Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics 312 (2005) 151–158
Chemical Physics
www.elsevier.com/locate/chemphys

Photophysical characterisation of some dipyrromethene dyes in ethyl acetate and covalently bound to poly(methyl methacrylate)

T. Susdorf [a], M. Álvarez [a,1], W. Holzer [a], A. Penzkofer [a,*], F. Amat-Guerri [b], M. Liras [b], A. Costela [c], I. García-Moreno [c], R. Sastre [d]

[a] *Institut II – Experimentelle und Angewandte Physik, Universität Regensburg, Universitätsstrasse 31, D93053 Regensburg, Germany*
[b] *Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*
[c] *Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain*
[d] *Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

Received 27 September 2004; accepted 27 November 2004
Available online 16 December 2004

Abstract

Analogues of the dipyrromethene-BF$_2$ dye PM567 modified at the 8-position by acetoxymethyl (P1Ac), *s*-acetoxypentyl (P5Ac), and *p*-acetoxymethylphenyl (PAr1Ac) groups are studied in ethyl acetate solution. PM567 modified at the 8-position by methacryloyloxymethyl (P1MA), *s*-methacryloyloxypentyl (P5MA), and *p*-methacryloyloxymethylphenyl (PAr1MA) groups have been copolymerized with methyl methacrylate (MMA), and these solid samples are also studied. The absorption cross-section and stimulated emission cross-section spectra are determined. The fluorescence quantum distributions and fluorescence lifetimes are measured. Saturable absorption measurements with picosecond laser excitation are carried out for excited-state absorption cross-section determination at the excitation wavelength. The photo-degradation of the dyes is studied under cw laser excitation conditions and quantum yields of photo-degradation are extracted.

Keywords: Dipyrromethene dyes; Dipyrromethene dyes covalently bound to PMMA; Absorption spectroscopy; Fluorescence spectroscopy; Saturable absorption; Excited-state absorption; Photo-degradation

1. Introduction

The dipyrromethene dyes are well-established laser dyes with low triplet absorption losses in the laser emission region [1]. They find application in solid-state dye lasers because of their high laser efficiency and high photo-stability [2–4]. Especially the commercially available pyrromethene dye PM567 has been applied in solid-state lasers [5–23]. For improvement of solid-state photo-stability and laser performance PM567 analogues have been synthesized by substitutions at the 8-position with acetoxypolymethylene chains consisting of *n* methylenes ($n = 1, 3, 5, 10, 15$) [4,24,25] (called P*n*Ac), methacryloyloxypolymethylene chains [4,24,25] (called P*n*MA), acetoxypolymethylene-phenyl chains [26] (called PAr*n*Ac, $n = 1, 3$), and methacryloxypolymethylene-phenyl chains [27] (called PAr*n*MA). The P*n*Ac dyes were doped into acrylic and methacrylic copolymers [4,24,26] and poly(methyl methacrylate) (PMMA) [24,25,28] matrices. The P*n*MA dyes were copolymerized with methyl methacrylate (MMA) [4,24,25,28] (called COP(P*n*MA–MMA)). The PAr*n*Ac dyes were investigated in various liquid solvents and in PMMA matrices [27], and the PAr*n*MA where copolymerized with MMA

---

[*] Corresponding author. Tel.: +49 941 943 2107; fax: +49 941 943 2754.
E-mail address: alfons.penzkofer@physik.uni-regensburg.de (A. Penzkofer).

[1] On leave from Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain.

0301-0104/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2004.11.035

(called COP(PAr*n*MA–MMA)) and then characterized [27].

In this paper, some photo-physical characterization (absorption and emission spectra, fluorescence quantum yields and lifetimes, saturable absorption, photo-degradation) of the model dyes P1Ac, P5Ac, and PAr1Ac dissolved in ethyl acetate and of the monomer dyes P1MA, P5MA, and PAr1MA copolymerized with MMA is carried out. The P*n*Ac and PAr*n*Ac dyes have the same chromophores as the copolymers COP(P*n*MA–MMA) and COP(PAr*n*MA–MMA). The behaviour of the chromophores in solution is compared with the behaviour in the copolymers.

