New Fluorene-Based Conjugated Copolymers Bearing Carboxylic Groups

*Stanislav Kukla, Petra Pavlačková, Věra Cimrová, Drahomír Výprachtický**

Summary: New conjugated copolymers containing 9,9-dioctylfluorene and terephthalate units (as dimethyl ester or free acid) were synthesized by the Suzuki coupling and characterized by GPC and NMR, FT-IR and UV-VIS spectroscopies. These copolymers proved to be good luminescent materials showing emissions in the blue region of the visible spectrum both in solution ($\lambda_{em} = 450$ nm) and in thin layers. Differences in the luminescence properties were attributed to various extents of aggregation. It was shown that interchain interaction can be avoided by the formation of the copolymer sodium salt. The copolymers were tested as active layers in light-emitting devices and the formation of their Eu(III) complexes was studied.

Keywords: aggregation; conjugated polymers; fluorene; luminescence; Suzuki coupling

Introduction

Fluorene-based polymers are promising blue-light-emitting materials with high photoluminescence efficiency and good thermal stability for application in optoelectronic devices such as light-emitting diodes (LEDs).[1–4] The undesirable tendency of these materials to generate long-wavelength emission[5] accompanied by a decrease in electroluminescence quantum efficiency might be overcome by introducing various structure units into the main chain or using polyfluorenes in polymer blends (for example with hole-transporting polymers [6]). Polyfluorene modification with suitable binding sites enables these materials also as potential energy donors for lanthanide metal ion (Eu^{3+}, Tb^{3+}) complexes.

In this article we report on the synthesis, characterization, photoluminescence (PL) and electroluminescence (EL) of novel alternating copolymers containing 9,9-dioctylfluorene and terephthalate units (as dimethyl ester or free acid) and on the formation of their Eu(III) complexes.

Experimental Part

Polymer Synthesis

F1: 9,9-dioctylfluorene-2,7-bis(trimethylborate) (3 g, 5.4 mmol), dimethyl 2,5-dibromoterephthalate (1.9 g, 5.4 mmol) and tetrakis(triphenylphosphine)palladium (0.13 g, 0.11 mmol, 2 mol. %) were introduced to a flask fitted with a reflux condenser and an argon inlet. Degassed aqueous solution of potassium carbonate (2 M, 27 ml) and degassed toluene (40 ml) were added to the flask and the reaction mixture was stirred and heated at 85 °C for 72 hours under argon atmosphere. After cooling to room temperature, the resulting solution was added dropwise into methanol (800 ml) to precipitate the polymer. The resulting grey material was collected by filtration and washed with methanol, water and methanol and dried. It was reprecipitated twice from tetrahydrofurane into methanol. Yield: 2.58 g (81%), ^{1}H NMR ($CDCl_3$, ppm): 7.91 (s, 2H), 7.81 (d, 2H, $J = 7.5$ Hz), 7.40 (d, 2H, $J = 7.5$ Hz), 7.32 (s, 2H), 3.65 (br, 6H,

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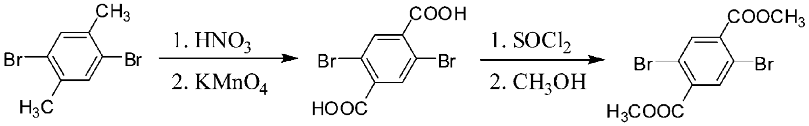
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2,
162 06 Prague 6, Czech Republic
Fax: (+420) 296 809 410;
E-mail: vyprach@imc.cas.cz



Scheme 1.
Synthesis of dimethyl 2,5-dibromoterephthalate.

$COOCH_3$), 1.99 (br, 4H, CH_2), 1.11 (br, 24H, CH_2), 0.80 (tr, 6H, CH_3), FT–IR (film from $CHCl_3$, cm^{-1}): 2927, 2855, 1735, 1463, 1435, 1278, 1230, 1106.

F2 : **F1** (2 g) was dissolved in tetrahydrofuran (50 ml) under argon atmosphere and refluxed with a solution of sodium hydroxide in methanol (10 wt. %, 50 ml). After the reaction mixture was cooled to room temperature, it was poured into 200 ml of distilled water. The resulting polymer was isolated by precipititating with ~200 ml of 0.5 M hydrochloric acid (to pH ~ 3), filtration and drying. It was reprecipitated from tetrahydrofurane into distilled water to obtain a yellow-green fibrous solid. Yield: quantitative, ^1H NMR ($CDCl_3$, ppm): 11.3 (br, 2H, COOH), 7.92 (s, 2H), 7.82 (d, 2H, $J = 7.5$ Hz), 7.49 (s, 2H), 7.41 (d, 2H, $J = 7.5$ Hz), 2.48 (br, 4H, CH_2), 1.13 (br, 24H, CH_2), 0.81 (tr, 6H, CH_3), IR (film from $CHCl_3$, cm^{-1}): 2956, 2855, 1728, 1698, 1463, 1436, 1412, 1279, 1236, 1122, 823.

