



Universidad
Carlos III de Madrid



This is a postprint version of the following published document:

González-Benito, J., Cabanelos, J. C., Aznar, A., Vigil, M. R., Bravo, J., Serrano, B., & Baselga, J. (1997).
Photophysics of a pyrene probe grafted onto silanized glass fiber surfaces. *Journal of Luminescence*, 72-74, pp. 451-453.

DOI: [10.1016/S0022-2313\(97\)00074-4](https://doi.org/10.1016/S0022-2313(97)00074-4)

© Elsevier, 1997



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.

Photophysics of a pyrene probe grafted onto silanized glass fiber surfaces

J. Gonzalez-Benito, J.C. Cabanelas, A. Aznar, M.R. Vigil, J. Bravo, B. Serrano, J. Baselga*

Departamento Ingeniería, U. Carlos III de Madrid, C/Butarque 15, 28 911 Leganes, Spain

ABSTRACT

Glass fibers have been silanized with γ -aminopropyltriethoxysilane. 1-pyrenesulphonyl chloride (PSC) has been grafted onto the fibers via adduct formation with the amine functionality. Absorption spectra from SPC stock solutions shows aggregation. Emission spectra from the fibers also reveal aggregation of the chromophore at extremely low concentration (10^{-9} mol/g).

KEYWORDS

Pyrene sulphonyl chloride; Glass fibers; Dimer emission; Fluorescent probes

1. Introduction

The knowledge of the structure of coupling regions around reinforcing glass fibers is actually of prime interest in composite material research. Photophysics of fluorescent probes grafted to the glass surfaces appears to be a very important tool for the characterisation of distribution of specific sites, microheterogeneity and solid solvent relaxation in this systems [1]. A great amount of work has been done using silica [2] or pore-controlled glass as substrates [3], and using pyrene as a fluorescent probe either adsorbed [3] or chemically bounded to the surface [2].

The aim of this work is to characterise the fluorescent response of a pyrene probe (pyrene sulfonyl chloride, PSC) grafted onto a glass silanized fibre

surface, and to identify the species which appear to account for the fluorescent behaviour. Although some work has been done on grafted PSC water soluble polymers [4], to our knowledge, there are no studies of the use of this probe on microheterogeneous synthetic systems such as silane coated glass fibers.

2. Experiments

Commercial glass fibres from Vetrotex were used as substrates. Details of the procedures for silanization, and sample conditioning can be found elsewhere [1].

PSC was grafted onto the fibre surface via adduct formation with the amine functionality of APES. Fibres were put in contact with a 10^{-4} M acetonitrile (AcN) PSC solution, for different periods of time to achieve different PSC concentrations, and extracted with dry toluene for 4 h to remove adsorbed probe. UV spectra were recorded with

*Corresponding author. Tel.: 34-1-624.94.67; fax: 34-1-624.94.30; e-mail: jbaselga@ing.uc3m.es.

a Perkin Elmer Lambda 14P with a solids sample accessory. PSC concentrations were in the range 5×10^{-10} - 10^{-9} mol/g. Fluorescent spectra were recorded with a Perkin-Elmer LS-SOB spectrometer.

3. Results and discussion

In Fig. 1, the emission spectra of the fibres for some probe concentrations are presented. At low concentration, the three bands centred at 377, 397 and 420 resemble the emission spectrum of pyrene, in which the bluest band is assigned to the 0-0 transition. At higher concentrations, a broad structureless 'excimer-like' band, centred around 470 nm, neatly appears; it presents several features that allow to assign it to preformed dimers. Firstly, a similar band is observed, but is shifted by 50 nm to the red in fluid aqueous systems [4]. Although a slight blue shift may be expected for excimer emission in solids, such a high displacement is difficult to explain. Secondly, the fluorescent ratio I_{470}/I_{397} changes with excitation wavelength, having its maximum value at 380 nm when excited; this is not a normal behaviour of excimer emission.

