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Syntheses of Special Monomers for π-Conjugated Polymers

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Summary: Tailored monomers based on the activated esters of 2,5-dibromo-benzoic and 2,5-dibromobenzene-1-sulfonic acids or 3-substituted 2,5-dibromothiophene suitable for the Suzuki, Yamamoto or Grignard metathesis (GRIM) coupling reactions were synthesized and characterized by the melting point, elemental analysis, ^{1}H NMR, FT IR, and TLC. The Horner-Wadsworth-Emmons reaction was utilized for the preparation of 3-(arylvinyl)-2,5-dibromothiophenes and the 4-nitrophenol or *N*-hydroxysuccinimide for the preparation of activated esters. A monomer with β-diketone active structure was prepared and characterized as well.

Keywords: activated ester; β-diketone; Horner-Wadsworth-Emmons reaction; pyrene derivative; quinoline derivative; substituted thiophene

Introduction

π-Conjugated polymers[1] are widely used in polymer light-emitting diodes, polymer field effect transistors and polymer photovoltaic cells. 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. To modify the electronic properties of polythiophene, such as redox cycling,[2] band gap,[3] and photovoltaic behavior,[4] aromatic substituents have been introduced into the polymers. Poly(3-arylthiophene)s have improved the doping capacity and cyclability in comparison with polythiophene.[4] To improve the photoconductivity, the 2-(4-nitrophenyl)vinyl group was introduced into the 3-position of polythiophene.[5] Although the polymers with attached conjugated 2-(nitro- or dinitrophenyl)vinyl side chains have been reported in the literature, they were synthesized by oxidation polymerization and they had irregular and random structure. Recently,[6] polythiophenes with conjugated phenylenevinylene side chains of different lengths were synthesized by the GRIM or Stille methods. Their backbone side chain conjugation was studied by UV-vis absorption spectroscopy. It was found that the polymers possess a strong and broad absorption in the visible region from 350 to 650 nm and hence are promising for the application in polymer solar cells. In this paper, we synthesized 2,5-dibromothiophene monomers containing conjugated pyrene or quinoline moieties in the 3-position. In search for new photovoltaic conjugated polymer materials, the monomers will be utilized for the syntheses of polythiophenes by the GRIM method or for syntheses of alternating thiophene copolymers by the Suzuki coupling. For the synthesis of activated esters of aromatic dibromo acids, see the discussion below.

Experimental Part

2,5-Dibromo-1,4-xylene, 2,5-dibromobenzene-1-sulfochloride, thionyl chloride, *N*-hydroxysuccinimide, 4-nitrophenol, 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione, *N*-bromo-succinimide (NBS), dibenzoyl peroxide (BPO), pyrene-1-carboxaldehyde (Pyr-CHO), triethyl

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phosphite, sodium methoxide, and quinoline-4-carboxaldehyde (4-Q-CHO) were commercial products (Aldrich, Fluka). Triethylamine was refluxed for 3 h with calcium hydride and distilled. Tetrahydrofuran (THF) was refluxed for 8 h with $Na/LiAlH_4$ and fractionally distilled. The other solvents and chemicals (Lach-Ner, Ltd., Neratovice, Czech Republic) were of analytical grade (p.a.) and were used as received.

^1H NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz in deuterated dimethyl sulfoxide (DMSO-d_6) or chloroform ($CDCl_3$) using hexamethyldi-siloxane 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.

Results and Discussion

Syntheses of Monomers with Activated Esters

The preparation of activated esters of 2,5-dibromo-4-methylbenzoic and 2,5-dibromobenzene-1-sulfonic acids was performed to obtain the materials for synthesis of π-conjugated polymer systems, where the second comonomer would be a heterocyclic or aromatic diboronic acid or its ester. The goal is to introduce a reactive group into the π-conjugated system for further modification with optical or photovoltaic active structures. There are two possibilities: (a) synthesis of the π-conjugated polymer with activated ester groups followed by modification reaction with an active structure; (b) comonomer synthesis from an activated ester and active structure followed by the Suzuki coupling giving an active π-conjugated polymer.

N-Hydroxysuccinimidyl 2,5-dibromo-4-methylbenzoate **(III)** was prepared after Scheme 1: 2,5-Dibromo-4-methylbenzoic acid **(I)** was prepared by oxidation of 2,5-dibromo-1,4-xylene with nitric acid and its chloride **II** by subsequent reaction with thionyl chloride. The intermediate **II** and *N*-hydroxysuccinimide in dry THF and in the presence of triethylamine give the ester **III**, which was characterized by the elemental analysis, ^1H NMR (DMSO-d_6), and FT IR. Yield: 50% (relative to **I**); m. p. 190 °C.

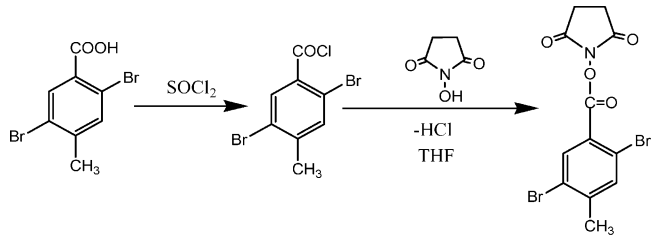
$C_{12}H_9Br_2NO_4$ (391.02): Calc. C 36.86, H 2.32, Br 40.87, N 3.58; Found C 37.05, H 2.43, Br 40.72, N 3.55.

