

Towards the template synthesis of conjugated pyrrole based oligo-heteroaryls

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Synthesis of polymers and Oligomers with various interesting physical properties is a rewarding task for the chemist. oligo-heteroaryls are a significant class of organic compounds due to their wide applicability in various fields. Here, in this article, the synthetic studies directed for the preparation of conjugated pyrrole based oligo-heteroaryls was reported. The successful synthesis of double stranded polymeric ladderphane using ring opening metathesis polymerizations (ROMP) and palladium catalyzed Suzuki coupling were the key feature of this work. Hydrolysis of the double stranded polymer was unsuccessful due to its insoluble nature. The effort to increase the solubility of the double stranded polymers by the incorporation of long-chain aliphatic counterpart is underway in our laboratory.

Keywords: Oligo-heteroaryls, ladderphane, conducting polymer, polypyrrole, ROMP.

Introduction

Conductive polymers are known as a class of organic materials containing exclusive electrical and optical properties. In 2000 three scientists Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa have received Nobel Prize for their discovery and development of conducting polymers. They established that if in a polymer structure alternating single and double bonds are linked with their carbon atoms, and electrons are either removed through oxidation or introduced through reduction then that polymer can able to conduct electricity. Conductive polymers¹ are an important class of materials since they show good electrical conductivity, chemical stability and have large applicability in numerous areas like sensing, biotechnology, supercapacitors, solar cells, electromagnetic shielding, corrosion protection, microwave shielding, electrochromism, printed electronic circuits, organic light-emitting diodes, etc.

It has been documented that, the photophysical and electronic properties of the conducting polymers can be changed after insertion of heteroaromatic rings in conjugation with polymers backbone². Different methods are known in literature for the synthesis of conjugated oligoaryls among them transition metal (generally Pd) catalyzed cross-coupling reactions and annulation protocols are generally used.

The use of thiophene is well documented as a useful unit in the preparation of conjugated polymers compare to its nitrogen analogue pyrrole³⁻⁶. Since nitrogen is more electronegative than sulphur, pyrrole shows high oxidation potential and low aromaticity than thiophene. The optical absorption of oligopyrroles is somewhat blue shifted relative to oligothiophenes. It has been found from theoretical calculations that the bandwidths, as well as intrinsic charge carrier mobility in case of oligothiophenes can be relatively similar to oligo-pyrroles. Therefore, we planned to synthesize and investigate the effect of N-heterocycle, pyrrole based heteroaryls oligomers in various photophysical studies (Fig. 1). Incorporation of various new pull moieties with cautiously selected push units was intended to implement using either Suzuki coupling or direct hetero-arylation polymerization process.

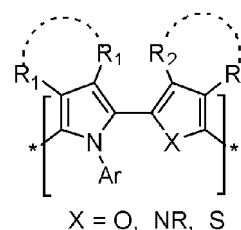


Fig. 1. Structure of oligo-heteroaryls.

Results and discussion

The previous work done by Prof. Luh's group proved the supremacy of the use of polynorbornene templates for living polymerization reactions with various pendant groups^{7–11}. Polynorbornenes have been appealing much interest as they show some characteristic properties that have thus been extensively studied for potential application in material science. Compared with double-stranded or triple-stranded polynorbornene, single-stranded polynorbornenes are more flexible, soluble which are easier to derive or modify for controlled synthesis. The most commonly used method to construct the single-stranded polynorbornene moiety is the ring-opening metathesis polymerization (ROMP) process. The ROMP of norbornenes initiated by Grubbs catalysts has proved to be living polymerization, and the formed linear polymers often have very low polydispersity index (PDI) values. These facts make it possible for one to controllably synthesize sharply-dispersed polynorbornenes by controlling the ratio of initiator and monomer. And the designedly introduced functional groups in the pendant moiety of such a kind of polynorbornenes can couple with each other to construct new polymeric backbones. It was assumed that the stereoselectivity of the polymerization process was controlled through the interactions between the pendent aryl groups in the backbone. Therefore, these polynorbornenes are used as a very suitable template for the synthesis of various functional polymers. The norbornene acid **1** (Fig. 2) was prepared (see, Supporting information) following Luh's methods¹² and used for the synthesis of monomer.

