Isomerization of Diphenyl Polyenes. Part VIII. Absorption and Fluorescence Properties of 1-Phenyl-4-diphenylthiophosphinyl Butadiene in Poly(vinyl alcohol) Film

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The effect of temperature (from 296 to 423 K) upon the absorption and fluorescence of 1-phenyl-4-diphenylthiophosphinyl butadiene (PDPB) and of the direct irradiation on the absorbance were investigated in poly(vinyl alcohol) film. It was found that for PDPB in PVA film the transition from cis to trans configuration is only possible as a result of thermal isomerization due to the softening of PVA polymer, whereas photoisomerization results in both cis-to-trans and trans-to-cis transitions. Similar as with 1,4-diphenyl-1,3-butadiene in PVA, the luminescence is due to two, trans-trans and cis-trans, PDPB conformers.

1. Introduction

In previous papers [1–8] the effect of temperature and light on the photophysical and photochemical properties of linear polyenes, Ph–$(CH=CH)_n$–Ph, $n = 2$, 3, 4, in poly(vinyl alcohol) (PVA) films were investigated. The behaviour of the polyene with $n = 2$, i.e. 1,4-diphenyl-1,3-butadiene (DPB), differs from that of the polyenes with $n = 3$, 4. In the latter cases, i.e. for 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatriene (DPO) in PVA, an unusual behaviour of absorbance and quantum yield was observed above the glass transition temperature (T_g = 358 K), which enabled the conclusion that above this temperature thermal cis-trans isomerization occurs in the ground state [1, 3, 5, 6]. In addition, based on quantum yield and mean fluorescence lifetime decay measurements it was found that for the three polyenes fluorescence emission is due to trans-trans and cis-trans conformers.

As demonstrated by investigating the effect of daylight and direct irradiation in the short- and longwave absorption band, DPB is the most photosensitive molecule among the three molecules examined. DPB in PVA has the greatest mobility, and following photoisomerization it undergoes cis-to-trans or trans-to-cis transitions. In the long DPO molecule such a transition upon photoisomerization under the same conditions is hindered.

In this part of our series of papers we report the results of investigating the effect of temperature and direct light irradiation upon the behaviour of absorbance and fluorescence of 1-phenyl-4-diphenylthiophosphinyl butadiene (PDPB) in PVA film. Compared to DPB, the PDPB molecule is more extended since in position 4 the single phenyl group is replaced with a much larger substituent (see Figure 1).

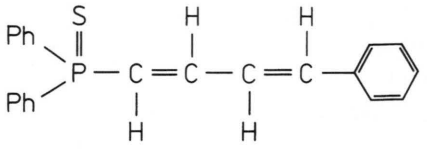

Fig. 1. Structure of the 1-phenyl-4-diphenylthiophosphinyl-trans, trans-butadiene (PDPB).

2. Experimental

The method of preparing PDPB samples in PVA and the measurements of absorption spectra at different temperatures were reported in [1]. PDPB was from Dr. D. Gloyna (Humboldt-Universität zu Berlin), poly(vinyl alcohol) (PVA, 100% hydrolyzed, molecular weight 106,000–110,000) was from Aldrich Chemie.

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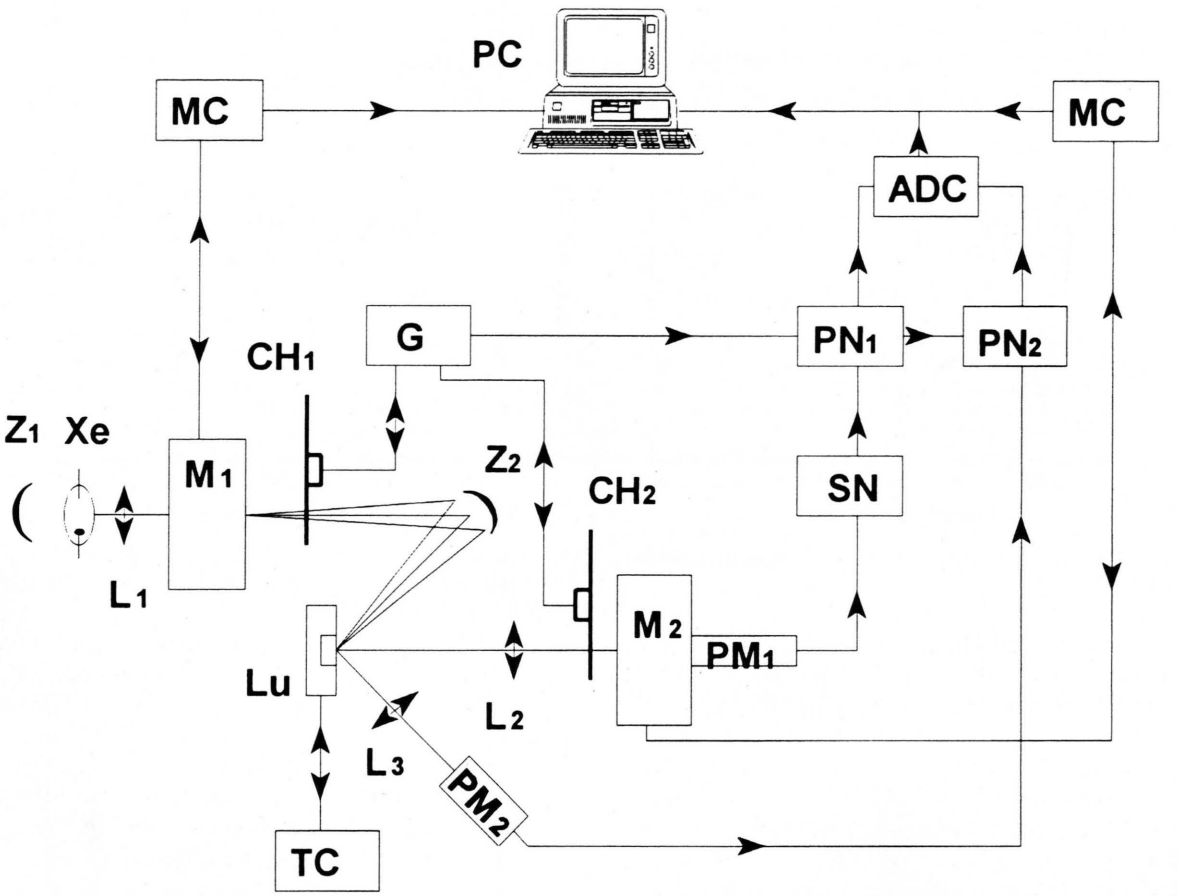


Fig. 2. Schematic diagram of the apparatus for fluorescence and phosphorescence spectra measurements: Xe: 250 W Osram Xenon lamp, L_1, L_2, L_3: lenses, Z_1, Z_2: mirrors, M_1, M_2: monochromators, SPM-2 Carl Zeiss Jena, CH_1, CH_2: choppers, Lu: luminophore, PM_1, PM_2: photomultipliers, FEU-79, G: generator, SN: selective nanovoltmeter, PN_1, PN_2: phase-sensitive nanovoltmeters, ADC: analog to digital converter, TC: temperature controller, MC: monochromators controllers, PC: personal computer.

Since the fluorescence of PDPB is very weak in both liquid solution and PVA film (very low fluorescence quantum yield), a highly sensitive modulation method was employed to measure the emission spectra. Figure 2 shows an improved version of our apparatus for measuring fluorescence and phosphorescence spectra [9]. The modification consists in the employment of choppers with variable rotation frequency, adjusted in the range 100–500 Hz, and in controlling the experimental and data collecting by the use of a computer with an IES 625 interface.

3. Results and Discussion

3.1. Water Induced Changes in PDPB Absorption in Methanol-Water Solutions

The longwave absorption band of PDPB in methanol (Fig. 3) is continuous with a maximum at 310 nm. Upon increasing the water content in a methanol PDPB solution, a distinct red-shift of the absorption band is observed, which results from intermolecular electrostatic interactions [10]. This bathochromic band shift may be due to a strong electronic interaction between the phenyl substituent in position 1 of

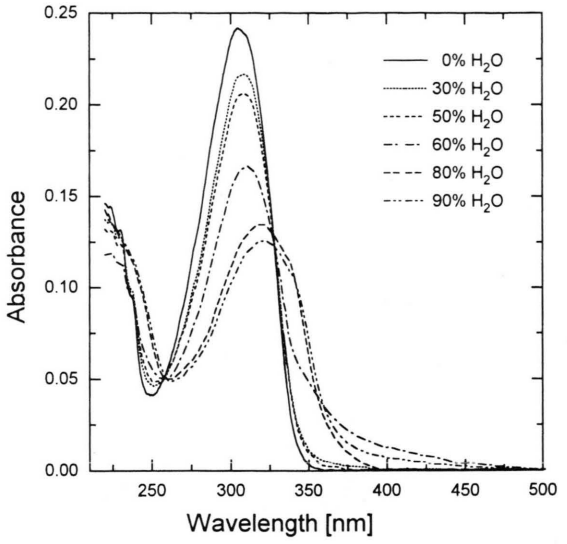


Fig. 3. Absorption spectra of PDPB in methanol-water mixtures.

