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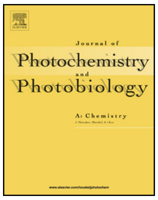

The interactions of probes based on substituted pyrene derivatives in polymer matrices; spectral study

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ABSTRACT

Two substituted pyrene derivatives with cholesterol ((3β)-cholest-5-en-3-ol) moiety as esters were synthetized. The spectral properties of the mono-substituted derivatives of pyrene as esters with different linkages to cholesterol via carboxy unit (**PyCACh1**) and methylene carboxy unit (**PyMECh2**) are compared with the mono-substituted pyrene derivatives and the parent pyrene in toluene at low concentration and doped in glassy polymer matrices of polystyrene (PS), poly(methyl methacrylate) (PMMA) and polyvinylchloride (PVC) in the concentration range of 0.002–0.06 mol kg^{-1}. Fluorescence spectroscopy of the pyrene derivatives in polymer matrices reveals changes in the shape of the fluorescence spectra with increasing concentration. Two limiting cases are observed: (1) a medium or large red shift of the entire fluorescence spectrum or (2) the formation of an emission band in the excimer emission region (approx. 500 nm). These changes are less pronounced in the pyrene-cholesterol esters in the PS matrix due to higher compatibility than in PMMA and PVC matrices. Exploitation of these emissions to estimate the interactions of the components in the polymer matrix is discussed.

1. Introduction

Probes based on fluorescence are widely used in different applications, such as chemosensors for various metal ions, monitoring of viscosity and polarity change-based processes, fluorescent imaging, etc. [1]. The advantage of these probes is that they combine high detection sensitivity with a specific sensing functions and can be used to monitor various microscopic properties of the immediate vicinity of the probe [2,3]. Pyrene and its various derivatives are the fluorophores of choice for this application because these derivatives exhibit interesting spectral properties. Namely, their spectral vibrational structures exhibit strong dependencies on polarity, and they possess the ability to form homo- and hetero-dimers in the excited state (excimers and exciplexes) [4–9]. Moreover, pyrene and its derivatives exhibit long lifetimes in non-polar media (ca. 200 ns). If these probes have more complex structures, aggregation might complicate, but sometimes facilitate, their application as a probe to characterize interactions in solution, micelles and, to a lesser extent, in the solid phase.

There has been a large body of literature produced concerning the spectral properties of pyrene since the discovery of excimer formation in solution at increasing pyrene concentration in the middle of the last century [10]. Several examples taken from the literature demonstrate how the changes in the vibrational structure of pyrene monomer fluorescence and the appearance of red-shifted excimer emission were used for characterization of interactions in simple [11] or more complex [12,13] systems. We and others have demonstrated that probes with pyrene as a fluorophore and hydrophilic and hydrophobic parts can aggregate even at low concentrations depending on the method of preparation. Under certain conditions, these probes formed aggregates that exhibit excimer-like emission in normal, pre-micellar and micellar solutions [14–16]. Pyrene-fluorescence probes and fluorescence labels were used to monitor the self-association of hyperbranched poly(sulfone-amine) in water [15]. Self-association results in hydrophobic domains where the pyrene probes are concentrated, yielding excimer fluorescence. In the case of complexation between poly(methacrylic acid) and poly(*N*,*N*-diethylacryl amide), the change occurs from compact micelle-like structures (hydrophobic domains) of both components to ladder-type structures due to complexation, which is more hydrophilic [16].

A recent development based on quantitative analysis of fluorescence decay was acquired using pyrene labeled macromolecules [17,18].

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Pyrene based probes with hydrophilic and hydrophobic parts were used to characterize non-polar [19] and polar matrices [20]. To characterize the superstructure of semi-crystalline polyethylene (PE), the static and dynamic spectroscopic properties of four α,ω-di(1-pyrenyl) alkanes were examined [21].

New host–guest materials have been prepared by incorporating a new fluorescence probe that has a pyrene motif and a phosphate function into a regular amphiphilic copolymer. Using powder X-ray diffraction, photoluminescence and FTIR spectroscopy, it was proofed that it is possible to study the interactions between the host matrix and the guest probe [22].

In this paper, the spectral properties of the parent pyrene and three substituted pyrene derivatives with substituents, i.e., carboxy, carboxy methyl ester and methylol, were compared with esters, which contain additional bulky cholesteryl groups. These pyrene based probes have been examined in media with different viscosities, such as liquid toluene and the common solid polymer matrix as polystyrene or more polar poly(methyl methacrylate) (PMMA) or polyvinylchloride (PVC). First, the influence of the environment (polymer matrix) on the absorption and emission spectra and the dynamic emission decay were examined at different probe concentrations. The static spectra and decay curves of pyrene – based probes are sensitive spectral parameters that reflect changes in the medium. By analyzing the fluorescence spectra and decay curves, resulting data allow us to estimate the interaction between the components of the polymer/probe mixture. The possibility of forming stacks (ground state dimers) due to hydrophilic interactions in a less polar matrix, such as PS, or alternatively, the formation of pre-formed ground state dimers was explored. In addition, the study was extended to other polymer matrices, i.e., PMMA and PVC, and comparing with PS.

The goal of the study is to characterize interaction (compatibility) between probe and polymer matrix. Compatibility can be characterized by degree of probe dispersity in polymer matrix. In limiting case of high dilution of the probe in the polymer matrix this interaction is in fact polymer solvent effect. At increasing concentration of the probe in the polymer matrix the interaction results in self – association or self – aggregation of the probes in various degree.