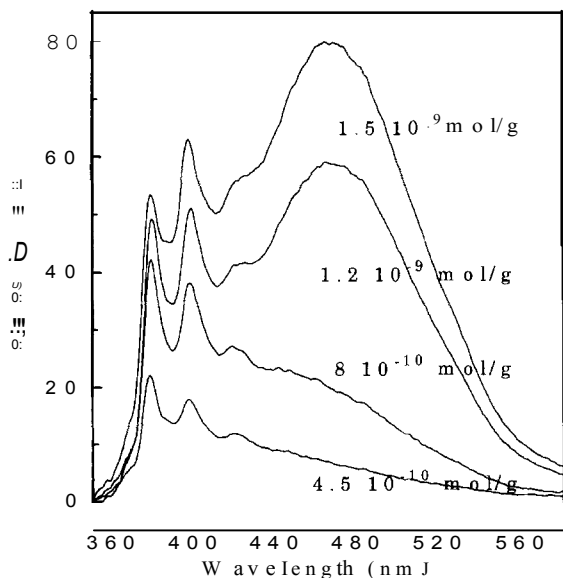


Fig. 1. Emission spectra of grafted PSC at different average surface concentrations ($\lambda_{exc} = 330$ nm).

In Fig. 2, the absorption spectra of PSC AcN solutions of different concentrations are compared with the absorption spectrum of an AcN PSC-propylamine adduct solution and with excitation spectrum of a typical fibre sample. The low concentration spectra of PSC in AcN, resembles the pyrene absorption spectrum with the same vibrational resolution, but it is red-shifted by about 7 nm. When the concentration is raised, the 345 nm band, that may be assigned to the 0-0 transition, decreases and the spectra broadens, and among others, a peak at 357 nm and a new band at 388 nm appear. This concentration effect is proposed to be due to ground-state aggregation. The same effect is observed when a stable adduct with propylamine is formed (see Fig. 2). In the lower part of Fig. 2, the excitation spectra of two fibre samples are presented; their shapes are almost similar, unlike the dissolved adduct spectrum, but a slight red shift of about 2 nm, attributable to an increased density, is found for all the bands.

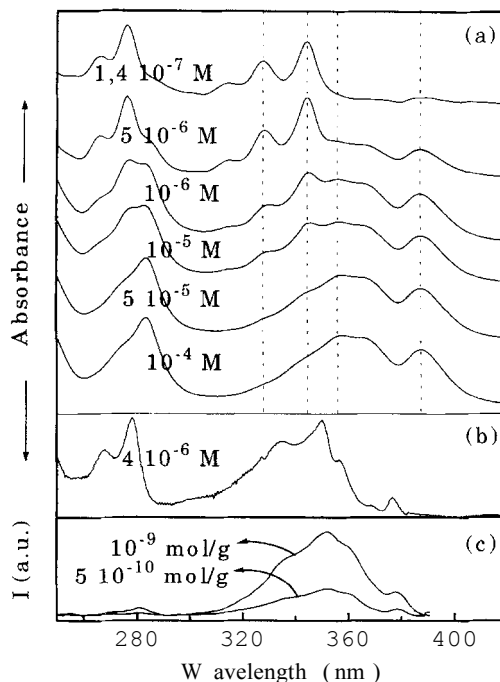


Fig. 2. (a) Absorption spectra of PSC AcN solutions at different concentrations; (b) absorption spectrum of an 4×10^{-6} M PSC-propylamine adduct AcN solution; (c) excitation spectra of PSC grafted glass fibers ($\lambda_{exc} = 397$ nm).

All these observations allow to conclude that the 378 nm band (in excitation spectra) is due to some kind of stable ground-state aggregates between the cromophores. Therefore, the most significant contribution to the excimer-like emission at 470 nm would then be the emission from the preformed excited dimers.

Dimers may be formed at the fibre surface in any of the following three ways: (a) direct grafting of dimers formed previously in the PSC AcN solution, (b) as a consequence of the APES inhomogeneous coating structures over the fibre surface or (c) by grafting two cromophores in the same nitrogen atom.

It must also be considered that the appearance of the red shift of the dimer absorption with respect to the monomer absorption and the blue shift of the dimer emission with respect to the reported excimer emission, may imply a high-energy-excited state, in which pyrene residues are not in a parallel conformation.

Acknowledgements

This work has been supported by projects CAM 247/92 and CICYT MAT93-0823.

References

- [1] J. Gonzalez-Benito, J.C. Cabanelas, A.J. Aznar, M.R. Vigil, J. Bravo and J. Baselga, *J. Appl. Polym. Sci.* 62 (1996) 375.
- [2] C.H. Lochmiiller and T.J. Wenzel, *J. Phys. Chem.* 94 (1990) 4230.
- [3] T. Fujii, A. Ishii, N. Takusagawa, H. Yamashita and M. Anpo, *J. Photochem. Photobiol. Part A* 86 (1995) 219.
- [4] K.D. Branham, G.S. Shafer, C.E. Hoyle and C.L. McCormick, *Macromolecules* 28 (1995) 6175.