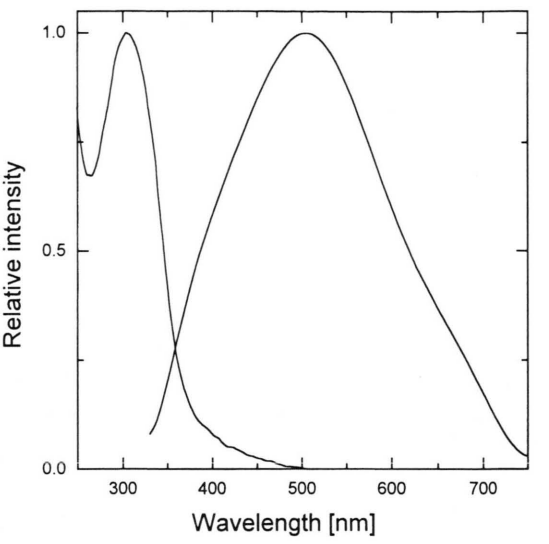


Fig. 5. Absorption and fluorescence spectra of PDPB in PVA film, measured at 296 K after previous heating to 423 K and cooling to room temperature.

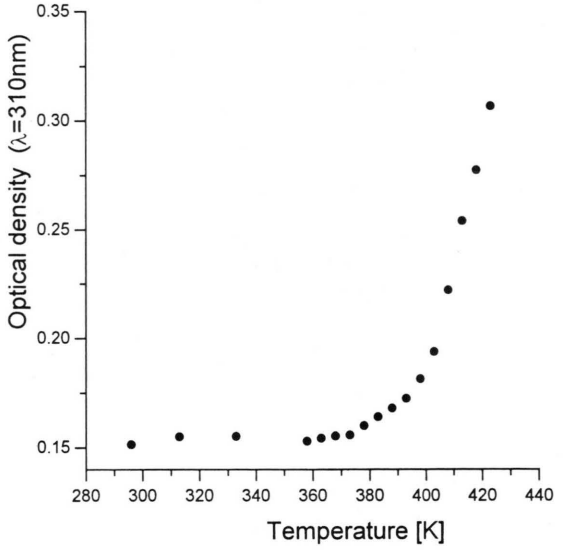


Fig. 4. Dependence of the long wavelength absorption maximum ($\lambda = 310$ nm) of PDPB in PVA film upon the temperature.

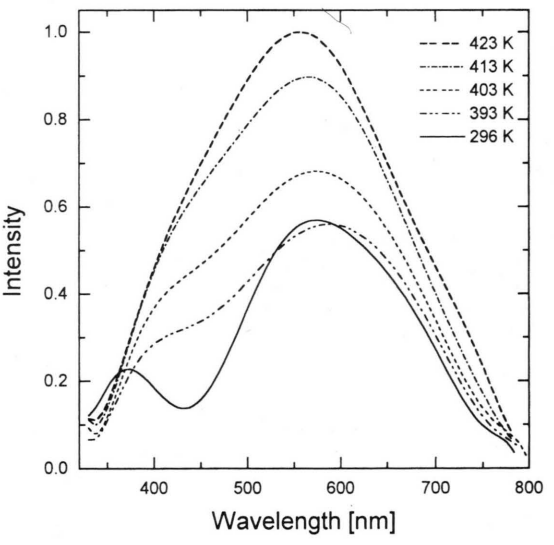


Fig. 6. Fluorescence spectra (arbitrary units) of PDPB in PVA film at different temperatures, excited ($\lambda_{exc} = 310$ nm) under the same conditions.

the styrene skeleton with the steric group in position 4 [11]. The isosbestic point located at the shortwave side of the band ($\lambda = 258.7$ nm) evidences the occurrence of trans-cis isomerization.

In mixtures with much higher water content, PDPB molecules exist in both trans and cis forms.

