

# Fluorescence Anisotropy and Decay Times of Pyrene and Pyrene Excimer in Cellulose Acetate Films at Various Temperatures\*

A. Kowski, I. Weyna, Z. Kojro, and A. Kubicki

Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland

Z. Naturforsch. **38a**, 1103–1106 (1983); received May 16, 1983

Investigations of fluorescence anisotropy and mean lifetime of pyrene and pyrene excimer in cellulose acetate films have shown that this environment can not be considered as a strictly rigid solution, being rather a medium consisting of empty spaces where small pyrene molecules have considerable freedom. It has been concluded that the mechanism of the excimer formation is the same as that in liquid solvents.

## 1. Introduction

The origin of the excimer fluorescence of pyrene in rigid amorphous polymer media is still an actual problem. As is known, in liquid solutions excimers are formed during the excited state of monomers, the process depending on the diffusion rates of the excited and unexcited monomers and their concentration. The concentration dependence is consistent with the hyperbolic Stern-Volmer formula [1]. The diffusion rate is inversely proportional to the solvent viscosity  $\eta$ . The relation between the monomer and excimer fluorescence quantum yields of pyrene and the solvent viscosity has been investigated by Förster *et al.* [2–4].

Excimer fluorescence of pyrene at high concentrations was also observed in doped aromatic crystals [5, 6]. For the fluorescence properties of pure pyrene monocrystals of the review articles of Förster [7] and Birks [8]. Mataga *et al.* [9] observed excimer fluorescence of pyrene in a cyclohexane matrix at 77 K and attributed it to the ground state dimer of pyrene. Oster *et al.* [10] were the first to observe excimer fluorescence in polymer solutions. During the sixties, attempts to explain the occurrence of the excimer fluorescence of pyrene in polystyrene were taken up at the Förster laboratory [11, 12]. Investigations of the excimer fluorescence of pyrene in polystyrene were also reported in Refs. [13, 14].

In the present paper we investigate the fluorescence anisotropy and decay time of pyrene and pyrene excimer in cellulose acetate films within a broad temperature range (93–303 K). We also explain the origin of the excimer fluorescence in polymer solutions.

## 2. Experimental results

Figures 1 and 2 show the fluorescence spectra of pyrene in cellulose acetate films at two concentrations ( $\sim 10^{-2}$  M and  $7 \times 10^{-1}$  M) and at different temperatures. At  $7 \times 10^{-1}$  M, the strong excimer band can be observed on the long wavelength side. Figure 3 shows the pyrene monomer fluorescence (360–420 nm) anisotropy,  $r$ , and life time,  $\tau$ , in the temperature range  $93 \text{ K} \leq T \leq 313 \text{ K}$  in cellulose acetate films.

We also have tried to find the excimer fluorescence anisotropy of pyrene in cellulose acetate films. For high concentrations, at which distinct excimer fluorescence occurs, no fluorescence anisotropy could be observed. At  $7 \times 10^{-1}$  M, the measured value  $r \approx 0.003$  is within the experimental error. Figure 4 shows that the mean lifetime  $\tau$  of the excimer fluorescence grows, similarly as the monomer fluorescence, with decreasing temperature.

The monomer fluorescence anisotropy was measured also as a function of concentration at different temperatures. To minimize reabsorption effects done  $r$  was measured on thin films ( $\sim 1 \mu\text{m}$ ). The intensities being too small at lower concentrations, Fig. 5 shows the results only for higher concentrations.

\* Carried out under Research Project MR.I.5.

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

0340-4811 / 83 / 1000-1103 \$ 01.3 0/0. — Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

