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Difunctional pyrene derivatives as fluorescent brightening agents for condensation polymers

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Abstract

Dimethyl esters of four pyrene dicarboxylic acids were synthesized and incorporated into poly(ethylene terephthalate). The spectroscopic properties of the polymers and monomers are assessed for their effectiveness and potential as covalently-bound fluorescent brightening agents. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Pyrene derivatives; Condensation polymers; Fluorescent brightening agents

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1. Introduction

Fused arenes have long been known to be strongly fluorescent and substituted arenes have been used extensively as brightening agents for polymers. However, except for the notable exceptions of 1-triazine substituted pyrenes [1–3] 1-hydroxy-3,6, pyrenetrisulphonic acid [3], and pyrenylamine derivatives [4], few pyrenes have been developed as fluorescent brightening agents (FBAs) for polymers. In particular, there are very few references to carboxyl functionalized pyrenes as brighteners [5]. Other fused aromatic brighteners include heteroarenes such as benzoxazoles, benzimidizoles, and benzfurans, and carbocyclics such as naphthalimides [6]. Some of the problems associated with using fused arenes as FBAs are poor adhesion to the polymer, poor light fastness, and difficult synthetic approaches. We have developed new synthetic strategies to provide stable difunctional pyrenes as luminophors **I–IV** which can be incorporated directly into the polymer backbone of condensation polymers (e.g. polyesters, polyamides). Potential advantages to having brighteners in the polymer backbone include elimination of wash-out of the brightener and elimination of a separate processing step to add the brightener to the fabric. These difunctional compounds will also serve as base compounds for other FBAs through modification of the carboxyl functional group (e.g. conversion to benzoxazoles, benzimidizoles, nitriles).

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2. Results and discussion

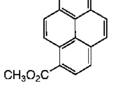
2.1. Synthesis

Bromination of pyrene [7] gave a mixture of 1,6- and 1,8-dibromopyrenes (ca. 3:2 by ^{1}H NMR) which were separated by repeated recrystallization from toluene. Lithiation of the individual isomers (BuLi, benzene, 80°C) followed by carboxylation (CO_2) gave the corresponding diacids **Ia** and **IIa** (Scheme 1). The diacids were methylated (methyl iodide, Li_2CO_3, DMF) [8] to give the dimethyl esters **Ib** and **IIb** which were purified by recrystallization from dioxane.

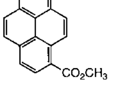
Functionalization of pyrene at the 2- (and 7-) position(s) is not possible by electrophilic aromatic substitution on pyrene itself [9,10]. Pyrene was subjected to hydrogenation (40 psi, wet EtOAc, 10% Pd/C, 3 d) to afford a mixture of 4,5,9,10 tetrahydropyrene and 1,2,3,6,7,8-hexahydropyrene (85:15 by 1H NMR). Acylation [11] (CH_3COCl, CH_2Cl_2, $AlCl_3$) gave 2,7-diacetyl-4,5,9,10-tetrahydropyrene and 4,10-diacetyl-1,2,3,6,7,8-hexahydropyrene. The soluble over-reduced product was easily separated by trituration (ether: benzene, 1:10). Oxidation of 2,7-diacetyl-4,5,9,10-tetrahydropyrene (NaOBr, dioxane) [12] followed by aromatization (Br_2, CS_2) [13] gave dimethyl 2,7-pyrenedicarboxylate, **III** (Scheme 2).

Reaction of pyrene with phthalic anhydride ($AlCl_3$, $C_2H_2Cl_4$, 70°C) gave the bis(diphthalic acid), **IVa**, which was separated from the 1,6-isomer by recrystallization from aqueous base. Methylation gave the dimethyl ester **IVb** (Scheme 3).

Monomers **I–III** showed strong florescence in the blue and violet, with **I** being the strongest. Monomer **IV** was essentially non-fluorescent.



I



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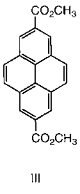
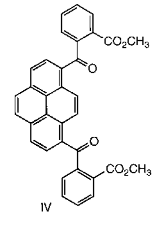
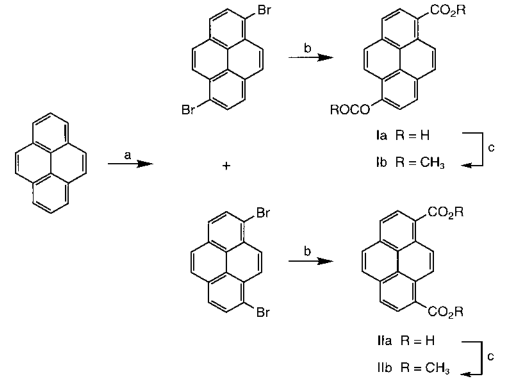


