

An Alternative Convenient Protocol for the Preparation of Regioregular Poly(3-hexylthiophene) via Thienylzincate Complex

Reuben D. Rieke and Seung-Hoi Kim^{†,*}

Rieke Metals, Inc., 1001 Kingbird Rd. Lincoln, NE 68521, USA

[†]Department of Chemistry, Dankook University, 29 Anseo Cheonan 330-714, Korea. *E-mail: kimsemail@dankook.ac.kr

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Regioregular head-to-tail poly(3-hexylthiophene), P3HT, has been found to be an unusual class of conducting polymer with good solubility, processibility, environmental stability, and high electrical conductivity.¹ It has been used for a broad range of chemical devices such as photovoltaics, electrochromic devices, optical sensors, organic light-emitting diodes and field-effect transistors.² Due to the significant role of this polymer in the field of functionalized material chemistry, many procedures have been developed and utilized for its production. To this aim, in general, two synthetic routes such as electrochemical methods and chemical methods have been developed.³ Chemical methods have extensively used for the synthesis of regioregular P3HT mainly because these methods generally provide high regioregularity of the polymer in excellent yields and can be readily carried out in large scale production.

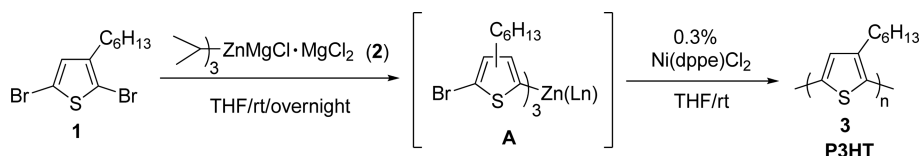
Among the chemical synthetic methods, organometallic reagents have been frequently employed as key intermediates. Among those, thienylzinc halides⁴ and thienylmagnesium halides⁵ are the most common reagents. In addition, a few other reports have exploited the Suzuki⁶ and Stille⁷ reagents. Although each protocol has provided the corresponding polymer with good qualities, the use of thienylzinc halide as an organometallic reagent has been proven to be the most reliable procedure for the preparation of regioregular P3HT. Rieke⁴ demonstrated the use of thienylzinc bromide intermediates prepared by the direct insertion of highly active zinc to 2,5-dibromo-3-alkylthiophenes. McCullough⁵ also reported the synthesis of the regioregular polythiophenes utilizing both thienylmagnesium halides and thienylzinc

halides prepared by the Grignard metathesis followed by transmetallation with zinc halides.

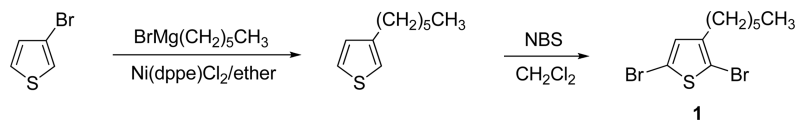
In our continuing studies on the preparation of P3HT, we next focused on the development of more practical synthetic procedures especially utilizing thienylzinc reagents. One of our studies was to use 2-bromo-3-hexyl-5-iodothiophene along with the dialkylzinc reagents.⁸ Recently, Higashihara also reported the use of 2-bromo-3-hexyl-5-iodothiophene along with a zincate complex of 'Bu₄ZnLi₂ for the synthesis of P3HT.⁹ Even though the use of 2-bromo-3-hexyl-5-iodothiophene provides a satisfactory route, it still requires the regio-selective halogenation which is consisted of two separate steps. Thus, to alleviate this difficulty, the use of 2,5-dibromothiophene derivatives as a monomer would be highly recommended especially in large scale production. Herein, we report a more practical synthetic route for the preparation of thienylzinc reagents and its subsequent polymerization in the presence of a Ni-catalyst affording the high head-to-tail regioregular P3HT. The schematic diagram for the preparation of P3HT used in this study is described in Scheme 1.

As depicted in Scheme 1, the monomer and trialkylzincate complex should be prepared prior to polymerization. 2,5-Dibromo-3-hexylthiophene was prepared by the literature procedure⁴; treatment of *n*-hexyl Grignard reagent with 3-bromothiophene in the presence of Ni(dppe)Cl₂, followed by bromination with NBS yielded **1**. Simple distillation afforded the pure product (**1**) in good yield (Scheme 2).

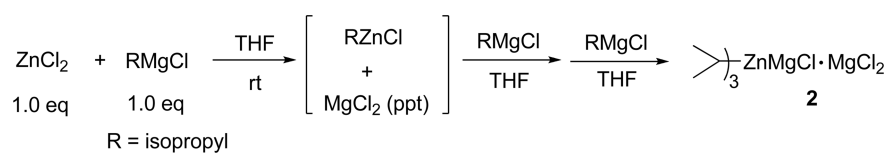
The trialkylzincate complex was also easily prepared as shown in Scheme 3. When zinc chloride was treated with 1.0



Scheme 1. Schematic diagram for the preparation of regioregular poly(3-hexylthiophene) (**3**).



Scheme 2. Preparation of 2,5-dibromo-3-hexylthiophene (**1**).