4-Nitrophenyl 2,5-dibromobenzene-1-sulfonate **(VI)** was prepared according to Scheme 2 by the reaction of 2,5-dibromobenzene-1-sulfochloride **(IV)** with 4-nitrophenol **(V)** in the presence of triethylamine. The product **VI** was characterized by the elemental analysis, ^1H NMR (DMSO-d_6), FT IR, and TLC (toluene). Yield: 95%; m. p. 135 °C.

$C_{12}H_7Br_2NO_5S$ (437.06): Calc. C 33.00, H 1.61, Br 36.56, N 3.20, S 7.34; Found C 33.21, H 1.69, Br 35.51, N 3.25, S 7.13.

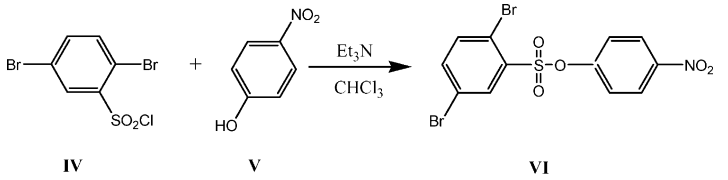
Synthesis of Monomer with Active β-Diketone Structure

2-(1,3-Dioxo-3-phenylpropyl)phenyl 2,5-dibromo-4-methylbenzoate **(VIII)** was synthesized after Scheme 3: 2,5-Dibromo-3-methylbenzoyl chloride **(II)** was reacted with a β-diketone, 1-(2- hydroxyphenyl)-3-



I II III

Scheme 1.



IV V VI

Scheme 2.

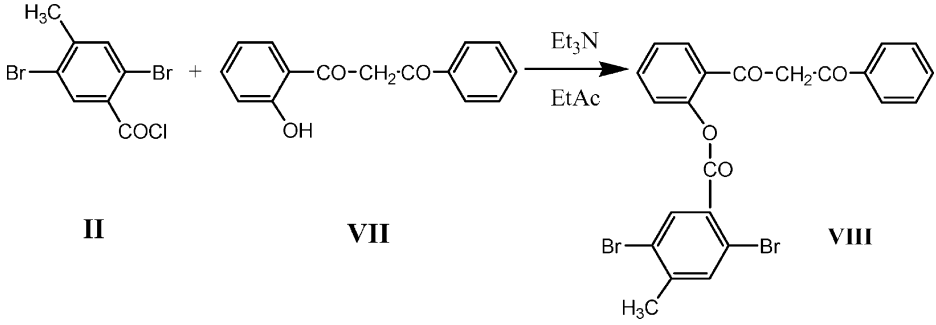
phenylpropane-1,3-dione **(VII)**, in ethyl acetate in the presence of triethylamine. The reaction mixture was washed with a saturated aqueous $NaHCO_3$ solution and water and then gradient-chromatographed on a column (40×3 cm) packed with silica gel (Silpearl, Kavalier Sázava, CZ) in toluene/hexane(1:1) → toluene. The product **VIII** was isolated in a yield of ca. 30%. An unreacted β-diketone **VII** and 2,5-dibromo-4-methylbenzoic acid **(I)** as a transformation product of chloride **II** were isolated from the reaction mixture as well. Product **VIII** was characterized by the elemental analysis, ^{1}H NMR (DMSO-d_6), FT IR, and TLC (toluene/butyl acetate 14:1 by vol.). From the spectra it was proved that **VII** reacts in the keto form rather than as enol form.

$C_{23}H_{16}Br_2O_4$ (516.20): Calc. C 53.52, H 3.12, Br 30.96; Found C 53.03, H 2.90, Br 31.34.

Synthesis of 2,5-dibromo-3-[2-(pyren-1-yl)vinyl]thiophene (XII)