2. Experimental

2.1. Materials

Cholesterol ((3β)-cholest-5-en-3-ol, or 10*R*,13*R*-10,13-dimethyl-17-(6-methyl-heptan-2-yl)-2,3,4,7,8,9,11,12,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol) and cholesteryl chloroformate analytical grade products were used as received (Sigma–Aldrich, Steinheim, Germany). Anthracene and pyrene (**Py**) were purity zone refined (Sigma–Aldrich, Steinheim, Germany). 1-Pyrenecarboxylic acid (**PyCA**) and 1-pyrenemethanol (**PyME**) used as received from Sigma–Aldrich, Steinheim, Germany. Tetrahydrofuran (THF, POCh Gliwice, Poland) was dried and freshly distilled from sodium/benzophenone and dichloromethane (analytical reagent, Centralchem, Slovakia) was dried over CaH_2 and distilled off. Toluene (Uvasol®, Merck, Germany) spectroscopic grade was used as received. All other solvents and chemicals were commercial materials and used without further purification. Methyl 1-pyrenecarboxylate (**PyCAMe**) was prepared by esterification of 1-pyrene carboxylic acid chloride with methanol in dry methylene chloride in the presence of triethylamine.

Experimental details for preparation of crystalline 1-pyrene-(3β)-cholest-5-en-3-yl-carboxylate (**PyCACh1**, m.p. 175 - 177 °C) were described in details in [23]. Its purity was confirmed by elemental analysis (Anal. calcd. for $C_{44}H_{54}O_2$: C 85.94, H 8.85; found: C 86.42, H 8.63)

1-Pyrenylmethyl (3β)-cholest-5-en-3-yl-carbonate (**PyMECh2**) was prepared according to the following procedure. To an ice cold solution containing 300 mg of cholesteryl chloroformate (0.67 mmol) and 0.2 mL of triethylamine in 5 mL of dried dichloromethane, was dropwise added (1-pyrenyl) methanol in 10 mL of dichloromethane over 30 min. The reaction mixture was stirred and allowed to warm to room temperature. After 30 h, the reaction mixture was poured into 1% aq. HCl and extracted with dichloromethane. The combined organic layers were washed with 15% aq. $NaHCO_3$, brine and water and then dried over $NaSO_4$. The dichloromethane was evaporated and the residue was passed through short pads of silica gel using dichloromethane/hexane/ethyl acetate 1/1/1 as the eluent. The purity of solid product was confirmed by elemental analysis (Anal. calcd. for $C_{45}H_{56}O_3$: C 83.81, H 8.75; found: C 84.38, H 9.15). Structural characteristics of both products was supported by ^1H and ^{13}C NMR analysis (given in Supporting information).

Polymer films doped with the probes were prepared via casting from solution. The following amorphous polymers were used as matrices: polystyrene (PS, Krasten, Kaucuk Kralupy a.s., CR, SEC (chloroform) $M_n = 93{,}700\ \mathrm{g\,mol^{-1}}$ $M_w/M_n = 2.7$, $M_w = 110{,}000\ \mathrm{g\,mol^{-1}}$ light scattering), polymethyl methacrylate (PMMA, Povazske Chemicke Zavody, a.s. Zilina, SR, $M_v = 101{,}000\ \mathrm{g\,mol^{-1}}$), polyvinyl chloride (PVC, Neralit 628, Spolana Neratovice, a.s., CR $M_v = 111{,}000\ \mathrm{g\,mol^{-1}}$). Self-holding films were prepared by casting 1 mL of the polymer solution (5 g/100 mL) with an appropriate amount of probe on a glass plate with an area of $10\ \mathrm{cm^2}$ (28 × 35 mm). Spectroscopy grade chloroform was used in the case of PS and PMMA and tetrahydrofuran in the case of PVC. The thickness of the transparent films was 50 μm. All polymers were precipitated from chloroform or tetrahydrofuran to the spectroscopy grade methanol prior to use and were free of processing or stabilizing additives.

2.2. Methods

Melting points were measured using a Kofler block and are uncorrected. ^1H NMR and ^{13}C NMR were recorded using a VARIAN VXR Unity instruments at 298 K. The chemical shifts are reported in ppm downfield from an internal standard TMS (0.00 ppm), and the solvent was used as a reference. The working frequency was 400 MHz for ^1H and 100 MHz for ^{13}C NMR. The coupling constants are given in Hz. The abbreviations used are: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Merck Silica Gel (60H) was used for flash column chromatography. Merck Silica Gel F254 plates were used for the thin layer chromatography, and the visualization was achieved with UV-light (254 nm). UV/vis absorption spectra were recorded on a UV 1650PC (Shimadzu, Japan) spectrometer. The emission spectra were recorded on a RF-5301PC (Shimadzu, Japan) spectrofluorophotometer. The excitation wavelength was set at 337 nm for pyrene, 344 nm for **PyME**, **PyCACh1** and **PyMECh2** and at 353 nm for **PyCA** and **PyCAMe** derivatives in all media. The fluorescence of the solutions were measured in 1 × 1 cm quartz cuvettes in the right angle arrangement or in a triangular cuvette in the case of a high probe concentration to partially suppress self-absorption. The fluorescence of the polymer films was taken in a front face arrangement using a standard solid sample holder where sample foil is positioned in 40° angle to the excitation light and 50° angle to the detector. The quantum yield of the fluorescence of the pyrene derivatives was determined in solution and in the polymer films using anthracene as a standard. The quantum yields of anthracene fluorescence in different media were determined by comparing with the anthracene fluorescence in cyclohexane (0.25) [10]. It was found to be 0.16 in toluene and PS, 0.20 in PMMA and 0.11 in PVC. The quantum yields in the solutions and films were corrected to the