Isomerization of Diphenyl Polyenes

Part I. Unusual Absorption Properties of 1,8-Diphenyl-1,3,5,7-octatetraene

A. Kawski *, Z. Gryczyński *, **, I. Gryczyński *, **, W. Wiczk **, and H. Malak **

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

** Center for Fluorescence Spectroscopy, Department of Biological Chemistry, University of Maryland, 660 West Redwood Street, Baltimore MD 21201, USA

Z. Naturforsch. **46a,** 621–624 (1991); received March 27, 1991

We describe an unusual temperature dependence of 1,8-diphenyl-1,3,5,7-octatetraene absorption in poly(vinyl alcohol) films. Upon heating above 80 °C, the optical density (in the long wavelength region) of this compound increases rapidly. A sample heated to 150 °C has a nearly twenty times higher optical density than a non-heated sample. This effect is not reversible: Once the sample is heated it retains its absorbance on cooling to room temperature. In our opinion, the effect has its origin in changes of the chromophore molecules from cis to trans conformation at the high temperature. Possible applications of these unique material properties should be improved temperature sensors, optical data storage, non-developed high resolution photography or typing, etc.

1. Introduction

Diphenyl polyenes, Ph–(CH=CH)$_n$–Ph, have anomalous luminescence properties: A large shift between the absorption and emission spectra and a marked difference in the natural lifetimes, determined from luminescence and integrated absorption [1]. The photophysics of diphenyl polyenes has extensively been investigated [2]. Trans-stilbene ($n=1$) was the subject of tens of publications, mostly about photoisomerization occurring in the excited state [3–7]. It is known that trans-stilbene absorbs more strongly in the 310 to 320 nm region whereas cis-stilbene absorbs more strongly in the 240–250 nm region, and the extinction coefficient is about 10 times greater in the long wavelength region than in the short wavelength region [2, 6]. Similar dependences occur for other diphenyl polyenes. Time-resolved fluorescence spectroscopy was used to study excited states of DPB [8], DPO [9, 10] and DPH – one of the most widely used fluorescence probes in studies of biological membranes [11–13]. In all trans-diphenyl polyenes the transition moments are lying along the long axis of the molecules. Thus they are convenient chromophores for dichroism and polarization studies in oriented systems (liquid crystals, stretched polymeric films) [14, 15].

In this paper we describe a new effect and its potentially useful applications utilizing the diphenyl polyene 1,8-diphenyl-1,3,5,7-octatetraene (DPO) doped into poly(vinyl alcohol) (PVA) films.

2. Experimental

Isotropic PVA films were prepared at room temperature by the method described in previous papers [16–18], introducing the substances under investigation into aqueous PVA solution through methanol.

PVA films without DPO were used as references in absorption measurements.

The purity of DPO (>99%) was checked by HPLC analysis.

3. Results and Discussion

3.1. *Water Induced Changes of DPO Absorption in Solutions*

The absorption spectrum of DPO in methanol (Fig. 1) is structured and has a maximum at 375 nm with a high extinction coefficient $\sim 10^5\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$. At short wavelengths (230–300 nm) DPO in methanol absorbs poorly. In methanol-water mixtures we observed significant changes in the DPO absorption. With addition of water, the 375 nm DPO absorption decreases and new absorption bands occur. In 90% of

---

Reprint requests to Prof. Dr. Alfons Kawski, Uniwersytet Gdański, Instytut Fizyki Doświadczalnej, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

0932-0784 / 91 / 0700-0621 $ 01.30/0. – Please order a reprint rather than making your own copy.