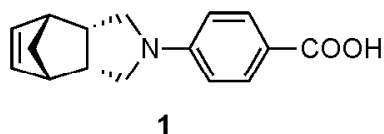
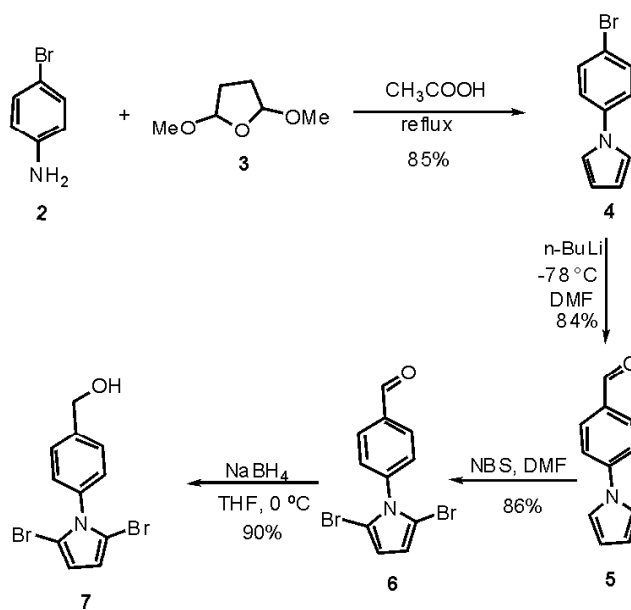


Fig. 2. Structure of norbornene acid **1**.

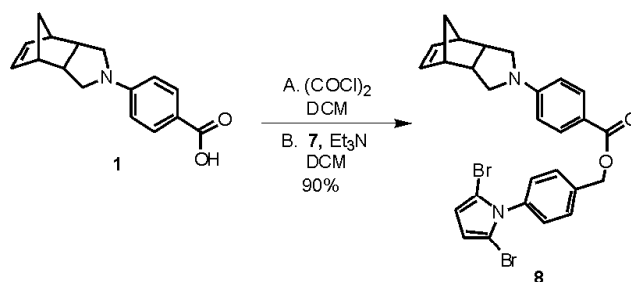
The synthesis of pyrrole partner was started by the reaction of 4-bromoaniline with compound **3** in presence of acetic acid which provide the N-aryl pyrrole **4** in good yield (Scheme 1). Now, the bromo-lithium exchange reaction of *n*-butyl lithium with aryl bromide **4** generates the phenyl lithium derivative which was quenched with DMF to obtain the aldehyde **5**. Bromination of compound **5** with *N*-bromosuccinimide (NBS) in DMF afforded the 2,5-dibromopyrrole



Scheme 1. Preparation of pyrrole partner.

derivatives **6** in good yield. Reduction of aldehyde **6** by sodium borohydride with careful monitoring the reaction (TLC), to prevent over reduced debrominated side-product, furnished the corresponding alcohol **7** in excellent yield.

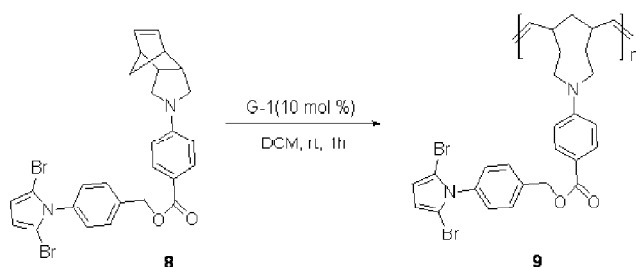
After successful synthesis of alcohol **7**, the required the monomer was prepared via esterification of alcohol **7** with norbornene acid **1** (Scheme 2). First, norbornene acid was converted to corresponding acid chloride with oxalyl chloride in dry DCM, which then reacts with alcohol **7** in presence of base triethylamine to afford the desired monomer in excellent yield.



Scheme 2. Synthesis of monomer **8**.

After the successful preparation of the monomer molecule, it was subjected to metathesis polymerization. Release of ring strain¹³ is the key factor for the ring opening

metathesis reactions. Ring opening metathesis polymerization reaction of monomer **8** in presence of 1st generation Grubbs catalyst (10 mol%) furnished the polymer **9** in good yield (Scheme 3). The ROMP reaction was terminated by the addition of electronically rich olefin ethyl vinyl ether. Gel Permeation Chromatography (GPC) results show that the polydispersity index (PDI) was 1.16 and the degree of polymerization (DP) is 10.040 (For GPC chromatogram and data, see Supporting information).



Scheme 3. ROMP of monomer **8**.

The preparation of double stranded polymer was performed via Suzuki coupling reaction with compound **10** (Scheme 4). The reaction of 2,5-thiophene diboronic acid with polymer **9** in presence of 2 mol% Pd(PPh₃)₄ afforded the insoluble double stranded polymer **11** in good yield. Hydrolysis of polymer **11** was unsuccessful and the starting material was returned completely. This is probably due to

