

FUNCTIONALIZATION OF REGIOREGULAR HEAD-TO-TAIL POLY(3-ALKYLTHIOPHENES) SIDE CHAIN

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Introduction

Conjugated polymers possess several intriguing properties including high electrical conductivity, fast and large nonlinear optical responses and visible wavelength chromaticity. Layer by layer conducting polymer structures are even more interesting because they offer many potential advantages in device application, including sensor application¹, state charge separated assemblies for photo voltaics² and light emitting diodes³. Polythiophene bearing carboxylic acid and amine side chains can be applied in constructing layer by layer polymer assemblies. Polythiophene with short acid side chains have been synthesized by McCullough et. al⁴, and Iraqi has functionalized the side chain of 3-hexylbromothiophene by 2-carboxyanthraquinone (Anth)⁵. However, polythiophenes bearing acid and amine side chains have not been synthesized by Post-polymerization Functionalization method yet.

We have synthesized 3-heptonic acid polythiophene by both Stille and post-polymerization functionalization method.

Experimental

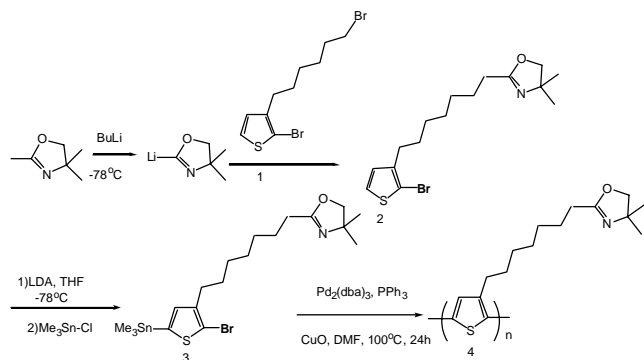
Materials. All the solvents were dried before using. 2,4,4-trimethyl-2-oxazoline(Aldrich) was dried over calcium hydride.

Stille Method. (Scheme 1) 2-Bromo-3-(2(4,4-dimethyloxazolin-2-yl)heptyl)-5-trimethylstannylthiophene **3** was dissolved in DMF and the solution was purged with nitrogen for 15 min.. Tris (dibenzylidene acetone) dipalladium(0) was added, followed quickly by copper(II) oxide and triphenylphosphine. The solution was heated to 100°C and stirred over night. The reaction was quenched by pouring into methanol.

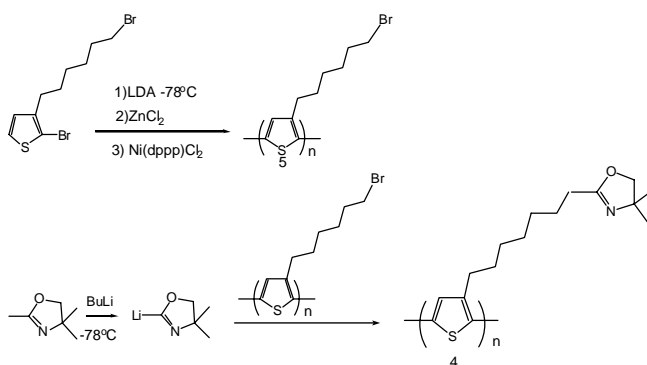
Post-polymerization Functionalization Method. (Scheme 2) Poly(3-bromohexylthiophene) **5** was made by McCullough Method⁶. 2,4,4-Trimethyl-2-oxazoline was dissolved in THF and cooled to -70°C. BuLi was added dropwise, maintaining the temperature below -65°C. This was stirred 1hr., then polymer THF solution was added quickly and the cooling bath was removed, stirred for 30 min. The reaction was quenched by adding methanol.

Hydrolysis of Polymer. (Scheme 3) Deprotection of polymer **4** was readily achieved by acid hydrolysis using hydrochloride acid aqueous solution.

