An Organozinc Route for the Preparation of Functionalized Poly-3-alkylthiophenes

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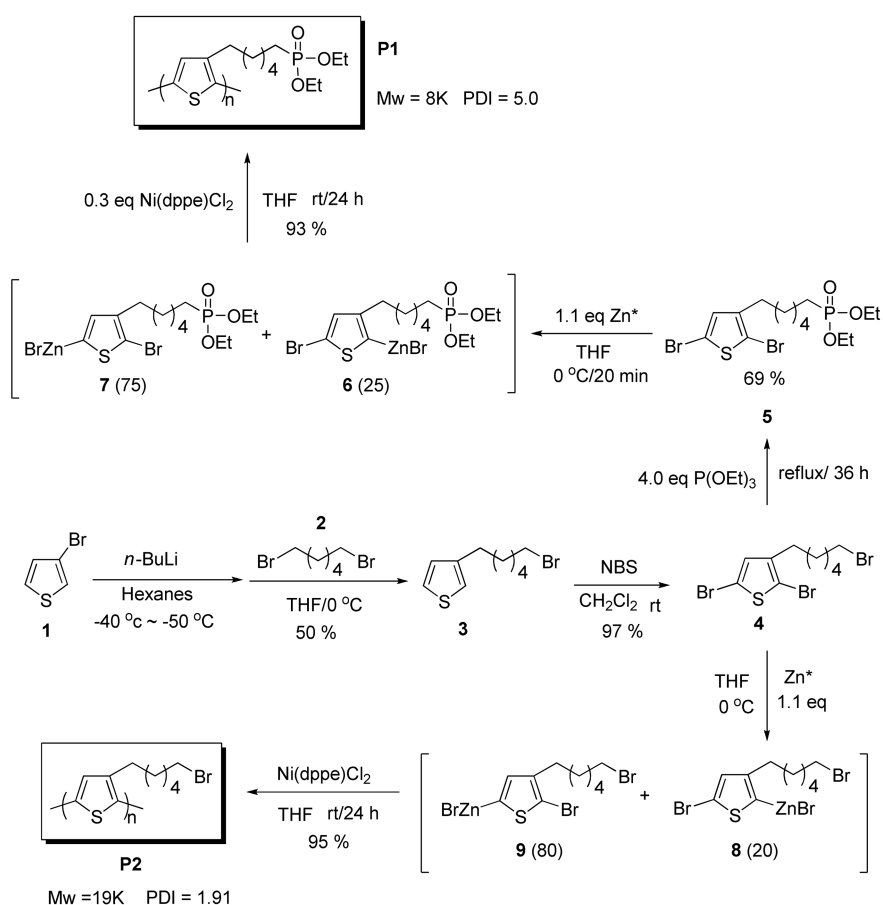
In 1980, two groups reported the synthesis of unsubstituted polythiophene utilizing 2,5-dibromothiophene *via* a Ni-catalyzed method.[1] Since then, several different types of catalysts were employed for the polymerization of 2,5-dibromothiophene.[2] Unfortunately, low molecular weight polymers generally resulted from these attempts. Even though these methods provided interesting materials, there was a big barrier to utilize this polymer due to the lack of processability. In order to overcome this difficulty, an alkyl chain was introduced on 3-position of the thiophene ring. Of the many methods, metal-catalyzed cross-coupling polymerization was most frequently used, and the synthesized polythiophenes containing an alkyl group equal or greater than C4 are soluble in common organic solvents.[3] This well-established method, however, has significant drawbacks generating inconsistent results and regiorandom polymers. As is known, the regioregularity of the 3-substituted polythiophene plays a critical role in electronic and optical devices.[4] Consequently, developing the efficient methods of preparing highly regioregular head-to-tail poly-3-alkylthiophenes is of high value. This goal was achieved by two research groups, seperately. Rieke and coworkers reported a synthetic approach to the preparation of regioregular poly-3-alkylthiophene utilizing thienylzinc bromide.[5] The other synthetic method, the McCullough method, was performed by using the Kumada cross-coupling method.[6]

Even though extensive studies have focused on the preparation and application of the linear alkyl-substituted polythiophenes, there is an increasing need to develop various types of polythiophenes because these polymers have a wide range of potential possibilities of being used in material chemistry. Recent reports also showed that the chemical composition of the P3HT significantly affect the device performance. Therefore, many efforts were devoted to finding new strategies for the preparation of functionalized P3HTs. One of the first attempts was to introduce a heteroatom on the thiophene ring. This has been accomplished wherein the thiophene has an oxygen atom directly attached to the ring.[7] Furthermore, polythiophenes containing other functionalities such as an alcohol, ester, and urethane were prepared.[8] In addition, thiophenes bearing a carboxylate or sulfonate functionality were introduced for the synthesis of water-soluble polythiophenes.[9] More importantly, a recent report showed that P3HT-phosphonic ester was employed to improve the power conversion efficiencies in hybrid solar cells.[10] We have developed a versatile synthetic method for polythiophenes bearing a phosphonic ester functionality on the 3-position. In addition, we wish to report more results obtained from the study on the preparation of polythiophenes bearing several different functional groups.