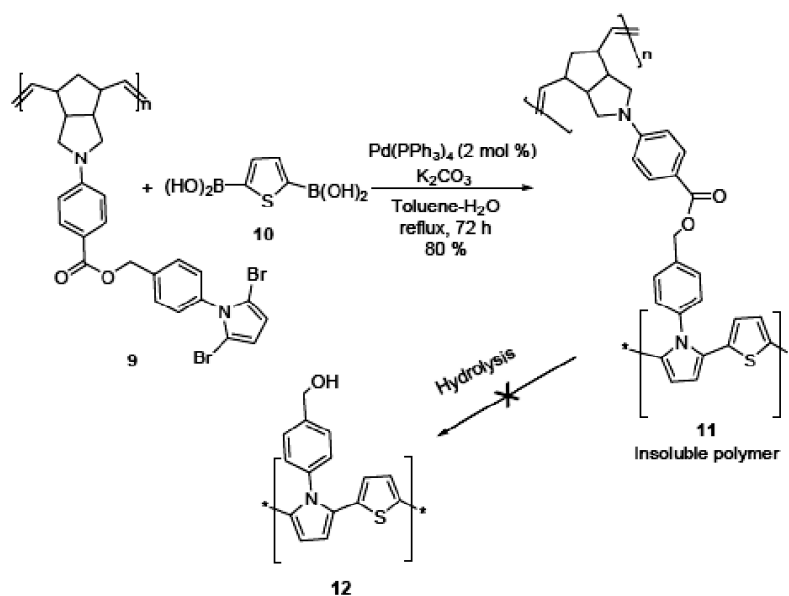
the solubility problem in the reaction milieu. At this end, our current work is focused to increase the solubility of the double stranded polymers by incorporation of long-chain aliphatic counterpart.

As expected, the signals in the ¹H NMR spectra are found to be broadened in the case of polymers compared to monomers. The integration of aromatic protons in the case of **8** and **9** are the same, only in case of **11** presence of two more protons proved the formation of double stranded polymer through the incorporation of thiophene moiety.

Experimental

Polynorbornene (9): Compound **8** (341 mg, 0.6 mmol) was dissolved in CH₂Cl₂ (3 mL) at room temperature under N₂ atmosphere. In this solution, a solution of Grubb's 1st generation catalyst (50 mg, 0.0607 mmol, 10 mol%) in CH₂Cl₂ (5 mL) was added. After the addition of the catalyst, stirring was continued for 1 h at room temperature and then ethyl vinyl ether (1 mL) was added to quench the reaction and stirred for 20 min. Then the volume of the reaction mixture was reduced under vacuum, and the residual solution was poured into ethyl acetate (30 mL) to get a crude precipitate. This precipitate was rinsed with EtOAc and dried under reduced pressure to obtain desired polymer **9** (324 mg, 95%).

¹H NMR (CDCl₃, 400 MHz): δ 7.91 (br, 2H), 7.50–7.48 (br, 2H), 7.31–7.18 (br, 2H), 6.54–6.46 (br, 2H), 6.36 (br, 2H),



Scheme 4. Synthetic effort for the preparation of oligo-pyrrole **12**.

5.34 (brs, 4H), 3.24 (br, 4H), 2.88 (br, 2H), 2.73 (br, 2H), 1.78 (br, 1H), 1.36 (br, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 166.5, 151.0, 137.9, 137.1, 131.9, 131.7, 131.5, 129.0, 128.6, 128.2, 128.0, 126.0, 116.5, 112.5, 111.5, 102.2, 65.8, 64.9, 49.5, 46.8, 46.6, 46.4, 44.8, 44.5, 15.2, GPC: M_n = 5706; PDI = 1.161.

Double stranded polymer (11): In a two-neck flask fitted with a condenser, compound **10** (258 mg, 1.5 mmol), polymer **9** (852 mg, 1.5 mmol), CsF (685 mg, 4.5 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (35 mg, 0.03 mmol, 2 mol%) and dry THF (20 ml) was added. The resulting solution was degassed with argon. Then it was refluxed for 48 h under an inert atmosphere and allowing cooling to room temperature to get a crude precipitate and washed with toluene, CH_2Cl_2 , and H_2O (2×50 mL each) to afford polymer **11** as brown solid (780 mg, 80%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.91–7.84 (br, 2H), 7.50–7.43 (br, 2H), 7.42–7.20 (br, 5H), 6.49 (br, 2H), 6.28 (br, 2H), 5.34 (brs, 4H), 3.23 (br, 4H), 2.89 (br, 2H), 2.73 (br, 2H), 1.79 (br, 1H), 1.37 (br, 1H).

Conclusion

The polynorbornene template containing pendant pyrrole moieties and followed by conjugated pyrrole based oligo-heteroaryl was successfully synthesized using palladium catalyzed Suzuki coupling. This synthetic effort will help the synthetic community for the synthesis of pyrrole monomer as well as polymers. In addition, pyrrole based oligo-heteroaryls were found to be very low solubility. The preparation of pyrrole compound bearing a long alkyl chain to resolve the solubility issues are currently underway in our laboratory.

Supporting information

NMR spectra of all unknown compounds were provided as supporting documents.

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