3.2. Temperature Induced Changes in PDPB Absorption and Fluorescence Intensity in PVA Films

The behaviour of the absorbance of PDPB measured in PVA film at different temperatures from 296 to 423 K is similar as that of DPB. Up to 358 K the

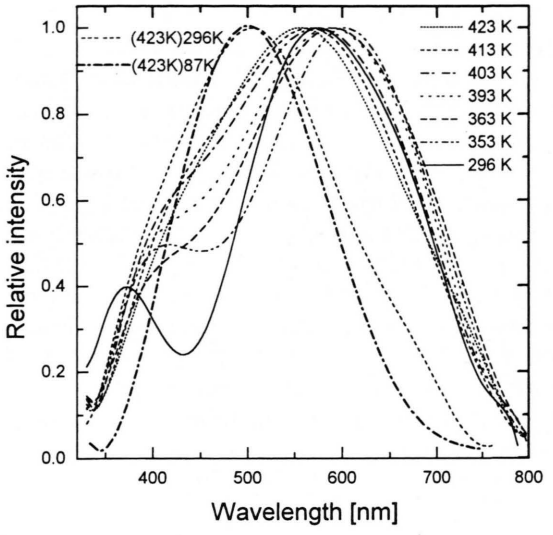


Fig. 7. Normalized fluorescence spectra of PDPB in PVA film at different temperatures for $\lambda_{exc} = 310$ nm. (423 K) 296 K and (423 K) 87 K denotes that the sample was measured at 296 K and 77 K after heating to 423 K.

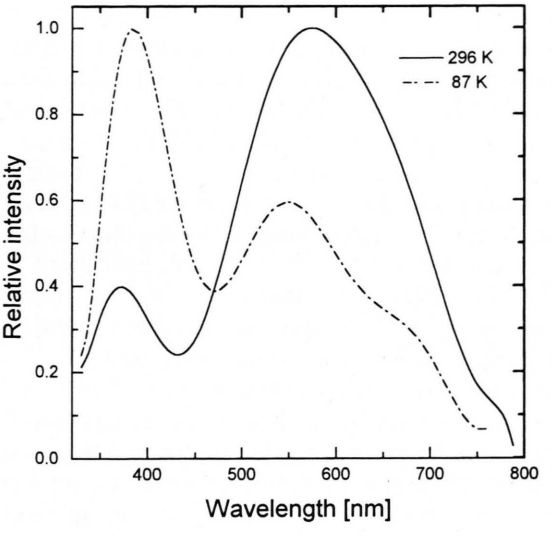
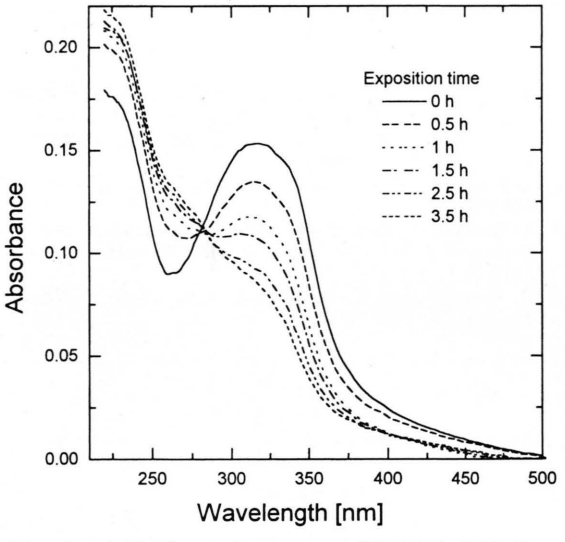
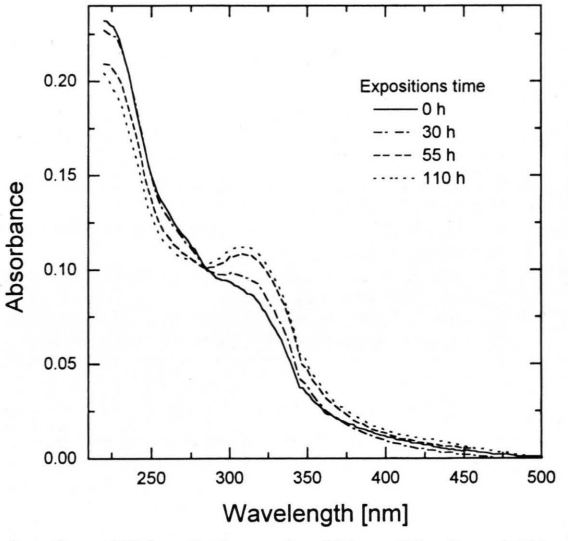


Fig. 8. Comparison of fluorescence spectra of non-heated sample of PDPB in PVA film at 296 K and 87 K.





