

Luminescent monomer of substituted tetrastrylpyrene and poly(*p*-phenylenevinylene) derivative with pyrene segments: Synthesis and photophysics

John A. Mikroyannidis*

Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece

Received 13 May 2005; accepted 27 June 2005

Available online 13 October 2005

Abstract

1,3,6,8-Tetrabromopyrene reacted with 1-*tert*-butyl-4-vinylbenzene to afford the luminescent monomer **M**. In addition, the reaction of 1,6-dibromopyrene with 1,4-didodecyloxy-2,5-divinylbenzene yielded a poly(*p*-phenylenevinylene) (PPV) derivative **P**. **M** dissolved partially in chloroform and completely in THF. **P** showed an excellent solubility being readily soluble in common organic solvents. **M** emitted intense blue–green light in THF solution with photoluminescence (PL) maximum at 507 nm and green–yellow light in thin film with PL maximum at 570 nm. Polymer **P** displayed in THF a PL maximum at 464 nm and a shoulder at 513 nm. Thin film of this polymer exhibited PL maximum at 572 nm. Both **M** and **P** emitted from excimers in solid state. The PL emission quantum yields in THF were 0.35 for **M** and 0.32 for **P**. The emission maximum of **M** thin film was red shifted by 9 nm after annealing at 150 °C for 24 h as a result of conformational changes of the molecules with increase in temperature.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Tetrastrylpyrene; Poly(*p*-phenylenevinylene); Pyrene; Light-emitting polymer; Photophysics; Synthesis

1. Introduction

The wide range of applications of electroactive and photoactive conjugated polymers has triggered intensive development of various types of application specific functional conjugated polymers in the last four decades. Great progress has been made particularly in the design of polymers for light-emitting-diodes [1–4] and photovoltaic cells [5–8], whereby poly(*p*-phenylenevinylene) (PPV) and its various derivatives have been at the centre of attention [9]. PPVs, as one kind of π -conjugated polymer, are ideal candidates for electroluminescence, because they exhibit high photoluminescence (PL) efficiency in solution, and do not significantly aggregate in the solid state. Although PPVs possess a hole transport capability, the hole mobility is not high enough to satisfy the need for effective hole injection and transporting in light-emitting devices [10,11].

Pyrene has been extensively used for the investigation of water soluble polymers with the fluorescence technique. The features of pyrene that make it an attractive chromophore include its well-characterized long-lived excited state, the sensitivity of its fluorescence to quenching, the sensitivity of its excitation spectra to microenvironment changes, and its propensity for forming excimers [12]. The various fluorescence properties of pyrene have been used to study a variety of different kinds of polymers. A literature survey revealed that there is a limited number of investigations concerning the attachment of pyrene to polymers [12,13]. Thin films of pyrene in polystyrene matrix have been prepared by the spin casting technique and their optical properties have been studied [14]. Pyrene containing polymers have been used as acceptors for energy transfer from various donors [15,16].

In this article a new luminescent monomer **M** and a PPV derivative **P** containing pyrene segments are presented. These were conveniently synthesized via the Heck coupling from dibromo or tetrabromopyrene in high yields. The *tert*-butyls that were attached to the four styryl units of **M** acted as solubilizing groups. On the other hand, the didodecyloxy side groups of **P**

* Tel.: +30 2610 997115; fax: +30 2610 997115.
E-mail address: mikroyan@chemistry.upatras.gr.

enhanced its solubility. The presence of the styryl units in the four side chains of the pyrene core of **M** gives rise for efficient fluorescence which makes the material candidate for light emissions. Moreover, the preparation of a PPV derivative with pyrene moieties along the backbone is of interest.

2. Experimental

2.1. Characterization methods

IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ^1H NMR (400 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer. The PL spectra were obtained with a Perkin-Elmer LS45 luminescence spectrometer with photoexcitation at the corresponding absorption maximum. GPC analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters 2410) as detector using polystyrene as standard and THF as eluent. The DSC thermograms were obtained at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere at a flow rate of $60\text{ cm}^3/\text{min}$. Dynamic TGA measurements were made at a heating rate of $20^\circ\text{C}/\text{min}$ in atmospheres of N_2 or air at a flow rate of $60\text{ cm}^3/\text{min}$. To measure the PL quantum yields (Φ_f) a degassed solution of polymer in THF was prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1. The excitation was performed at the corresponding absorption maximum and a solution in $1\text{ N H}_2\text{SO}_4$ of quinine sulfate, which has a Φ_f of 0.546 ($\lambda_{\text{ex}} = 365\text{ nm}$), was used as a standard.

2.2. Reagents and solvents

Dimethylformamide (DMF) and triethylamine were dried by distillation over CaH_2 and KOH, respectively. The Stille reaction was used to prepare 1,4-bis(dodecyloxy)-2,5-divinylbenzene [17]. The latter was prepared by reacting 1,4-bis(dodecyloxy)-2,5-dibromobenzene with tributylvinyltin in the presence of the catalyst $[\text{PdCl}_2(\text{PPh}_3)_2]$, and a few crystals of 2,6-di-*tert*-butylphenol using toluene as solvent. All other reagents and solvents were commercial of analytical-grade quality and were used without further purification.