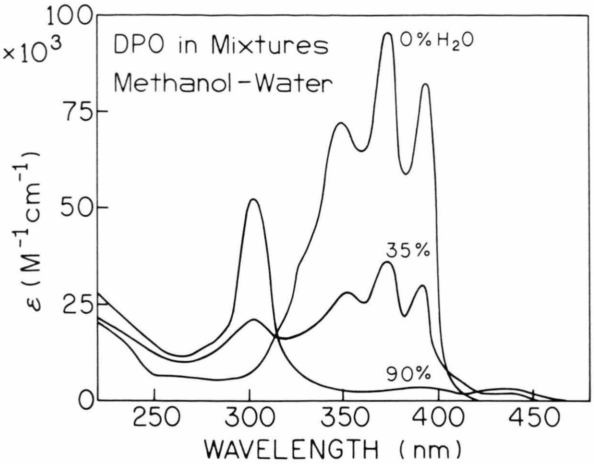

Fig. 1. Absorption spectra of 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in methanol-water mixtures.

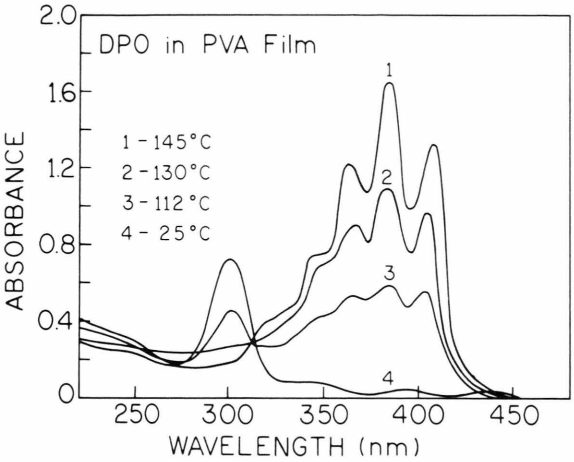

Fig. 2. Absorption spectra of 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in poly(vinyl alcohol) (PVA) film at different temperatures.

water we observed a strong absorption band at 305 nm and two week bands at 390 nm and 430 nm. We did not observe any crystallization, and this effect does not depend on the concentration of DPO. In our opinion, like in the stilbene case, the observed absorption changes can be explained by trans-cis isomerisation of the DPO molecules.

In mixtures containing much water, the DPO molecules exist mostly in cis-form(s). Water induced trans-cis isomerisation of DPO is monitored also in fluorescence changes (cis form(s) of diphenylpolyenes display poor fluorescence), which will be described in detail in a separate publication.

3.2. Temperature Induced Changes of DPO Absorption in PVA Films

Several years ago, during an experimental study of the linear dichroism and polarization of diphenyl polyenes in PVA films, we observed an unusual increase of DPO absorption in stretched PVA films. Initially, we thought that the stretching of the films is responsible for the effect, but this was not the reason. Later we found that unstretched PVA films containing DPO show also an increase of absorption after heating (it should be noted that PVA films are heated in the stretching procedure).

In PVA aqueous solution, the DPO molecules (introduced by methanol) exist in the cis form(s). These cis-conformations are trapped in the polymeric matrix during the vaporizing procedure and cannot change into the natural (in nonaqueous solution) trans-form because of the high viscosity of the PVA film.

During the PVA film preparation the inversion of the conformational states of DPO and/or other diphenylpolyenes can be distinguished.

The absorption spectrum of DPO in PVA film does not change at all up to 80 °C. Above 80 °C we observed a dramatic increase in the long wavelength (300–440 nm) absorption of the sample. No changes in the position of the spectrum were detected (Figure 2). In the temperature range of 80–150 °C the absorption increases progressively (Fig. 3), displaying an Arrhenius dependence. At 150 °C the optical density of the sample is nearly 20 times higher than at room temperature. The data points (●) in Fig. 3 represent the absorption of DPO in PVA films when the sample is heated from room temperature up to 150 °C. Once heated, the sample retains its absorption after cooling. This effect is demonstrated by heating the sample to a given temperature and then cooling it to room temperature before measuring its absorption (■). Small differences between the points in these two data sets can easily be explained by geometrical changes in the PVA film when it is cooled. The temperature dependent increased absorption is independent of the concentration of DPO in the films and the molecular weight of PVA. We have observed this effect in films prepared from PVA with molecular weights of 10,000 and 100,000. The absorption of the sample is not dependent on the heating time. Samples that were heated for 2 minutes or 20 minutes at the same high

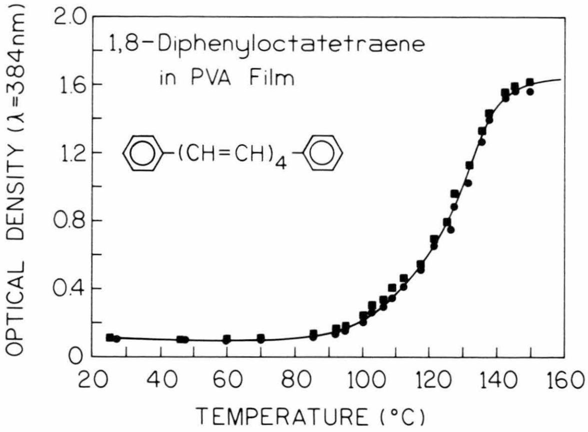

Fig. 3. Dependence of the long wavelength absorption maximum ($\lambda = 384$ nm) of DPO in PVA film upon the temperature. The data points are from two independent measurements; (●) the sample was heated from room temperature up to 150 °C; (■) the sample was heated to a given temperature and then cooled to room temperature before measuring its absorption.

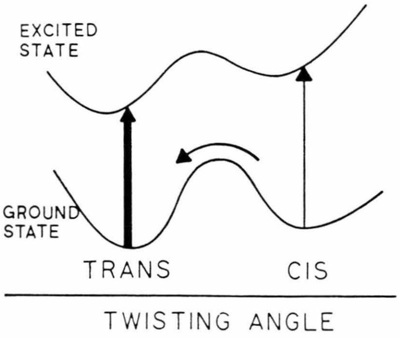

Fig. 4. Possible energy diagram describing cis-trans isomerization of DPO in PVA films in the ground state. During the film preparation procedure, DPO molecules are trapped in the polymer matrix mostly in the cis-form(s). The cis-trans isomerization is activated by temperature which results in a viscosity decrease. The polymer chain dynamics occurring in the plastic phase of PVA film and the resulting internal mechanical tension are additional factors effecting isomerization. The intensity of the absorption transition in trans-diphenyl polyene is much higher than in its cis-form.

temperature (100, 120 or 140 °C) show essentially the same elevation in absorbance.

It should be noted that the PVA films used as reference do not show absorption changes after heating up to 150 °C, however heating to higher temperatures (>170 °C) can introduce color changes of the films.

In an aqueous PVA solution we did not observe any significant temperature-dependent changes in DPO absorption between 20 and 150 °C (these measurements were done in a pressure cell). Likewise, in other solvents, such as propylene glycol and hexadecane, we did not observe any unexpected changes in absorption. As an additional experiment, we dissolved a heated sample of DPO in PVA film which displayed high optical density, in a small amount of hot water and repeated the procedure of PVA film preparation. This sample behaves like normally prepared DPO in PVA film, i.e. it shows low absorption at room temperature and high absorption during and after heating. The shape of the fluorescence spectra for non-heated and heated samples of DPO in PVA film is the same. The mean fluorescence lifetimes of the two samples are the same as well, ~8 ns, with the fluorescence intensity of the heated sample being much higher than that of the non-heated sample.

We have also tested other diphenyl polyenes, Ph$-$(CH$=$CH)$_n-$Ph. Diphenyl butadiene (DPB, $n=2$) shows an effect similar to DPO with about 4-fold maximal increase of absorption. Another well known member of diphenyl polyenes, 1,6-diphenyl-1,3,5-hexatriene (DPH, $n=3$), displays only a 50% increase in absorbance after heating.