Figs. 9 and 10. Absorption spectra of PDPB in PVA film exposed to direct UV irradiation at $\lambda = 334$ nm (Fig. 9) and 234 nm (Figure 10).

absorbance does not change. It is only above the glass transition temperature ($T_g = 358$ K) that a two-fold increase in optical density of the longwave band occurs (250–350 nm, Figure 4). This rise is five-fold in the case of DPB. Figure 5 shows absorption and fluorescence spectra of PDPB in PVA film, measured at 296 K following heating to 423 K and cooling to room temperature. In this case the fluorescence band is much broader than the absorption band. Figure 6 shows the effect of temperature on the fluorescence intensity in the range from 296 to 423 K for $\lambda_{exc} =$ 310 nm under the same conditions (geometry of the

experiment, excitation light intensity etc.). At 296 K two distinct emission bands are observed. Upon increasing the temperature to 423 K these two emission bands merge. After heating the sample to 423 K and cooling it to 296 K the band shifts to the shortwave side with a simultaneous narrowing (the fluorescence band half-width, $\Delta\lambda_{1/2}$, decreases from 273.3 to 221.2 nm), see Fig. 7. The figure shows also the fluorescence band recorded at 87 K for the sample pre-heated to 423 K. It is clearly seen that the fluorescence maximum overlaps with the spectrum measured at 296 K; the band, however, was further narrowed ($\Delta\lambda_{1/2}$ = 182.9 nm). No dependence of the intensity distribution in the fluorescence band upon excitation light wavelength was observed for this sample at 296 K and 87 K, which evidences the occurrence of only one trans-trans conformer. For a non-heated sample two fluorescence bands are observed (Fig. 7), which manifests the presence of two emission centres, i.e. trans-trans and cis-trans conformers. The reduction of temperature from 296 to 87 K results in a marked rise of the fluorescence intensity of the shortwave band corresponding to the cis-trans conformer (Fig. 8).

These investigations confirm that similar to DPB, DPH and DPO, thermal cis-trans isomerization in the ground state occurs also for PDPB in PVA film above the glass transition temperature (T_g = 358 K). The behaviour of the longwave absorption band at 296 K of a fresh PDPB sample in PVA film was also investigated upon irradiation with light of λ_{exc} = 334 nm and λ_{exc} = 234 nm. After 3.5 h, the longwave absorption band intensity distinctly decreased while that of the short wave band increased (Fig. 9). A reverse cis-trans process occurs only after longer direct irradiation with λ_{exc} = 234 nm (Fig. 10). As a result of photoisomerization, PDPB, similar to DPB in PVA film, undergoes transitions from trans to cis configuration and reversely.

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[1] A. Kawski, Z. Gryczyński, I. Gryczyński, W. Wiczk, and H. Malak, Z. Naturforsch. **46a,** 621 (1991).
[2] A. Kawski, A. Kubicki, B. Kukliński, I. Gryczyński, and Z. Gryczyński, Z. Naturforsch. **47a,** 1017 (1992).
[3] A. Kawski, B. Kukliński, A. Kubicki, and I. Gryczyński, Z. Naturforsch. **47a,** 1204 (1992).
[4] A. Kawski, B. Kukliński, A. Kubicki, and G. Piszczek, Z. Naturforsch. **48a,** 759 (1993).
[5] A. Kawski, A. Kubicki, B. Kukliński, and G. Piszczek, Z. Naturforsch. **48a,** 861 (1993).
[6] A. Kawski, A. Kubicki, B. Kukliński, and I. Gryczyński, J. Photochem. Photobiol. A: Chem. **71,** 161 (1993).
[7] A. Kawski, A. Kubicki, B. Kukliński, and G. Piszczek, Z. Naturforsch. **48a,** 947 (1993).
[8] A. Kawski, B. Kukliński, and A. Kubicki, Z. Naturforsch. **48a,** 1177 (1993).
[9] A. Kawski and K. Nowaczyk, Acta Phys. Polon **A** 78, 379 (1990).
[10] A. Kawski, in: Progress in Photochemistry and Photophysics, Vol. V (J. F. Rabek, ed.), CRC Press Boca Raton, 1992, p. 1–47.
[11] D. Gloyna and K.-G. Berndt, Acta Phys. et Chem. (Szeged) **26,** 155 (1980).