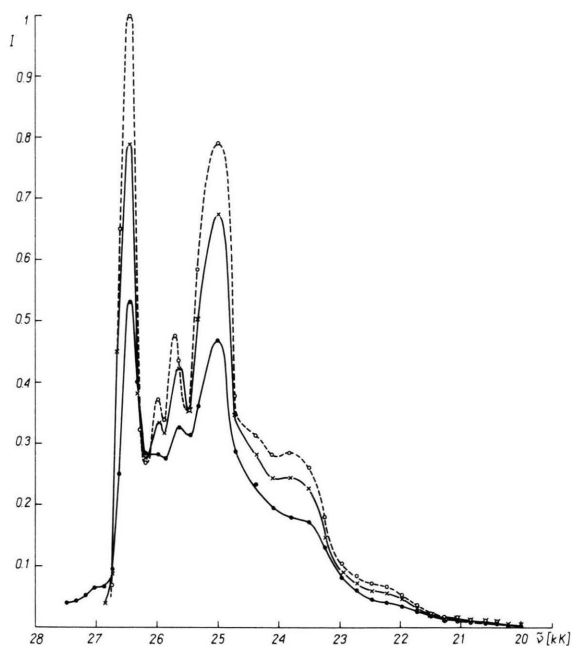


Fig. 1

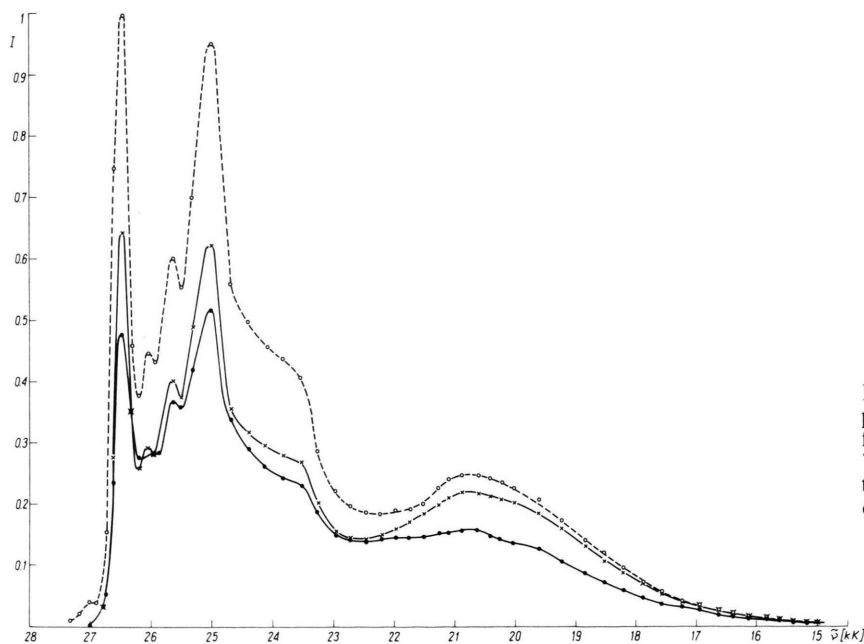


Fig. 2

for a rigid solution  $\frac{r_0}{r} = 1 + \frac{kT\tau}{v\eta}$  should become unity for  $\eta \rightarrow \infty$ . The experimental limiting value  $r'_0(T \rightarrow 0)$  differs from  $r_0$  according to the relation  $r'_0 = r_0(1 - \frac{3}{2}u)^2$ , where

$$u = \langle \sin^2 \gamma \rangle \approx \frac{\hbar}{I\omega} + \frac{2kT}{I\omega^2};$$

$u$  is the mean square angle deviation of the excited oscillators by torsional vibrations [15, 17].

If,  $r$  for the cellulose acetate films were given by the Perrin and Jablonski relations with  $\eta \rightarrow \infty$  in the case of low concentrations, one would measure  $r'_0$ , which should decrease with growing temperature. The observed  $r$  values (Fig. 3) show an opposite temperature dependence and the absolute values deviate very strongly from the limiting value  $r'_0$ .

We believe that the small  $r$  values can be interpreted as a rotation effect of the luminescence

Figs. 1–2. Fluorescence spectra of pyrene in cellulose acetate films for  $c = 10^{-2}$  M (Fig. 1) and  $c = 7 \times 10^{-1}$  M (Fig. 2) at different temperatures: ○ – 93 K, × – 173 K, ● – 303 K.

### 3. Discussion

The observed low value of  $r$  for pyrene monomer molecules and its temperature dependence are not consistent with the theoretical predictions of Jablonski [15]. According to the Perrin [16] theory,

molecules sitting on special free places [18]. The rotation will be hindered not by the macroscopical but by a microscopical viscosity. The small increase – in contrast to the expected decrease – of  $r$  with temperature may be caused by the decrease of  $\tau$ . Such an increase of  $r$  with  $T$  has been observed in a

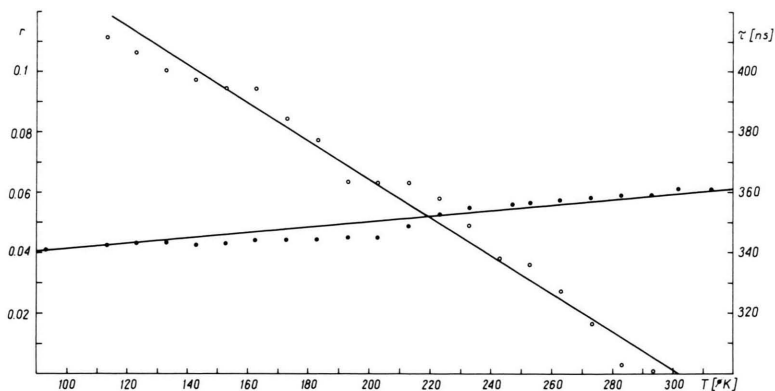


Fig. 3. Plot of  $r$  (●) and  $\tau$  (○) of pyrene in cellulose acetate film for  $c = 10^{-2}$  M vs. temperature.