Methods

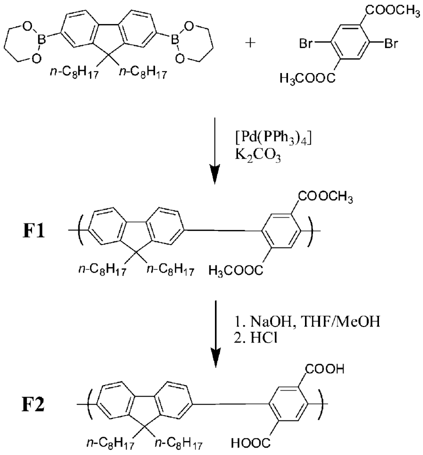
^1H NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz in deuterated chloroform or tetrahydrofuran using hexamethyldisiloxane as an internal standard. FT IR spectra were measured using a Perkin-Elmer Paragon 1000 PC Fourier transform infrared spectrometer as a film on a KBr pellet. Thin polymer films were prepared by spin coating from THF solutions. All solutions were filtered with 0.45 μm Millex-FH13 Millipore syringe filters prior to spin-coating. Thin films for optical studies were spin-coated onto fused silica substrates. UV-vis spectra were taken on a Perkin-Elmer Lambda 20 spectrometer. PL spectra were measured under ambient conditions with a home-made spectrofluorometer with a single-photon-counting detection using a 300 W xenon lamp as the excitation source.

Results and Discussion

The first monomer, 9,9-dioctylfluorene-2,7-diyl propane-1,3-diyl bisboronate, was purchased from Aldrich. The second monomer, dimethyl 2,5-dibromoterephthate, was synthesized according to Scheme 1.

The route involves a two-step oxidation of the starting 2,5-dibromo-1,4-xylene with nitric acid followed by treatment with potassium permanganate, giving the highest yield of 2,5-dibromoterephthalic acid[7]. This intermediate was converted to the dimethyl ester by a reaction with thionyl chloride and methanol.

The Suzuki reaction[8] was employed for the synthesis of copolymer **F1** with ester groups (Scheme 2).The advantages of this



Scheme 2.
Synthesis of copolymers **F1** and **F2**.

Table 1.
GPC data of the synthesized copolymers.

Polymer	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
F1	1.77	2.20	1.25
F2	2.34	2.82	1.20

type of coupling include mild reaction conditions, low sensitivity to steric hindrance, higher conversions and higher degrees of polymerization when compared with the Yamamoto reaction, for example. The dicarboxylic acid was obtained by alkaline hydrolysis of ester groups of **F1** in a methanol-THF solution and subsequent acidification, yielding copolymer **F2** (Scheme 2). A comparison of the data obtained from GPC measurements (Table 1) suggests that the copolymer **F1** was further purified during conversion to the diacid. Both the number- and weight-average molecular weights of the copolymer increased after hydrolysis, while its polydispersity decreased.

In the UV-vis spectra measured in a dilute THF solution, both copolymers show a single maximum at 350 nm ($\pi \rightarrow \pi^*$) with molar absorption coefficients (per monomer unit) $\varepsilon_{350} = 31\ 500$ L mol^{-1} cm^{-1}. Both copolymers proved to be good luminescent materials with emission in the blue spectral region. PL spectra of both copolymers in a diluted THF solution are the same and show a single band in the excitation spectrum ($\lambda_{exc} = 350$ nm) and a single band without vibronic structure in the emission spectrum ($\lambda_{em} = 450$ nm). PL quantum yields were measured in a diluted THF solution relatively to 9,10-diphenylantracene[9] (in cyclohexane) and it was found out that copolymer **F1** exhibited a higher quantum yield ($\Phi = 0.53$) than **F2** ($\Phi = 0.39$).

UV-vis and PL behaviors of the two copolymers differ when measured in a thin layer. The $\pi \rightarrow \pi^*$ band in UV-vis spectra is generally broader than in the spectra measured for dilute solutions. In the case of **F2** the maximum is slightly red-shifted and consists of two bands. Optical bandgaps (E_g) were calculated from the edges of the absorption spectra, and as can be seen from Table 2, the E_g value of **F2** is smaller than that of **F1**. These two observations suggest that the interchain interaction is greater in the **F2** thin layer, which can be understood on the chemical basis by formation of hydrogen bonds between COOH groups on different **F2** chains. When the a sodium salt (**F2Na**) was formed prior to spin-coating, the effects of the chain interaction and aggregation in the UV-vis spectra were not observed (Figure 1a and Table 2).

Similar behavior was observed when PL emission spectra in thin layers were measured (Figure 1b). The emission spectrum of **F2** is broader and red-shifted compared with the spectrum of **F1**. This supports the hypothesis of strong interchain interaction in **F2**. When the sodium salt **F2Na** is formed, its emission maximum shifts back to the value measured for **F1** in thin layer or for both **F1** and **F2** in the dilute solution. The PL emission intensity of **F2Na** in thin layer drops to one fourth of the value for both **F1**, **F2** (Figure 1b). **F1** and **F2** were also tested in light-emitting devices (LEDs). LEDs with indium-thin oxide (ITO) and aluminium electrodes made of **F1** and **F2** emitted green light with a maximum at 520 and 510 nm, respectively. Though the PL efficiency in thin films of both **F1** and **F2** polymers is similar, LEDs made of **F2** exhibited much better performance than those of **F1**. Their relative efficiency was 35 times higher than for **F1** LEDs.

Table 2.
UV–vis, PL and EL characteristics of the polymer thin layers.

Polymer	λ_{absmax} (nm)	α_{max} (10^7 m^{-1})	E_g (eV)	λ_{PLmax} (nm)	Relative efficiency of PL	λ_{ELmax} (nm)	Relative efficiency of EL
F1	352	1.534	3.18	441	1	520	1
F2	358	1.121	3.02	477	0.97	510	35
F2Na	344	1.726	3.22	455	0.25	–	–

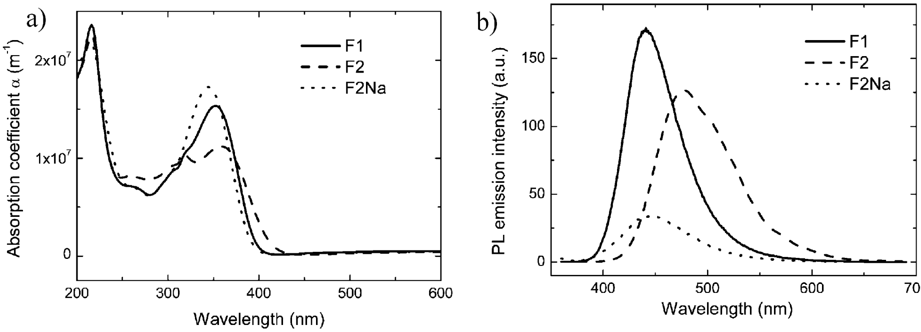
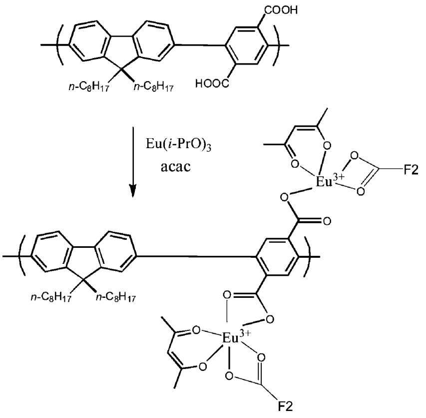


Figure 1.
(a) UV-vis and (b) PL spectra of **F1**, **F2** and **F2Na** thin films.



Scheme 3.
The Eu(III) ion complex with copolymer **F2** and pentane-2,4-dione.

By the reaction of highly reactive Eu triisopropoxide[3] with ligand **F2** in the presence of coligand (pentane-2,4-dione) we prepared a crosslinked material (Scheme 3), which exhibited a strong red and sharp luminescence with the dominant emission at $\lambda_{em} = 613$ nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III). The preparation of a soluble Eu(III)-**F2** complex is under study. We believe that a more efficient coligand will probably decrease crosslinking and, consequently, the insolubility of the polymer. Also, conversion of one of terephthalic carboxy group to ester or amide could increase the solubility as well. For better solubility of the polymer, we need to decrease the functionality of either metal (Eu^{3+}) or ligand (**F2**).

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