Scheme 3. Preparation of triisopropylzincate complex (**2**).

equiv of the Grignard reagent, magnesium chloride salt precipitated out. The supernatant only was used for the next steps and, interestingly, no more precipitates were obtained.

For the preparation of the intermediate, thienylzincate complex (**A**), 2,5-dibromo-3-hexylthiophene was reacted with triisopropylzincate complex (**2**) at room temperature. After being stirred at ambient temperature overnight, monomer (**1**) was totally converted to the intermediate (**A**) which consisted of a 73:27 ratio of regio-isomers. This ratio is the similar result observed in the previous reports.⁸ The resulting thienylzincate complex (**A**) was then polymerized in the presence of a Ni-catalyst under mild conditions.

As described in the previous report,⁴ the catalyst choice was critical in determining the regioregularity in the resultant polymer. In this report and other related studies, Ni(dppe)Cl₂ was superior over the other catalysts such as Ni[P(Ph)₃]₂Cl₂, Ni[P(Me)₃]₂Cl₂, Fe(dppe)Cl₂, and Co(dppe)Cl₂ in terms of yield and regioregularity of the polymer. Accordingly, the polymerization of thienylzincate complex (**A**) was carried out with 0.3 mol % Ni(dppe)Cl₂. Results from the additional catalyst screening test will be described later in this manuscript. Also, since a recent example of using thienylmanganese halides for the preparation of P3HT showed an interesting correlation between the order of addition of Ni-catalyst and molecular weight,¹⁰ the polymerization of the resulting thienylzincate complex was carried out in two different ways. As described in Table 1, the first approach was to add the Ni-catalyst into the solution of thienylzincate (route **I** in Table 1). A catalytic amount of Ni(dppe)Cl₂ was added into the solution of the thienylzincate complex through a powder funnel in one portion while being stirred at room temperature. Upon the addition of the catalyst, the reaction mixture usually turned a dark solution, and the formation of polymer was observed in a few minutes. To complete the polymerization, the resulting reaction mixture was allowed to stir at ambient temperature for 24 h. Work up and purification gave

the title polymer in good yields (78%, entry 1, Table 1). The second approach utilized the reverse addition of a Ni-catalyst (route **II** in Table 1). The thienylzincate solution was cannulated into the Ni(dppe)Cl₂ solution dissolved in THF and allowed to react at ambient temperature. Apparently, almost the same reaction occurred, but lower yield (40%) and low molecular weight (17 k) were obtained (entry 3, Table 1). This result clearly indicated that the order of addition of a catalyst significantly affected the chemical properties of the polymer. As shown in Table 1, higher yields were generally obtained from the route **I**. No significant improvement was achieved from an elevated reaction temperature (entries 2 and 4, Table 1) in both cases. Instead, significantly reduced yield, molecular weight and regioregularity were obtained from the reaction performed by route **II**. At this point, no concrete evidence on the origin of the results above was available. We also studied the effect of the concentration of the reaction mixture (entries 5 and 6, Table 1). The results clearly showed no profound difference other than a slightly reduced yield and molecular weight.

In addition, we also examined a catalyst screening test using several different catalysts such as Ni(dppp)Cl₂, Ni[P(Ph)₃]₄, Ni(dppe)Cl₂/SPhos, Ni[P(Ph)₃]₂Cl₂/SPhos, Pd(dppf)Cl₂, and

Table 2. Catalyst screening

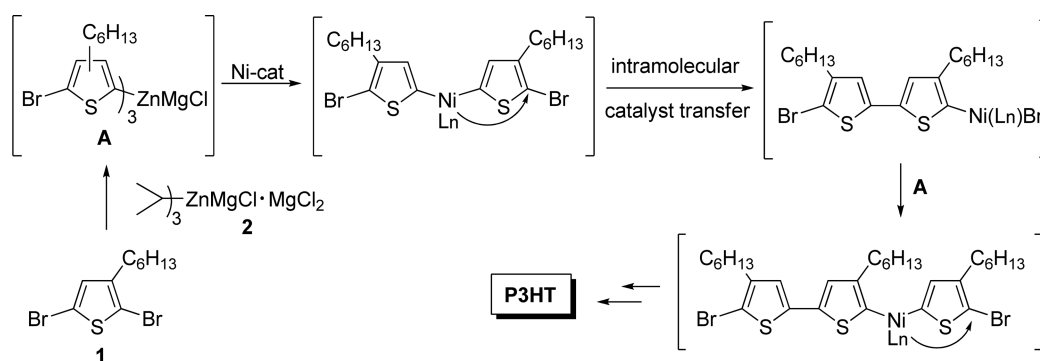
Entry	Catalyst ^a	Mw/Mn (kDa) ^b	PDI ^b	Yield (%) ^c
1	Ni(dppp)Cl ₂	18/11	1.64	44
2	Ni[P(Ph) ₃] ₂ Cl ₂	5/3	1.44	24
3	Ni(dppe)Cl ₂ /SPhos	20/12	1.62	58
4	Ni[P(Ph) ₃] ₂ Cl ₂ /SPhos	no polymer		
5	Pd(dppf)Cl ₂	no polymer		
6	Pd[P(Ph) ₃] ₄	no polymer		

^a0.3 mol % used. ^bDetermined by GPC analysis (eluent: THF, calibration: polystyrene standards). ^cBased on 2,5-dibromo-3-hexylthiophene

Table 1. Summary of the results

Entry	Conditions			Results ^b			
	Molarity	Temp/Time	Addition ^a	Yield (%)	Mw/Mn (kDa)	PDI	Regularity
1	0.25	rt/24 h	I	78	36/20	1.90	96
2	0.25	reflux/24 h	I	83	27/15	1.79	94
3	0.25	rt/24 h	II	40	17/9	1.43	88
4	0.25	reflux/24 h	II	56	18/9	1.47	90
5	0.20	rt/24 h	I	72	25/14	1.77	96
6	0.15	rt/24 h	I	69	24/14	1.79	96

^a**I**: addition of Ni-catalyst solution into thienylzinc solution. **II**: addition of thienylzinc solution into Ni-catalyst solution. ^bYield: based on 2,5-dibromo-3-hexylthiophene. Mw, Mn and PDI: determined by GPC analysis (eluent: THF, calibration: polystyrene standards). regularity: calculated by the integration of 2-methylene proton in ¹H NMR spectrum



Scheme 4. Proposed chain-growth polymerization.

$\text{Pd}[\text{P}(\text{Ph})_3]_4$. Unfortunately, as shown in Table 2, no significant improvement was observed even though some Ni-catalysts afforded the title polymer. Interestingly, a nickel-catalyst (entry 4, Table 2) and some Pd-catalysts used in this study did not provide any polymer compound (entries 5 and 6, Table 2).

Based on the results observed in this study, we proposed a chain-growth mechanism which is generally accepted for a transition metal-catalyzed polymerization of thienylmetallic reagents.¹¹

Finally, an additional investigation was carried out to see the effect of steric bulkiness of the alkyl group in zincate complex. For this aim, an alkylzincate complex was prepared using cyclohexylmagnesium chloride under the same fashion used in the case of isopropyl Grignard. The resulting cyclohexylzincate complex was reacted with 2,6-dibromo-3-hexylthiophene (1) resulting in the formation of the intermediate A at the same ratio (75:25) as observed from using isopropylzincate complex. The subsequent polymerization of this mixture, however, was apparently slower than the previous one and accordingly carried out at room temperature for 3 days affording the desired polymer P3HT in 42% yield ($M_w = 11 \text{ k}$, $\text{PDI} = 1.38$).¹²

In conclusion, we demonstrated a new facile and general procedure for the preparation of well-defined high regular poly(3-hexylthiophene). It should be emphasized that 2,5-dibromo-3-hexylthiophene and trialkylzincate complex which are readily available have been utilized in this protocol. Interestingly, the order of addition of a Ni-catalyst is critical for obtaining a high molecular weight polymer.

Experimental

Materials. 3-Bromothiophene, *n*-hexylmagnesium bromide, zinc chloride, isopropylmagnesium chloride, NBS, cyclohexylmagnesium chloride, $\text{Ni}(\text{dppe})\text{Cl}_2$ and other chemicals were purchased from Aldrich and used without any further purification.

General. All the reactions were carried out under argon gas. ^1H NMR spectra were recorded using a Varian FT-NMR (500 MHz) spectrometer with tetramethylsilane as internal standard. GPCs were obtained from a Waters 510 solvent delivery system using THF as eluent and polystyrene

standards for calibration.

Preparation of Thienylzincate Complex (A). An oven-dried 250 mL round-bottomed flask was charged with 2,5-dibromo-3-hexylthiophene (16.0 g, 50.0 mmol) and then 50 mL of THF was added into the flask. Next, 87 mL of triisopropylzincate solution (0.6 M in THF, 50.0 mmol) was cannulated into the flask with a steady-stream rate while being stirred at room temperature. The reaction temperature was reached up to 38 °C. Then, the mixture was allowed to stir at room temperature overnight. (The reaction was monitored by GC analysis of the reaction mixture). The resulting light yellow thienylzincate solution was used for polymerization.

Preparation of Poly(3-hexylthiophene) (3). In an oven-dried 500 mL round-bottomed flask, thienylzincate solution (50.0 mmol) was placed and 50 mL of fresh THF was added. Next, $\text{Ni}(\text{dppe})\text{Cl}_2$ (0.08 g, 0.3 mol %, based on thienylzincate complex) was added into the flask in one portion, and then the mixture was stirred at ambient temperature for 24 h. The whole mixture was then poured into 1.0 L of MeOH while being stirred at room temperature. The precipitated polymer was filtered and washed with MeOH until clear MeOH was observed. The obtained dark black polymer was dried under high vacuum pressure, then used for Soxhlet extraction.

General Procedure for Soxhlet Extraction with Hexanes. The polymer was placed in a Soxhlet extractor and then extracted with hexanes over 24 h. The resulting polymer was dried under high vacuum pressure affording 6.50 g of P3HT in 78% yield.

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12. Determined by the same manner as described in Table 1 in this study.
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