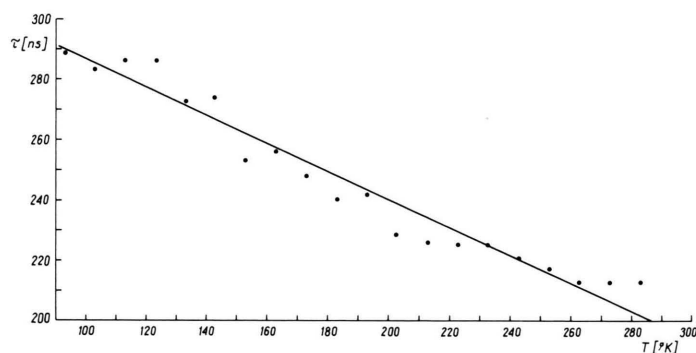


Fig. 4. Plot of  $\tau$  (●) of pyrene in cellulose acetate film for  $c = 7 \times 10^{-1}$  M vs. temperature.

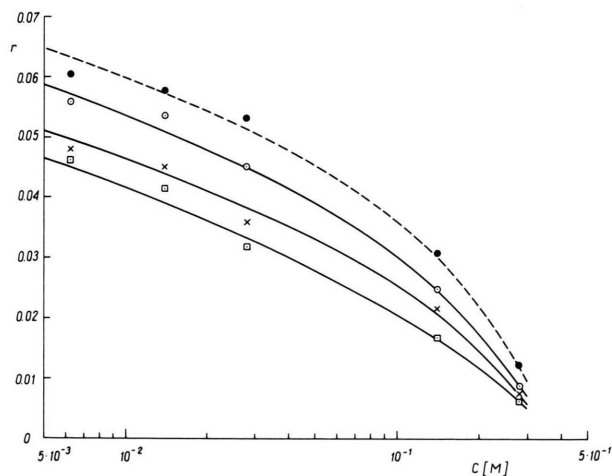


Fig. 5. Fluorescence anisotropy  $r$  of pyrene in cellulose acetate film versus concentration  $c$  for different temperatures (● — 293 K, ○ — 223 K, × — 173 K, □ — 93 K).

previous paper [19] (the denotations in [19] Fig. 4 are correct; the legend is faulty). At higher concentrations  $r$  will be reduced, as seen in Fig. 5, by energy migration.

The excimer fluorescence emission of pyrene is not polarized and the mechanism of the excimer

formation is the same as in liquid solvents. But in this case, both molecules, the excited and unexcited one are neighbored and unbound in the ground state. If, according to Mataga *et al.* [9], a ground state dimer of pyrene with fluorescence ability had existed in our case, we would have observed at high

concentrations an anisotropic fluorescence comparable to the monomer fluorescence anisotropy. Our conclusion – excimer and not dimer emission – is in accordance with Loewenthal *et al.* [20].

The author (A.K.) wishes to thank Prof. Dr. A. Schmillen for his valuable discussion and remarks during a stay at the University in Giessen and the DAAD for a grant.

- [1] O. Stern and M. Volmer, *Phys. Z.* **20**, 183 (1919).
- [2] Th. Förster and K. Kasper, *Z. Phys. Chem. NF* **1**, 275 (1954).
- [3] Th. Förster and K. Kasper, *Z. Elektrochem.* **59**, 976 (1955).
- [4] E. Döller and Th. Förster, *Z. Phys. Chem. NF* **34**, 132 (1962).
- [5] A. Schmillen, *Z. Naturforsch.* **16a**, 5 (1961).
- [6] A. Schmillen, *J. Phys. Chem.* **69**, 751 (1965).
- [7] Th. Förster, *Angew. Chem.* **81**, 364 (1969).
- [8] J. B. Birks, *Reports on Progress in Physics* **38**, 903 (1975).
- [9] N. Mataga, Y. Torihashi, and Y. Ota, *Chem. Phys. Lett.* **1**, 385 (1967).
- [10] G. Oster, N. Geacintov, and A. U. Khan, *Nature* **196**, 1089 (1962).
- [11] K. A. Bauer, Dissertation T. H. Stuttgart (1964).
- [12] G. Leuschner, Dissertation Univ. (T. H.) Stuttgart (1967).
- [13] P. Avis and G. Porter, *Faraday Trans. II*, **70**, 1057 (1974).
- [14] B. Polacka and I. Weyna, *Bull. Acad. Polon. Sci. Ser. Sci. Math., Astro. et Phys.* **26**, 935 (1978).
- [15] A. Jabłoński, *Acta Phys. Polon.* **10**, 193 (1950).
- [16] F. Perrin, *Ann. Phys. Paris* **12**, 169 (1929).
- [17] A. Jabłoński, *Z. Phys.* **96**, 236 (1935).
- [18] A. Kowski, M. Stoń, and I. Janič, *Z. Naturforsch.* **38a**, 322 (1983).
- [19] J. Kamiński, A. Kowski, and A. Schmillen, *Z. Naturforsch.* **32a**, 1335 (1977).
- [20] E. Loewenthal, Y. Tomkiewicz, and A. Weinreb, *Chem. Phys. Lett.* **2**, 29 (1968).