2.3. Preparation of monomers and polymer

2.3.1. 1,3,6,8-Tetrabromopyrene (**1**)

Compound **1** was prepared according to the literature procedure [18,19] that was modified as follows. A flask was charged with a solution of pyrene (0.50 g, 2.47 mmol) in nitrobenzene (10 mL). Bromine (2.37 g, 14.82 mmol) diluted with nitrobenzene (5 mL) was added dropwise to the stirred solution at 80°C . The mixture was subsequently stirred and heated at 120°C overnight. Then, it was cooled at room temperature and the whitish precipitate was filtered off, washed thoroughly with *n*-hexane and dried to afford **1** (1.21 g, yield 95%, $\text{mp} > 300^\circ\text{C}$).

IR (KBr, cm^{-1}): 3438, 1590, 1464, 1356, 1270, 1226, 1052, 984, 872, 810, 674, 496.

The ^1H NMR spectrum could not be recorded due to the limited solubility of **1** in DMSO-d_6 .

Anal. Calcd. for $\text{C}_{16}\text{H}_6\text{Br}_4$: C, 37.11; H, 1.17. Found: C, 36.85; H, 1.23.

2.3.2. 1,3,6,8-Tetrakis(*E*)-*tert*-butylstyryl)pyrene (**M**)

Compound **1** (0.5360 g, 1.03 mmol) was dissolved by heating in DMF (35 mL). 1-*tert*-Butyl-4-vinylbenzene (0.8287 g, 5.17 mmol), $\text{Pd}(\text{OAc})_2$ (0.0094 g, 0.042 mmol), and $\text{P}(o\text{-tolyl})_3$ (0.0247 g, 0.081 mmol) were added to the solution. The mixture was degassed and flashed with N_2 . It was stirred and heated at 110°C for 24 h. The orange precipitate was filtered off, washed with *n*-hexane and dried to afford **M**. It was dissolved in THF, the solution was filtered and precipitated into methanol (0.36 g, yield 42%, $\text{mp} > 300^\circ\text{C}$).

IR (KBr, cm^{-1}): 2956, 2866, 1592, 1510, 1464, 1362, 1268, 1119, 1052, 958, 856, 810, 676, 560.

^1H NMR (DMSO-d_6 , δ): 7.68–7.21 (m, 16H, aromatic of phenylene, and 6H, aromatic of pyrene, and 8H, vinylene); 1.56–1.25 (m, 36H, aliphatic).

Anal. Calcd. for $\text{C}_{64}\text{H}_{66}$: C, 92.03; H, 7.96. Found: C, 91.85; H, 8.04.

2.3.3. 1,6-Dibromopyrene (**2**)

This compound was prepared according to the literature procedure [20].

2.3.4. Polymer **P**

A flask was charged with **2** (0.1297 g, 0.36 mmol), 1,4-didodecyloxy-2,5-divinylbenzene (0.1793 g, 0.36 mmol), $\text{Pd}(\text{OAc})_2$ (0.0034 g, 0.015 mmol), and $\text{P}(o\text{-tolyl})_3$ (0.0252 g, 0.083 mmol). The flask was degassed and purged with N_2 . DMF (8 mL) and triethylamine (2 mL) were added, and the mixture was stirred and heated at 110°C for 24 h under N_2 . Then, it was filtered and the filtrate was poured into methanol. The reddish precipitate was filtered, washed with methanol and dried to afford **P** (0.20 g, yield 80%).

IR (KBr, cm^{-1}): 2922, 2852, 1600, 1500, 1462, 1420, 1384, 1202, 1030, 964, 842, 714.

^1H NMR (CDCl_3 , δ): 7.70–6.90 (m, 10H, aromatic and 4H, vinylene); 4.03 (m, 4H, OCH_2); 1.86, 1.25, 0.86 (m, 46H, other aliphatic).

Anal. Calcd. for $(\text{C}_{50}\text{H}_{64}\text{O}_2)_n$: C, 86.15; H, 9.25. Found: C, 85.96; H, 9.13.

3. Results and discussion

3.1. Synthesis and characterization

Monomer **M** was prepared as shown in Scheme 1. In particular, pyrene reacted with an excess of bromine in nitrobenzene to give 1,3,6,8-tetrabromopyrene (**1**) in excellent yield [18,19]. The Heck coupling of **1** with 4-*tert*-butylstyrene gave monomer **M**. The latter precipitated during the reaction, when DMF was used as reaction medium. However, **M** was completely soluble

Download English Version:

<https://daneshyari.com/en/article/10619116>

Download Persian Version:

<https://daneshyari.com/article/10619116>

[Daneshyari.com](https://daneshyari.com)