In contrast to other organic solvents, in aqueous PVA solution as well as in PVA films DPO exists mostly in cis-form(s) and displays low absorption and fluorescence. At high temperatures (80–150 °C) the concentration of the trans-form grows rapidly, and the observed absorption and fluorescence intensities are greater. During the film preparation procedure, DPO molecules are trapped in the polymer matrix mostly in the cis-form(s). In the PVA film (after water vaporation from the PVA film), trans-isomers of DPO should occur (due to their lower energy, as in other nonaqueous organic solvents); however, the cis-trans isomerization process is stopped by the high viscosity of the film.

In the non-heated PVA film, molecules of DPO exist in a conformational state with higher energy due to the inversion of states created by the film preparation (Figure 4). When the polymer reaches its glass temperature ($T \approx 100$ °C for PVA) and becomes less viscous, the DPO molecules relax to the state with the lowest energy (trans-isomer). The polymer chain dynamics occurring in the plastic phase of PVA film and the resulting internal mechanical tensions are additional probable factors effecting isomerization.

The effect we described may have wide future applications. A non-reversible temperature sensor (80 to

150 °C) is only one of them. It should be possible to use this effect for optical data storage of information. The property of high absorbances of PVA films in the infra-red (IR) and ultra-violet (UV) regions give possibilities to use the described effect for non-developed high resolution photography or typing purposes. A properly colimated light beam (UV or IR) can easily heat a sample to the necessary temperature (the sample can also be preheated to 80 °C). Texts or pictures on film may be obtained by using direct contact of hot elements (for example pins) with film. Read out of stored information, texts, or pictures can be achieved by absorption (transmission) and/or fluorescence measurements.

Acknowledgement

We thank P. S. Eis for HPLC analysis of DPO. This work was performed partially at the Center for Fluorescence Spectroscopy, NSF DIR-8710401.

[1] I. B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Second edition, Academic Press, New York and London 1971.
[2] For review, see: G. R. Fleming, Chemical Applications of Ultrafast Spectroscopy; Oxford University Press, New York 1986.
[3] G. Orlandi and W. Siebrand, Chem. Phys. Lett. **30,** 352 (1975).
[4] B. I. Green, R. M. Hochstrasser, and R. B. Weisman, Chem. Phys. Lett. **62,** 47 (1979).
[5] F. E. Doany, B. I. Green, Y. Liang, D. K. Neus, and R. M. Hochstrasser, in: Picosecond Phenomena, 2nd ed., Springer, New York 1980.
[6] M. Sumitani and K. Yoshihara, Bull. Chem. Soc. Japan **55,** 85 (1982).
[7] S. H. Courtney and G. R. Fleming, J. Chem. Phys. **83,** 215 (1985).
[8] D. J. S. Birch and R. E. Imhof, Chem. Phys. Lett. **88,** 43 (1982).
[9] J. B. Birks and D. J. S. Birch, Chem. Phys. Lett. **31,** 608 (1975).
[10] T. C. Felder, K. J. Choi, and M. R. Topp, Chem. Phys. **64,** 175 (1982).
[11] L. A. Chen, R. E. Dale, S. Roth, and L. Brand, J. Biol. Chem. **252,** 2163 (1977).
[12] J. R. Lakowicz and F. G. Prendergast, Science **200,** 1399 (1978).
[13] G. S. Beddar and M. A. West (eds.), Fluorescence Probes, Academic Press, London 1981.
[14] L.B. A. Johanson, Chem. Phys. Lett. **118,** 516 (1985).
[15] A. Kawski and Z. Gryczyński, Naturforsch. **41a,** 1195 (1986); **42a,** 617 (1987); **42a,** 1396 (1987).
[16] Y. Tanizaki, Bull. Chem. Soc. Japan **32,** 75 (1959).
[17] Y. Matsuoka and B. Norden, J. Phys. Chem. **86,** 1378 (1982).
[18] A. Kawski, Developments in Polarized Fluorescence Spectroscopy of Ordered Systems, in: Optical Spectroscopy in Chemistry and Biology-Progress and Trends (D. Fassler, ed.), VEB Deutscher Verlag der Wissenschaften, Berlin 1989.