In 2003, McCullough *et al.* reported the synthesis of poly[3-(6-diethylphosphorylhexyl)thiophene] utilizing the Stille method.[11a] This synthesis required a difficult monobromination as well as cryogenic condition (−70 °C) for the preparation of the reactive organometallic intermediate. This study also pointed out that the GRIM and Kumada methods are not reliable for the preparation of polythiophenes containing the phosphonic ester moiety. Although poly[3-(11-diethylphosphorylundecyl)thiophene] was also synthesized by Kowalik and Tolbert using an organozinc route,[11b] we have focused on a more practical synthetic method. It was accomplished starting with readily available 2,5-dibromo-3-(6-bromohexyl)thiophene (**4**), which is easily prepared by known literature methods. The use of this route provided a huge advantage over the previously reported studies requiring a regioselective monobromination of thiophene ring. As shown in Scheme 1, in our study, the phosphonate ester group was easily provided by the Michaelis-Arbuzov reaction with **4** which was readily obtained by the simple bromination of **3** with NBS. The oxidative addition of active zinc to **5** was completed in 20 min at 0 °C showing 75:25 ratio regioselectivity.[12] The resulting mixture of thienylzincs (**6** and **7**, Scheme 1) were polymerized in the presence of 0.3 mol % of Ni(dppe)Cl$_2$ at room temperature yielding the title polymer (**P1**) in 93%. The UV-vis analysis exhibited a λ_{max} of 440 nm in chloroform solution. This is compatible with the literature value (λ_{max} 442 nm).[11a] Analysis by MALDI-TOF MS showed peaks separated by 302 g/mol, which is the molecular weight of the repeating unit. GPC analysis (eluent: THF, calibration: polystyrene standard) of the chloroform fraction of the title polymer showed Mw of 8K with a PDI of 5.0.

Dibromothiophene **4** was also readily used for the preparation of poly[3-(6-bromohexyl]thiophene (**P2**, Scheme 1). Again, this procedure has a profound advantage specifically in large scale production over the reported procedures performed *via* either multiple step or under cryogenic conditions. The same conditions (0 °C in THF) as used for the polymer **1** in this study were employed for the preparation of organozinc reagents (**8** and **9**, Scheme 1) resulting in the
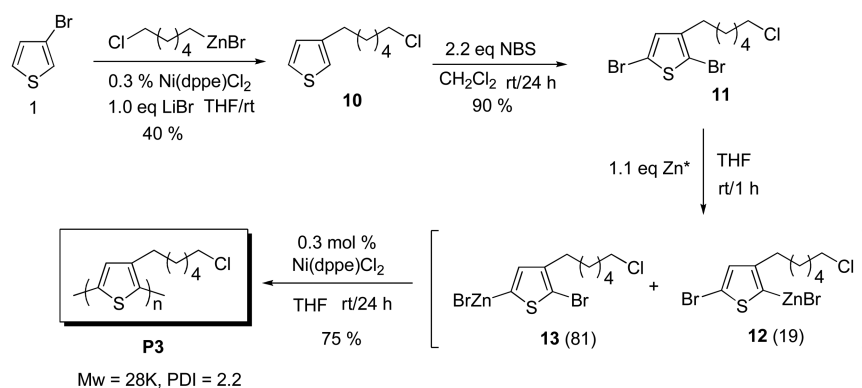
Scheme 1. Preparation of Poly[3-(6-diethylphosphorylhexyl)thiophene] (**P1**) and poly[3-(6-bromohexyl]thiophene (**P2**).

