# A METHOD FOR MEASURING PHOTOPYROELECTRIC SPECTRA OF DYES IN A POLYMER PYROELECTRIC MATRIX

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A method for measuring pyroelectric spectra of a dye admixed to a pyroelectric matrix has been described. Spectra obtained in the visible range by photopyroelectric and photoacoustic methods have been compared for rhodamine B in the pyroelectric PVDF matrix.

## 1. Introduction

In recent years many steady-state methods for measuring radiationless transitions in dyes embedded in polymer matrices have been developed [1]. The temperature changes occurring in samples due to absorption of light with modulated intensity can, among others things, be detected by the investigation of the photoacoustic effect or by using a pyroelectric transducer attached to the sample. Another method of measuring the radiationless transitions mentioned above has been described hereunder for rhodamine B introduced into the PVDF matrix. The investigations of the spectral characteristics of radiationless transitions were carried out using the technique outlined in the present paper and the photoacoustic method.

#### 2. Measurement method

In our previous report [2] a model of a pyroelectric transducer with a volumetrically admixed dye was presented. The model considered therein consists of a luminophore containing a pyroelectric layer with thickness of l and of light-transmitting electrodes adjoining both its sides. It has been assumed that light can only be absorbed by a dye with a nonzero coefficient of radiationless transitions, and that the matrix is transparent for light in the spectral region where the dye absorbs. The transfer of energy absorbed by the dye to the matrix results in the heating of the latter. Hence an electric potential

difference is created between the electrodes due to the pyroelectric properties of the matrix.

Basing on this method, the measurements of the pyroelectric response were carried out for the pyroelectric PVDF matrix with rhodamine B. A dyed pyrofilm was placed between the electrodes which transmitted light in the optical range and illuminated with monochromatic light of modulated sinusoidal intensity.

## 3. Samples

The samples of films with rhodamine B were prepared using the method of casting in the Research Branch of the Nitrogen Works in Tarnów. The films, with a rhodamine B concentration of  $10^{-4}$ mol/kg, were subjected to mechanical and electrical treatment under the following conditions: stretching at  $80^{\circ}$ C, hardening at  $120^{\circ}$ C, and polarization in the electric field with intensity  $\geq 500$  kV/cm at  $80^{\circ}$ C.

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Photopyroelectric spectra were examined by means of a photoacoustic measuring system built in the Institute of Experimental Physics by A. SIKORSKA and J. SZURKOWSKI, with a suitably changed measuring cell. The transverse cross-section of the cell used in photopyroelectric measurements is shown schematically in Fig. 1. The dyed PVDF pyrofilm was placed between glass plates coated with optically transparent electrodes. The measuring cell was insulated electrically and acoustically from the environment by placing it in an earthed casing with a window for the illuminating beam. The sample investigated was illuminated with a rectangular light beam with dimensions 0.5 cm × 1.0 cm. The block diagram of the system used to measure photopyroelectric spectra is shown in Fig. 2. Similarly as in photoacoustic measurements, a classical optical system with a continuous light source with intensity modulated electromechanically at a frequency of 8 Hz was employed. An 150 W XHP xenon

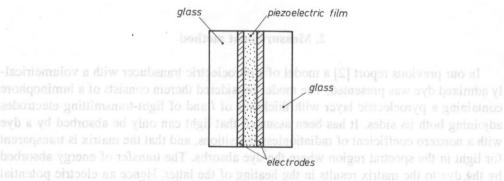


FIG. 1. Construction of the photopyroelectric cell.

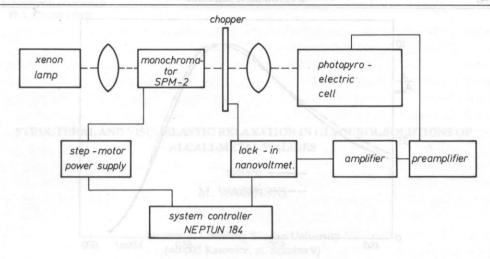


FIG. 2. Block scheme of the experimental set-up.

lamp was used as light source. Following the illumination of the sample with light with selected wavelength and modulated intensity, the obtained pyroelectric signal was fed supplied to a B and K type 2625 transducer, measured by a lock-in nanovoltmeter and, finally recorded on a microcomputer disk in a digital form. The whole measurement was computer-controlled. This enabled the current response of the pyroelectric transducer to be measured automatically as a function of the light wavelength. The photoacoustic signal was received using a B and K condenser microphone.

#### 5. Results and discussion

Photopyroelectric and photoacoustic spectra were measured in the range varying from 400 to 700 nm for the sample films dyed with rhodamine B and treated mechanically and electrically. The electric response obtained as a function of the illumination spectrum from photopyroelectric and photoacoustic measurements were corrected by dividing the values obtained from measurements by the spectral lamp characteristics recorded upon the light transmission through the optical system. The examples of photopyroelectric and photoacoustic spectra of rhodamine B in the pyroelectric PVDF matrix, corrected and normalized to the maximum value, are shown in Fig. 3. The comparison of both spectra implies that similar spectral characteristics are obtained by the two methods employed. Slight differences between photopyroelectric and photoacoustic spectra might be attributed to the volumetric effects, e.g., inhomogeneous distribution of the pyroelectric coefficient throughout the film thickness. Such pyroelectric coefficient distribution has already been observed for PVDF film [3].

Bearing in mind the above results and considerations, the conclusion can be drawn that for dyes embedded in pyropolymer films the photopyroelectric method can, on the

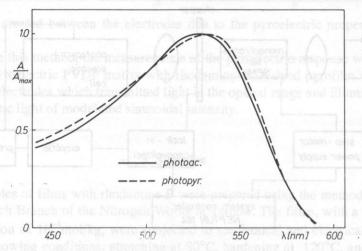


FIG. 3. Photoacoustic and photopyroelectric spectra of rhodamine B in the PVDF pyrofilm.

one hand, be employed, similarly as the photoacoustic method, for the investigation of spectroscopic properties of dyes, and, on the other hand, for the investigation of thermal and electrical properties of the matrix itself.

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#### References

- H. VARGAS, L.C.M. MIRANDA, Photoacoustic and related photothermal techniques, Physics Reports 161, 2 (1988).
  - [2] S. ŁĘTOWSKI, A. ŚLIWIŃSKI, C. LEWA, Analiza odpowiedzi prądowej przetwornika piroelektrycznego z PVDF domieszkowanego barwnikiem, Proc. Open Sem. Acoust. 1988 p. 112–117.
  - [3] R.L. PETERSON, G.W. DAY, P.M. GRUZENSKY, R.J. PHELAN, Analysis of response of pyroelectric optical detector, J. Appl. Phys. 45, 8, p. 3296–3303 (1974).