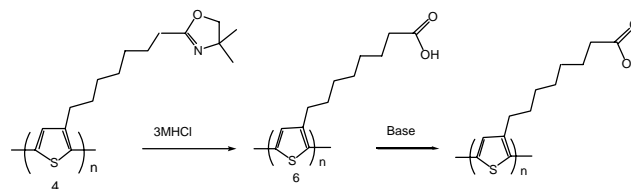
Amine Functionalization of Poly(3-bromohexylthiophene). (Scheme 4) Poly(3-bromohexylthiophene) **5** was dissolved in THF. After the solution was heated to refluxing temperature, sodium bis(trimethylsilyl)amide was added and stirred for 30min., then hydrochloride aqueous solution was added. The solution was stirred for 30min. and quenched in hexane.



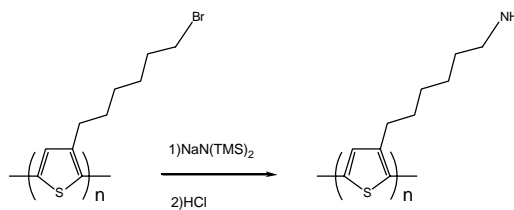
Scheme 1. Synthesis of PTHA (in protected form) by using a modified Stille cross-coupling route.



Scheme 2. Synthesis of PTHA (in protected form) by using post-polymerization functionalization method.



Scheme 3. Hydrolysis of the Poly(3-(2(4,4-dimethyloxazolin-2-yl)heptyl)thiophene).



Scheme 4. Synthesis of Polythiophene with Amine Substituted Side Chain.

Results and Discussions

Poly(3-hexylbromothiophene) **5** and Poly(3-(2(4,4-dimethyloxazolin-2-yl)heptyl)thiophene) **4** were analyzed by ¹H-NMR, MALDI-TOF and GPC. The polymer made from post-polymerization functionalization method proved to have higher molecular weight and better regioregularity than the polymer made from Stille method. The NMR of polymer **4** and **5** (Figure 2 and Figure 1) showed that all bromide groups were converted to 2,4,4-trimethyl-2-oxazoline groups in post-polymerization functionalization because the triplet of the methyl group adjacent to bromine completely disappeared in Figure 2. Treatment of polymer **6** with a variety of inorganic and organic bases yielded water-soluble salts. Solutions of the salts varied from purple to red. These results showed that post-polymerization functionalization method was efficient to modify side chains of polythiophene.

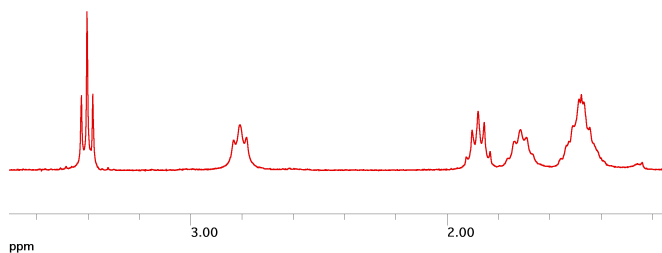


Figure 1. $^1\text{H-NMR}$ of poly(3-hexylbromothiophene).

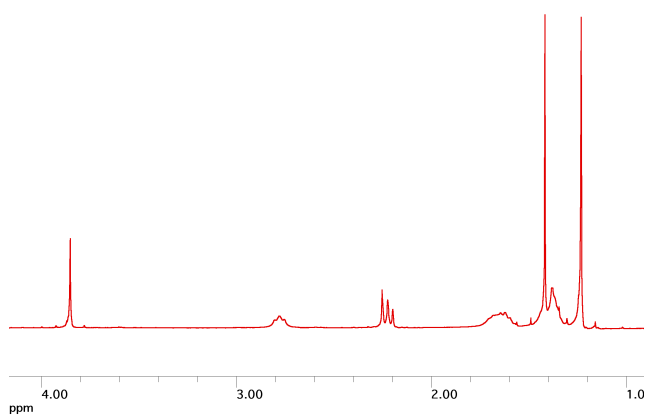


Figure 2. $^1\text{H-NMR}$ of Poly(3-(2(4,4-dimethyloxazolin-2-yl)heptyl)-thiophene).

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References

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