III

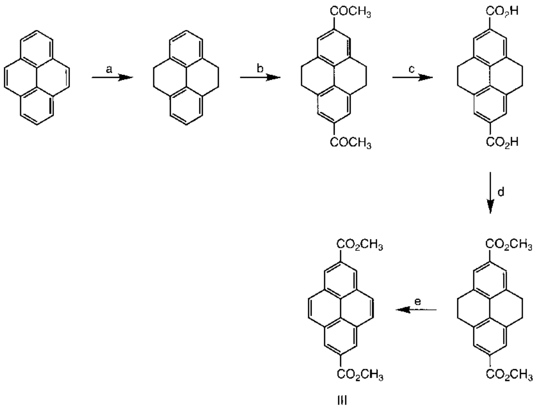


IV



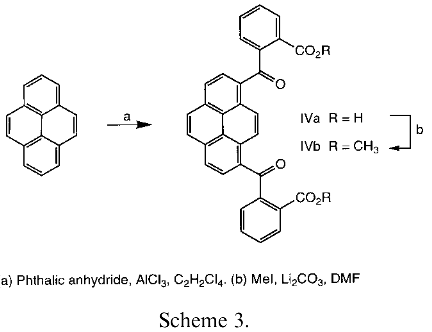
(a) Br_2, CCl_4. (b) n-BuLi, CO_2. (c) MeI, Li_2CO_3, DMF.

Scheme 1.



(a) H_2, 10% Pd/C, EtOAc. (b) AcCl, $AlCl_3$, CH_2Cl_2. (c) Br_2, NaOH, dioxane. (d) MeI, Li_2CO_3, DMF. (e) Br_2, CS_2.

Scheme 2.



(a) Phthalic anhydride, $AlCl_3$, $C_2H_2Cl_4$. (b) MeI, Li_2CO_3, DMF

Scheme 3.

Table 1
Monomer absorption and fluorescence data

FBA	I	II	III	IV
λ_{abs} (nm)	360	358	273	376
ε (1 mol^{-1} cm^{-1})	3.24×10^4	2.75×10^4	1.29×10^5	2.76×10^4
λ_{fl} (nm)	399	389	411	412
Stokes' shift (nm)	39	31	138	36
τ_{f1}	0.74	0.76	0.90	–
τ_{f2}	6.5	8.5	24	–

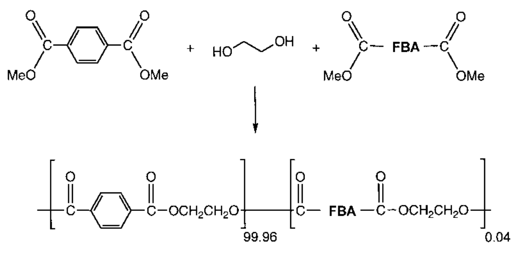
2.2. Copolymerization of FBAs in PET

The dimethyl ester FBA monomers **I–IV** were copolymerized with poly(ethylene terephthalate), PET, by the standard melt polymerization procedure [14] at 285°C on a 4 mol scale (Scheme 4). Copolymers were prepared containing 0.04 mol% of each fluorescent comonomer, **I–IV**. High molecular weight polymer (ca. 20,000 g/mol) was produced which had the same clarity and color as homopolymer lacking FBAs. Polymers **I–III** were strongly fluorescent.

2.3. Spectral data

The absorption spectra of **I, II**, and **IV** are similar, with all three molecules absorbing strongly between 350 and 380 nm (Table 1). The 2,7-pyrene derivative, **III**, is electronically distinct from the other FBAs [15] and its absorption is blue shifted to 273 nm.

FBAs **I–III** give a strong violet-blue fluorescence (Table 2). FBA **IV** is only very weakly fluorescent, probably due to excitation into a triplet state (common for ketone-substituted fused arenes). All the FBAs had long fluorescent lifetimes which could make them susceptible to oxygen quenching, although the polymer matrix would shield the FBAs from high concentrations of oxygen.



Scheme 4.

Thin films of polymers incorporating 0.04 mol% of **I-III** give a strong violet–blue fluorescence which are significantly red-shifted from the monomers in cyclohexane. The emissions are much broader than for the monomers due to the heterogeneity of the polymer matrix. Polymer containing **IV** as a comonomer does not fluoresce and is less bright than even PET homopolymer. The polymer containing 1,6-Pyrene, **I**, had the brightest fluorescence and would be the best candidate of the four for use as a FBA.

3. Experimental

UV–rv is spectra of the monomers (10^{-5} M solutions in cyclohexane) were collected on a Shimadzu 2401PC Spectrophotometer. Fluorescence data for the monomers (10^{-7} M solutions in cyclohexane) was collected on a Shimadzu RF-5301 PC Spectrofluorophotometer, while the reflectance fluorescence spectra on the polymers films was collected on a home-built instrument. Polymer samples were spin coated from a 10% trifluoroacetic acid solution onto glass slides for fluorescence measurements. Details of the synthesis of **III** have been reported [16]. Complete details of the synthesis of compounds **I, II**, and **IV** will be reported elsewhere.

Table 2
Polymer fluorescence emission maxima

FBA	I	II	III	IV
λ_{fl} (nm)	407	398	425	426

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