (2) 24 hours, (3) 240 hours and (4) 360 hours (measured at 293 K, $\lambda_{\text{exc}} = 366$ nm).

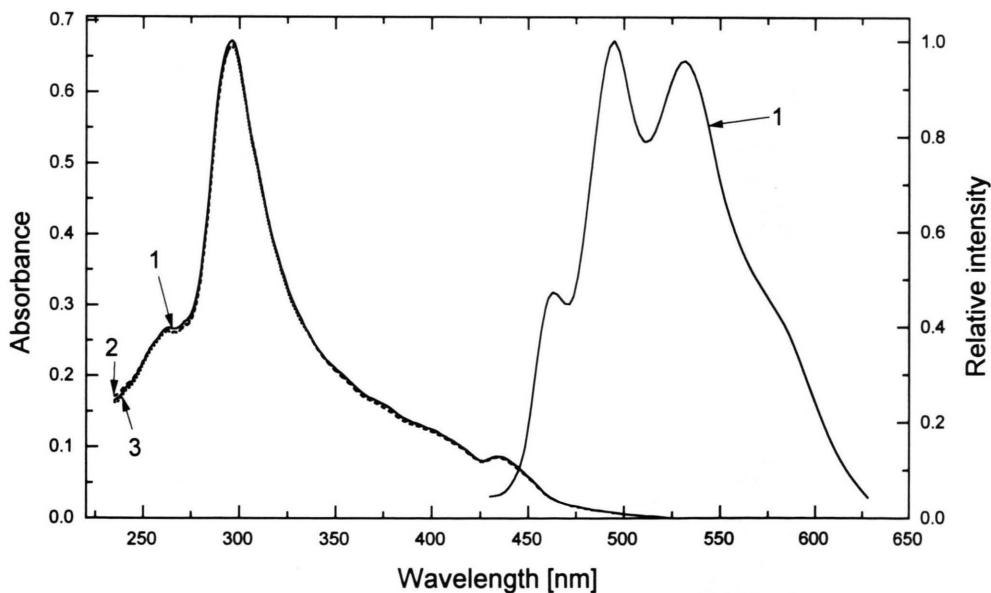


Fig. 6. Absorption and fluorescence spectra of DPO in PVA film (before heating) exposed to the daylight for: (1) 0 hours, (2) 96 hours, and to the UV irradiation at $\lambda = 295$ nm for (3) 20 hours (measured at 293 K, $\lambda_{\text{exc}} = 390$ nm).

From among the polyenes investigated, the DPB molecule ($n=2$) is the smallest and has a considerable mobility within the PVA polymer cavities. This conclusion is in agreement with the results of the studies on the emission anisotropy [8, 9].

3.2. Spectral properties of DPH and DPO in PVA films

In contrast to DPB in the PVA film (Fig. 4), the absorption spectra of DPH and DPO exposed to day-

light do not undergo such a rapid modification. In particular, no absorbance changes can be observed for DPO in PVA heated to 423 K (Figure 5). A slight change in the absorbance was noted after 240 hours (about 4%) but after 460 hours the spectrum remained unchanged. Similar, for DPO in nonheated PVA no changes in the absorption and fluorescence spectra were observed following daylight and ultraviolet (300 nm) irradiation (Fig. 6), which shows that the *cis-trans* transition takes place by thermal and not by photoisomerization.

In the case of DPH in PVA heated to 423 K, a distinct change in the absorbance (see Fig. 5) and fluorescence intensity (Fig. 7) is observed.

4. Conclusions

1. DPB, DPH and DPO polyenes embedded in the PVA polymer cavities are in identical conditions. They differ only in size and rotational freedom as regards

both the molecule as a whole and the double bond. The smallest molecule DPB has the greatest mobility and, as a result of photoisomerization, readily transforms from *cis* to *trans* or *trans* to *cis* configuration. Under the same conditions, photoisomerization of the DPH molecule is less efficient, and for the largest DPO molecule the *cis-trans* and *trans-cis* conversion by photoisomerization is hindered. The *cis-trans* conversion of DPO in PVA is only possible by thermal isomerization as a result of the softening of the PVA polymer at high temperatures.

2. From among the polyenes studied, only DPO in the PVA film heated to 423 K can serve as a fluorescence standard. Its fluorescence characteristics were previously given [3, 4, 7].

Acknowledgement

The authors wish to thank eng. T. Nowosielski for his assistance in the measurements.

This work was supported by Grant No. 2 0283 91 01 from the Committee for Scientific Research, Warsaw.

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