2. Experimental

The structural formulae of the dyes and copolymers are shown in Fig. 1. The synthesis of P*n*Ac and COP(P*n*MA–MMA) is described in [24], and the synthesis of PAr1Ac and COP(PAr1MA–MMA) is described in [27]. The dyes were dissolved in ethyl acetate ($CH_3COOCH_2CH_3$). The concentration of the dyes covalently bound to PMMA was adjusted to around 2×10^{-4}, 1×10^{-4}, and 1.5×10^{-6} mol dm^{-3}. The solid PMMA discs with 11–14 mm diameter and 2 mm thickness were polished to optical quality.

The absorption cross-section spectra were determined from transmission measurements with a conventional two-beam spectrophotometer (Beckman type ACTA M IV). The liquid solutions were measured with dye concentrations of around 1×10^{-4} mol dm^{-3} and the cell length was adjusted to the absorption strength. A cell filled with ethyl acetate was used in the reference beam. For the solid polymer discs in regions of low absorption the highly concentrated samples were used and in regions of high absorption the samples of low concentration were used. An un-doped PMMA disc was used in the reference beam. No concentration-dependent absorption effect was observed on the samples.

The fluorescence quantum distribution, $E_F(\lambda)$, and fluorescence quantum yield, ϕ_F, measurements were carried out with a self-assembled fluorimeter in front-face fluorescence collection arrangement [29,30] (excitation wavelength 500 nm). Rhodamine 6G in methanol was used as reference dye for the determination of absolute internal fluorescence quantum yields (its quantum yield is $\phi_F = 0.94$ [31]). The degree of fluorescence polarization, $P_F = (S_{F,\parallel} - S_{F,\perp})/(S_{F,\parallel} + S_{F,\perp})$ was determined

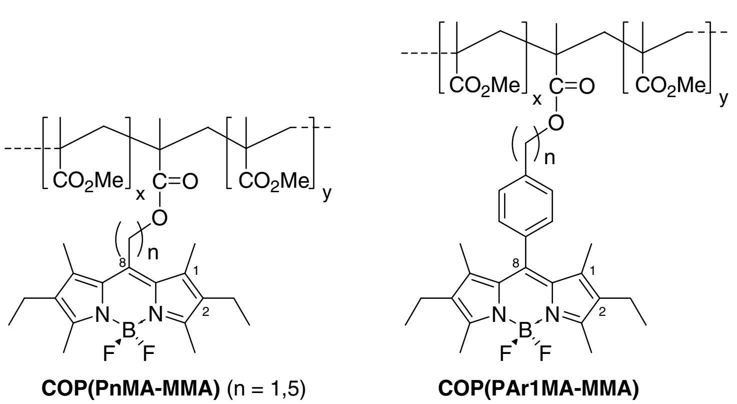

Fig. 1. Structural formulae of P1Ac (molar mass $M = 376.25$ g mol^{-1}), P5Ac ($M = 432.35$ g mol^{-1}), PAr1Ac ($M = 452.34$ g mol^{-1}), COP(P1MA–MMA), COP(P5MA–MMA), and COP(PAr1MA–MMA). The IUPAC names of the dyes are as follows. For P1Ac: 8-acetoxymethyl-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a, 4a-diaza-*s*-indacene; P5Ac:8-(5′-acetoxypentyl)-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a, 4a-diaza-*s*-indacene; PAr1Ac: 8-(*p*-acetoxymethylphenyl)-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene; P1MA: 2, 6-diethyl-4,4-difluoro-8-methacryloyloxymethyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene; P5MA: 2,6-diethyl-4,4-difluoro-8-(5′-methacryloyloxypentyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene; PArlMA: 2,6-diethyl-4,4-difluoro-8-(*p*-methacryloyloxymethylphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene.