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Syntheses of Conjugated Polymers for Photonics

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Summary: By the Suzuki coupling reaction of 9,9-dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl)fluorene (**I**) and 3,5-di-tert-butylphenyl 2,5-dibromobenzenesulfonate (**II**) the alternating poly{[9,9-dioctylfluoren-2,7-diyl]-*alt*-[2-(3,5-di-tert-butyl-phenoxysulfonyl)-1,4-phenylene]} (**III**) was synthesized. Alkaline hydrolysis of **III** gave a conjugated polyelectrolyte carrying sulfonic acid groups (**IV**). Monomers 2,5-dibromo-3-[2-(pyren-1-yl)vinyl]thiophene and 2,5-dibromo-3-[2-(quinolin-4-yl)vinyl)thiophene were prepared and copolymerized with **I** to afford poly{[9,9-dioctylfluoren-2,7-diyl]-*alt*-[3-(2-(pyren-1-yl)vinyl)thiophen-2,5-diyl]} (**V**) and poly{[9,9-dioctylfluoren-2,7-diyl]-*alt*-[3-(2-(quinolin-4-yl)-vinyl)thiophen-2,5-diyl] (**VI**), respectively. Conjugated backbone of **V** contains the conjugated pyrene unit in the side chain. Similarly the side chain of **VI** contains the conjugated quinoline structure unit which can be for instance protonated. By the Suzuki polycondensation reaction of **I** and of the prepared methyl 3-(2,7-dibromocarbazole-9-yl)propionate (**VII**) the new poly{[9,9-dioctylfluorene-2,7-diyl]-*alt*-[9-(2-methoxycarbonylethyl)carbazole-2,7-diyl]} (**VIII**) was synthesized and characterized.

Keywords: cis and trans isomers; conjugated polymer; conjugated polyelectrolyte; Horner-Emmons reaction; polycarbazole; polythiophene; pyrene; quinoline

Introduction

π-Conjugated polymers[1], such as polyphenylenes, polythiophenes, polyfluorenes, fluorene-thiophene copolymers, polycarbazoles, and their modifications have recently attracted great attention due to their potential applications in optoelectronics including light-emitting devices, photovoltaic cells, thin-film transistors, electrochromic devices, and switches. Polythiophenes in particular are utilized in polymer photovoltaic cells because of their higher charge carrier mobility. Most of the modifications of polythiophenes were focused on side-chain substitution or end-group functionalization. Here the preparation of several tailored monomers and their conjugated polymers or copolymers is reported. The synthesized materials were or will be utilized for construction of organic light-emitting devices or solar sells.

Experimental Part

^{1}H NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz in deuterated tetrahydrofuran or deuterated chloroform using hexamethyldisiloxane as internal standard. FT IR spectra were measured on a Perkin-Elmer Paragon 1000 PC Fourier transform infrared spectrometer, in KBr pellets or as a film on a KBr pellet. SEC measurements were performed using Pump Deltachrom (Watrex Comp.), autosampler Midas, with two columns PL gel MIXED-B LS, particle size 10 μm. Evaporative light scattering detector PL-ELS-1000 (Polymer Laboratories) was used and THF was the mobile phase. Polystyrene standards were used for calibration.

9,9-Dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl)fluorene, *N*-bromosuccinimide (NBS), triethyl phosphite, dibenzoyl peroxide

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(BPO), sodium methoxide, 3,5-di-tert-butylphenol, methyl acrylate, 2,5-dibromobenzene-1-sulfochloride, quinoline-4-carboxaldehyde (4-Q-CHO) and 1-octanal were commercial products (Aldrich, Fluka). 2,7-Dibromocarbazole was prepared according to published procedure.[2] Triethylamine was refluxed for 3 h with calcium hydride and distilled. Tetrahydrofuran (THF) was refluxed (8 h) with Na/$LiAlH_4$ and fractionally distilled. Toluene was refluxed with sodium (12 h) and distilled. The other solvents and chemicals (Lach-Ner, Ltd., Neratovice, Czech Republic) were of analytical grade (p.a.) and were used as received.

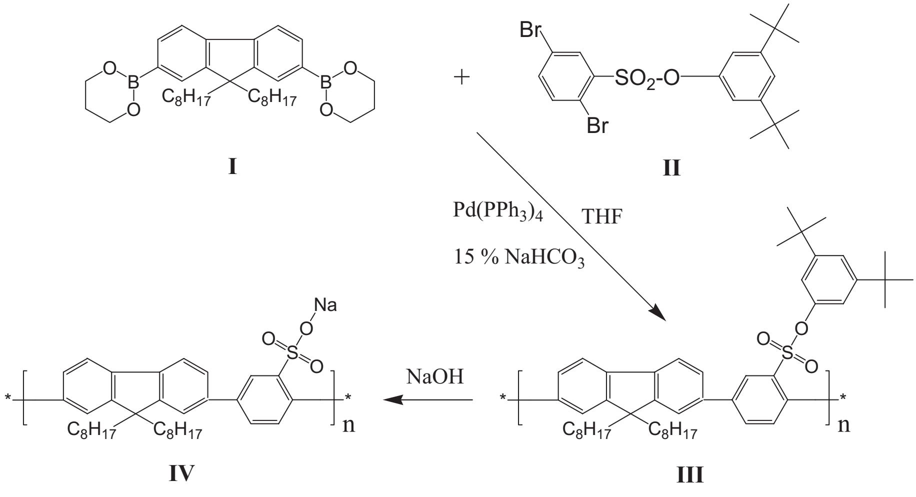
Methyl 3-(2,7-dibromocarbazole-9-yl)propionate

2,7-Dibromocarbazole (0.93 g, 2.86 mmol) and methyl acrylate (30 ml, 0.33 mol) was cooled (0–5 °C) and benzyltrimethylammonium hydroxide (0.2 ml of 35% methanolic solution) was added. The temperature increased slightly (ca. 2 °C) and a white crystalline material precipitated out of the solution. The starting 2,7-dibromocarbazole was not detect (TLC in toluene) in the reaction mixture after 1 h. The excess of methyl acrylate was vacuum evaporated and the residue was crystallized from methanol. Yield: 1.07 g (91%), m. p. 137–138 °C. Anal. for $C_{16}H_{13}Br_2NO_2$ (411.09): Calc. C 46.75, H 3.19, N 3.41, Br 38.87; Found C 46.78, H 3.22, N 3.38, Br 38.59. ^{1}H NMR (THF-d_8, δ ppm): 7.96 (d, 2H, arom.), 7.77 (s, 2H, arom.), 7.32 (d, 2H, arom.), 4.62 (t, 2H, N-CH_2), 3.57 (s, 3H, CH_3), 2.82 (t, 2H, CH_2-CO).

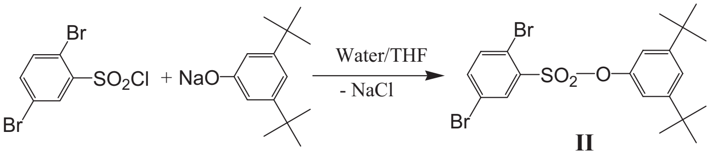
Results and Discussion

Synthesis of poly{[9,9-dioctylfluoren-2,7-diyl]-*alt*-[2-(3,5-di-tert-butylphenoxysulfonyl)-1,4-phenylene]} (III)

Conjugated rigid-rod polyelectrolytes are important materials for photonic elements.[3–5] To obtain a new conjugated polyelectrolyte the preparation of polymer **III** was performed by means of Suzuki coupling (Scheme 1) of commercially available 9,9-dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl)fluorene (**I**) with the prepared 3,5-di-terc.butylphenyl 2,5-dibromobenzenesulfonate (**II**). The reaction took place (reflux ~80 °C, 66 h) in an aqueous 15% $NaHCO_3$/THF (1:1 by vol.) two phase system under argon in the presence of tetrakis(triphenylphosphin)palladium catalyst. The polymer was isolated by precipitation into methanol/water (3:2 by vol.) and purified by a double reprecipitation from THF into methanol. The structure of **III**



Scheme 1.



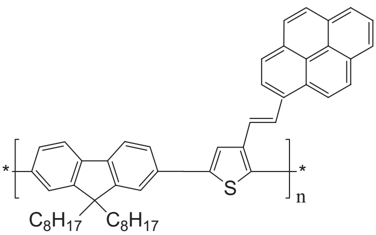
Scheme 2.

was confirmed by ^{1}H NMR and FT IR spectroscopy and the $M_w = 6\,500$, $M_n = 3\,700$ and $p = 1.75$ values were determined by GPC in THF. The saponification of **III** was performed by heating (70 °C, 12 h) in the 0.4 M NaOH prepared in a mixture of THF/ethanol/water (3:2:1 by vol.). Then the resulting solution was filtered and dialyzed (Spectra/Por 6, MWCO = 2000) against water. The conjugated polyelectrolyte **IV** was isolated by freeze drying. The nearly complete hydrolysis (> 95%) of sulfonic acid esters was confirmed by ^{1}H NMR (loss in methyl protons). The synthesis of 3,5-di-terc.butylphenyl 2,5-dibromobenzenesulfonate (**II**) was accomplished either according to a published procedure[6] or by our procedure depicted in Scheme 2.

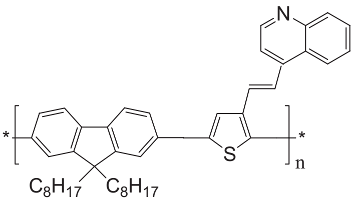
In the published procedure the 2,5-dibromobenzenesulfonyl chloride reacts with 3,5-di-tert-butylphenol in the presence of organic base (pyridine). Unfortunately, some byproducts were detected (TLC) in the reaction mixture and a column chromatography (Silica gel 60, Merck) in toluene/heptane (1:1) had to be used to separate **II**. The byproducts can be formed by the reaction of sulfonate with phenol (alkylation) or pyridine (pyridinium salt). We improved the procedure (Scheme 2) to avoid the column chromatography. First, the sodium 3,5-di-tert-butylphenolate was prepared by the reaction of 3,5-di-tert-butylphenol with sodium hydroxide in water and then the 2,5-dibromo-benzenesulfonyl chloride in THF was added. Reaction temperature slightly increased (~40 °C) and the **II** was extracted from the reaction mixture by chloroform. After solvent evaporation the product **II** was recrystallized from heptane to get colorless crystals, m. p. 100 – 102 °C (lit.[6] 100 °C). The structure of **II** was also confirmed by ^{1}H NMR and FT IR spectroscopy and by elemental analysis.

Syntheses of poly{[9,9-dioctylfluoren-2,7-diyl]-*alt*-[3-(2-(pyren-1-yl)vinyl)thiophen-2,5-diyl]} (V) and poly{[9,9-dioctylfluoren-2,7-diyl]-*alt*-[3-(2-(quinolin-4-yl)-vinyl)-thiophen-2,5-diyl] (VI)

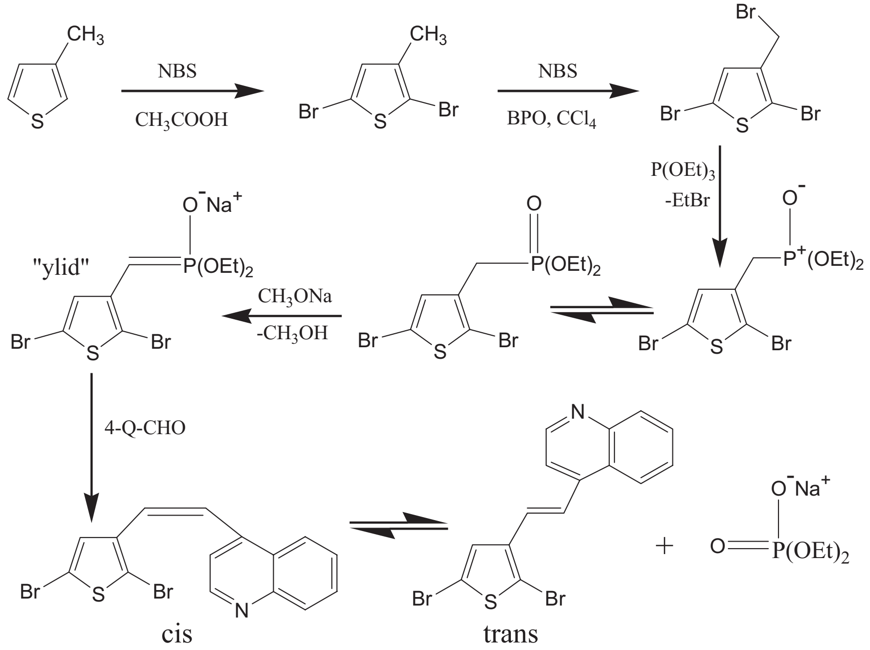
The preparation of polymer **V** was performed by means of Suzuki coupling of 9,9-dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl)-fluorene (**I**) and the 2,5-dibromo-3-[2-(pyren-1-yl)vinyl]-thiophene. Synthesis of the latter was published recently.[7] The coupling proceeded (reflux 85 °C, 48 h) in an aqueous 15% $NaHCO_3$/THF (1:1 by vol.) two phase system under



V



VI

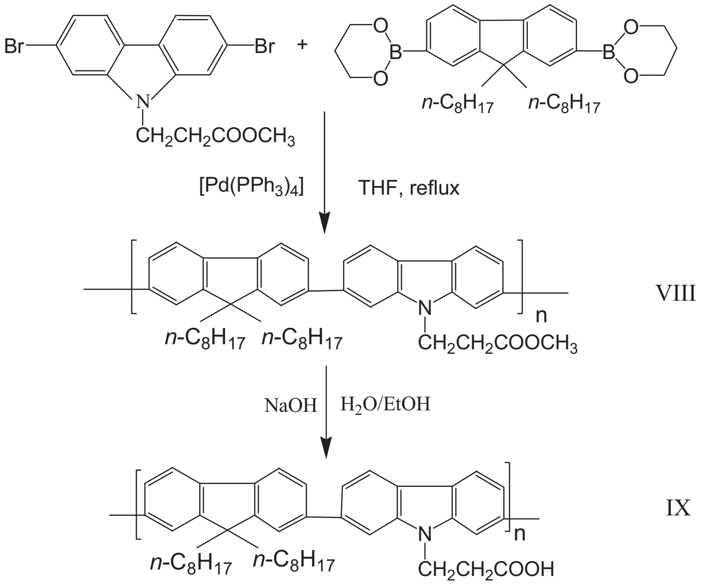


Scheme 3.

argon in the presence of tetrakis(triphenylphosphin)palladium catalyst. After end-capping (**I**: 5 h at 85 °C; 2-ethylhexylbromide: 12 h at 75 °C) the reaction mixture was poured into methanol/water (5:1 by vol.), the crude **V** was filtered off and purified by a double reprecipitation from THF into methanol. The structure of **V** was confirmed by ^{1}H NMR and FT IR spectroscopy and the $M_w = 12\,800$, $M_n = 4\,500$ and $p = 2.84$ values were determined by GPC in THF.

For the synthesis of polymer **VI** it was necessary to prepare the 2,5-dibromo-3-[2-(quinolin-4-yl)vinyl)thiophene (Scheme 3). 3-Methylthiophene was brominated with *N*-bromosuccinimide in two steps to get 2,5-dibromo-3-(bromomethyl)thiophene. Following the Horner-Wadsworth-Emmons reaction mechanism[8,9], the 2,5-dibromo-3-(bromo-methyl)thiophene reacts with triethyl phosphite to form 2,5-dibromo-3-thienylmethyl diethylphosphonate, which was converted to (2,5-dibromo-3-thenyliden)-diethoxynatrium-oxyphosphoran ("ylid") by sodium methoxide. Without isolation of these intermediates, the 2,5-dibromo-3-[2-(quinolin-4-yl)vinyl]thiophene was obtained after addition of quinoline-4-carboxaldehyde (4-Q-CHO). The product was characterized by the elemental analysis, ^{1}H NMR ($CDCl_3$), FT IR, and TLC. Yield: 22%, m. p. 154–155 °C. The TLC indicated the presence of two conformers (cis and trans) immediately after reaction. By means of GC-MS it was found out that after reaction the sample contains 60% of cis- and 40% of trans-isomer, whereas 24 h later, there was 1% of cis- and 99% of trans-isomer. In the case of 2,5-dibromo-3-[2-(pyren-1-yl)vinyl]thiophene the cis form was not detected at all, probably because of steric reason caused by bulky pyrene. On the other hand, in the case of 2,5-dibromo-3-(non-1-enyl)thiophene, i. e. for alkyl chain, the ratio of trans:cis isomers was found to be 2:1 (GC-MS, ^{1}H NMR) and stable in time. The 2,5-dibromo-3-(non-1-enyl)thiophene was prepared according to Scheme 3 replacing the 4-Q-CHO by the 1-octanal.

The polymer **VI** was prepared by Suzuki polycondensation of **I** and the 2,5-dibromo-3-[2-(quinolin-4-yl)vinyl]thiophene. The reaction proceeded (90 °C, 16 h) in an



Scheme 4.

aqueous 2 M K_2CO_3/toluene (3:2 by vol.) two phase system under argon and in the presence of tetrakis(triphenylphosphin)-palladium catalyst. After end-capping (**I**: 2 h at 90 °C; 2-ethylhexylbromide: 2 h at 90 °C) the reaction mixture was poured into methanol and a yellow polymer was filtered off. The crude material was extracted in a Soxhlet apparatus with acetone to remove the oligomers ($M_w = 1\,700$, $M_n = 1\,460$ and $p = 1.17$) and with THF to obtain the main fraction of **VI** ($M_w = 8\,400$, $M_n = 5\,860$ and $p = 1.43$). The structure of **VI** was further confirmed by ^{1}H NMR and FT IR spectroscopy.

Synthesis of poly{[9,9-dioctylfluorene-2,7-diyl]-*alt*-[9-(2-methoxycarbonylethyl)-carbazole-2,7-diyl]} (VIII)

Polymer **VIII** was synthesized by means of Suzuki coupling of 9,9-dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl)fluorene (**I**) and the methyl 3-(2,7-dibromocarbazole-9-yl)propionate (Scheme 4). The coupling reaction proceeded (90 °C, 64 h) in an aqueous 15% $NaHCO_3$/toluene (1:1 by vol.) two phase system under argon and in the presence of tetrakis(triphenyl-phosphin)palladium catalyst. After end-capping (I: 3 h at 90 °C; 2-ethylhexylbromide: 4 h at 90 °C) the reaction mixture was poured into methanol/water 5:1 (by vol.) and a yellow-green polymer was filtered off and dried. The crude material was reprecipitated from THF into methanol to get a yellow fluorescent polymer **VIII**. The structure of **VIII** was confirmed by ^{1}H NMR and FT IR spectroscopy and the $M_w = 18\,500$, $M_n = 8\,400$ and $p = 2.20$ values were determined by GPC in THF.

The conjugated polyacid **IX** was prepared by alkaline hydrolysis (10% NaOH in methanol/water (3:1 by. vol.)) of **VIII.** The hydrolysis took place at 80 °C for 5 h. After cooling and acidification (HCl) the yellow cloudy polymer precipitated from the solution. The ^{1}H NMR (loss of -O-CH_3 protons) and FT IR (-COOH at 1713 cm^{-1}) spectroscopy confirmed a complete hydrolysis of the ester groups.

The monomer methyl 3-(2,7-dibromocarbazole-9-yl)propionate was synthesized by nucleophilic addition of 2,7-dibromocarbazole to double bond of methyl acrylate (Michael addition – see Experimental).

Conclusion

The synthesis of 3,5-di-terc.butylphenyl 2,5-dibromobenzenesulfonate was improved and its copolymer with 9,9-dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl)fluorene was prepared and characterized. The methyl 3-(2,7-dibromocarbazole-9-yl)propionate and 2,5-dibromo-3-[2-(quinolin-4-yl)-vinyl]thiophene as new monomers for conjugated polymers were synthesized and their copolymers with 9,9-dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl)fluorene were prepared and characterized. The poly{[9,9-dioctylfluorene-2,7-diyl]-*alt*-[9-(2-methoxycarbonylethyl)-carbazole-2,7-diyl]} was used as an active layer in organic light-emitting device.[10]

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