same ratio (20:80).[12] The subsequent polymerization was also carried out with 0.3 mol % of Ni(dppe)Cl$_2$ leading to the polymer (**P2**) in 95% isolated yield. The UV-vis spectral analysis of the polymer in chloroform solution showed an absorption band of λ_{max} 447 nm. The molecular weight was Mw of 19K by GPC (PDI = 1.91). The ^{1}H-NMR spectroscopy indicated 93% regioregularity.
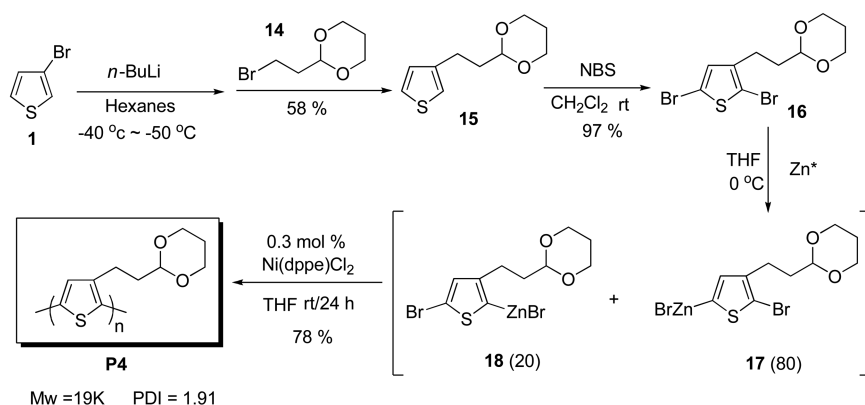
Poly[3-(6-chlorohexyl)thiophene] (P3). A schematic diagram is described in Scheme 2. The preparation of the title polymer (**P3**) was started with the coupling reaction of 3-bromothiophene and 6-chlorohexylzinc bromide which was readily prepared from the oxidative insertion of active

zinc to the corresponding alkyl halide. The subsequent reactions were carried out under either the same conditions (for bromination) or similar conditions (for metallation) giving rise to the corresponding products with satisfactory results. The typical conditions used for the polymerization of other thienylzinc reagents were employed in this study resulting in the formation of the desired polymer (**P3**) in 75 % isolated yield. The followings are the analytical data of **P3**: Mw = 28 K and PDI = 2.2 (GPC), λ_{max} = 445 nm (UV-vis), regioregularity = 94% (^{1}H-NMR), repeating unit = 200 (MALDI-TOF MS).

Poly[3-(2-propyl-1,3-dioxanyl)thiophene] (P4). The
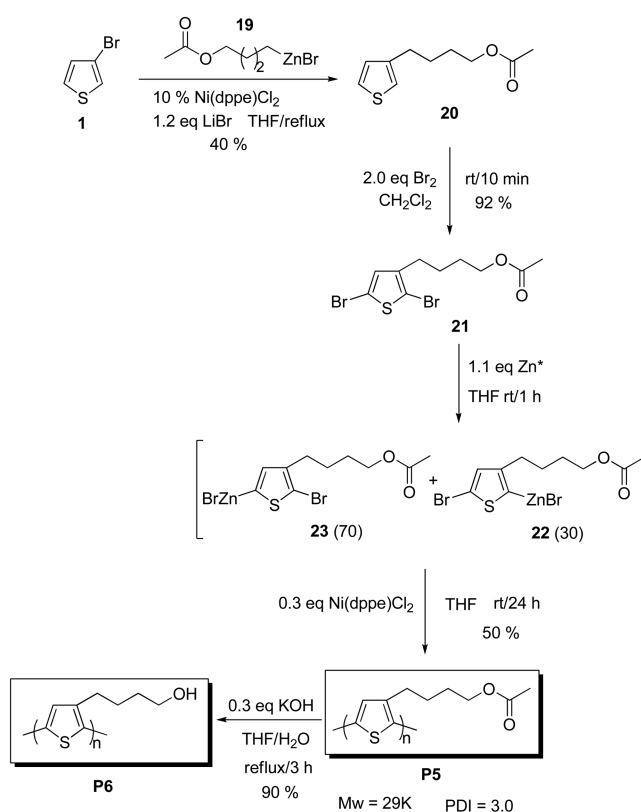

Scheme 2. Preparation of poly[3-(6-chlorohexyl)thiophene] (**P3**).

Scheme 3. Preparation of poly[3-(2-propyl-1,3-dioxanyl)thiophene] (**P4**).

synthetic strategy used for the preparation of aforementioned polymers **P1-P3** was expanded to develop polythiophenes containing different functional groups. First, as depicted in Scheme 3, an 1,3-dioxane functionality was successfully introduced to the polythiophene. It was accomplished utilizing the monomer 2,5-dibromo-3-(1,3-dioxanylethyl)thiophene (**16**) which was obtained by a two step-reaction; coupling reaction of 3-thienyl lithium with 2-(2-bromoethyl)-1,3-dioxane (**14**) leading to the coupling product **15** and then bromination with NBS. The resulting dibrominated thiophene **16** was treated with active zinc at 0 °C in THF providing two organozinc reagents, **16** and **17** with a ratio of 80:20.[12] In this case, Ni-catalyst worked very effectively for the subsequent polymerization leading to the regioregular polythiophene **P4** in 78% isolated yield. The polymer exhibited Mw of 19 K, by GPC (PDI = 1.9), and ^{1}H NMR analysis showed a high degree of regioregularity (98%) examined by the integration of methylene peak directly connected to the thiophene ring. The UV-vis spectroscopic analysis provided λ_{max} 442 nm in chloroform. A repeating unit of **P4** is 196 which is the corresponding value of the monomer confirmed by MALDI-TOF MS.