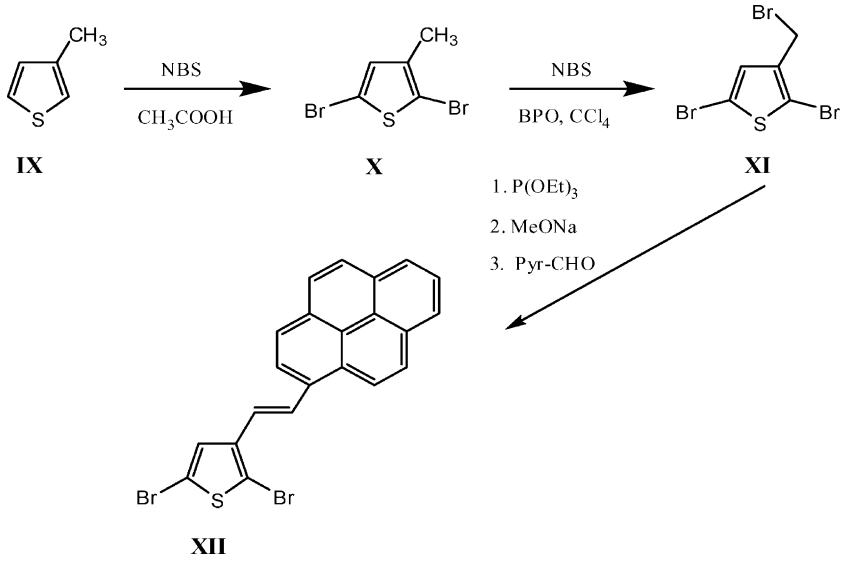
The monomer **XII** was prepared for the synthesis of π-conjugated polymers containing a thiophene moiety in the backbone and pyrene fluorophore in the side chain. The pyrene is conjugated with the thiophene backbone via vinylene linkage. 3-Methylthiophene **(IX)** was brominated with *N*-bromosuccinimide in two steps (Scheme 4). First, we brominated the thiophene ring in polar solvent ($CHCl_3$/acetic acid) to get 2,5-dibromo-3-methylthiophene **(X).** In the second step we brominated the methyl group in nonpolar tetrachloromethane in the presence of dibenzoyl peroxide to get 2,5-dibromo-3-(bromomethyl)thiophene **(XI)**.

The pyrene derivative of thiophene **XII** was synthesized by the reaction of **XI** with pyrene-1-carboxaldehyde in the presence of triethyl phosphite and sodium methoxide following the Horner-Wadsworth-Emmons reaction mechanism (Scheme 4).[7,8] Reaction products were chromatographed on a column (50×4 cm) packed with silica gel (Silpearl, Kavalier Sázava, CZ) in toluene/hexane (1:1) → toluene → $CHCl_3$/butyl acetate (1:1). The product **XII** was isolated from the first eluate and crystallized from toluene/heptane (1:1). Yield: 32%, m. p. 177–178 °C. The unreacted Pyr-CHO followed. The **XII** was characterized by the elemental analysis, ^{1}H NMR ($CDCl_3$), FT IR, and TLC (toluene).

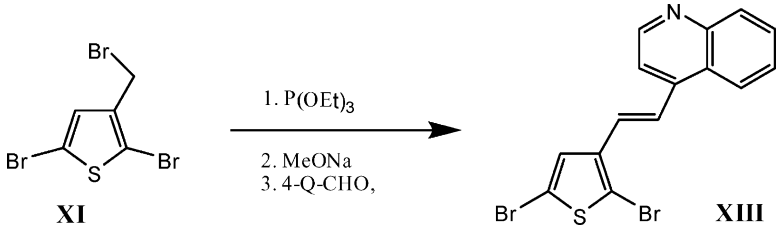


II VII VIII

Scheme 3.



Scheme 4.



Scheme 5.

$C_{22}H_{12}Br_2S$ (468.22): Calc. C 56.44, H 2.58, Br 34.13, S 6.85; Found C 56.46, H 2.48, Br 34.10, S 6.88.

Synthesis of 2,5-dibromo-3-[2-(quinolin-4-yl)vinyl]thiophene (XIII)

In a close analogy to the preparation of 2,5-dibromo-3-[2-(pyren-1-yl)vinyl]thiophene we synthesized also the 2,5-dibromo-3-[2-(quinolin-4-yl)vinyl]thiophene **(XIII)** using quinoline-4-carboxaldehyde (4-Q-CHO) (Scheme 5). It was characterized by the elemental analysis, ^{1}H NMR ($CDCl_3$), FT IR, and TLC (toluene/butyl acetate/triethylamine 70:70:1 by vol.). Yield: 22%, m. p. 154–155 °C.

$C_{15}H_9Br_2NS$ (395.12): Calc. C 45.60, H 2.30, Br 40.45, N 3.54, S 8.12; Found C 46.12, H 2.28, Br 39.94, N 3.75, S 7.95.

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[1] T. A. Skotheim, J. R. Reynolds, Eds., *Conjugated Polymers, Handbook of Conducting Polymers*, 3rd ed., CRC Press Taylor & Francis Group, Boca Raton **2007**.
[2] P. G. Pickup, *Mod. Aspects Electrochem.* **1999**, *33*, 549.
[3] Q. T. Zhang, J. M. Tour, *J. Am. Chem. Soc.* **1998**, *120*, 5355.

[4] G. Casalbore-Micely, M. C. Gallazzy, S. Zecchin, N. Camaiony, A. Geri, C. Bertarelli, *Adv. Funct. Mater.* **2003**, *13*, 307.
[5] Y. Greenwald, G. Cohen, J. Poplawski, E. Ehrenfreund, S. Speiser, D. Davidov, *J. Am. Chem. Soc.* **1996**, *118*, 2980.
[6] Hou, L. Huo, C. He, C. Yang, Y. Li, *Macromolecules* **2006**, *39*, 594.
[7] L. Horner, H. Hoffmann, J. H. G. Wippel, G. Klahre, *Chem. Ber.* **1959**, *92*, 2499.
[8] W. S. Wadsworth, Jr., W. D. Emmons, *J. Am. Chem. Soc.* **1961**, *83*, 1733.