Poly[3-(4-acetoxylbutyl)thiophene] (P5) and Poly[3-(4-hydroxybutyl)thiophene] (P6). The synthesis of regioregular polythiophene bearing an ester (**P5**) or hydroxyl (**P6**) group is described in Scheme 4. As depicted, a hydroxyl-containing polymer was easily accomplished by the hydrolysis of the corresponding polymer **P5**. The synthesis of **P5** required the attachment of an ester functional group, which was accomplished using readily available 4-acetoxybutyl-zinc bromide (**19**) providing **20** in 40% isolated yield. Compound **21** was synthesized by treating **20** with bromine in CH$_2$Cl$_2$. In this case, despite of lower selectivity of the active zinc toward the brominothiophene (**21**), high regioregularity was observed in the title polythiophene (**P5**) (> 95%, by ^{1}H-NMR) with a moderate yield (50%). Analytical data are: Mw = 29 K, PDI = 3.0 (GPC), λ_{max} = 441 nm (UV-vis), and repeating unit = 196 (MALDI-TOF MS). As mentioned above, hydrolysis of polymer **P5** with KOH in a mixed solvent (H$_2$O/THF) at refluxing temperature led to polymer **P6**. Unfortunately, we were unable to collect reliable

Scheme 4. Preparation of poly[3-(4-acetoxylbutyl)thiophene] (**P5**) and Poly[3-(4-hydroxybutyl)thiophene] (**P6**).

spectroscopic data due to its poor solubility in organic solvents such as chloroform, THF, and methylene chloride.

Conclusions

In conclusion a versatile synthetic method for polythiophenes bearing a phosphonic ester functionality at the 3-position has been developed. In addition, this methodology has been employed for the preparation of polythiophenes bearing several different functional groups such as bromine, chlorine, an ester, and dioxane. The results are summarized in the Table below.

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Notes

Table 1. Properties of the polymers (**P1-P5**)

Polymer	Mw	PDI	Regioregularity	UV-Vis (nm)
P1	8 K	5.00	80%	440
P2	19 K	1.91	93%	447
P3	28 K	2.20	94%	445
P4	19 K	1.90	98%	442
P5	29 K	3.00	95%	441

Experimental Section

A representative procedure is described below.

Oxidative Addition of Active Zinc: Preparation of (5-bromo-3-(6-(diethoxyphosphoryl)hexyl)thiophen-2-yl)-zinc(II) bromide (6)/(5-bromo-4-(6-(diethoxyphosphor-yl)hexyl)thiophen-2-yl)zinc(II) bromide (7). In a 25 mL round-bottom flask, active zinc (0.72 g in THF, 11 mmol) was placed. And then, the flask was cooled down to 0 ºC using an ice-bath. With being stirred at 0 ºC, diethyl 6-(2,5-dibromothiophen-3-yl)hexylphosphonate (**5**, 4.6 g, 10 mmol) dissolved in 5.0 mL of THF was cannulated into the flask. Upon stirring at 0 ºC for 20 min, the oxidative addition was completed. Then, the dark black solution was allowed to settled-down at ambient temperature overnight. The supernatant was used for the subsequent polymerization.

Polymerization: Preparation of 2,5-poly-3-(6-hexyl-(di-ethylphosphanate)thiophene (P1). To a three-neck round-bottom flask was added Ni(dppe)Cl$_2$ (0.015 g, 0.3 mol %) and 5.0 mL of THF. Next, the organozinc solution prepared above was cannulated into the catalyst solution while being stirred at room temperature. Upon addition, reaction temperature reached at 59 ºC. After 24 h at ambient temperature, the resulting solution was then poured into water then extracted with chloroform. The combined chloroform solution was washed with water. The organic solvent was rotavapped down until a thick solution was obtained. The concentrated solution of polymer was precipitated in hexanes. The polymer was filtered and then Soxhlated with hexanes, then dried to give 2.8 g (93%) of an opaque black polymer.

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12. All the ratios were determined by GC and GC-MS analyses of the corresponding reaction mixtures.