Research Article

Utilization of Zinc Dust for a Core Monomer 2-Bromo-3-hexylthien-5-ylzinc Bromide: Its Synthesis and Application for the Preparation of Regioregular Poly(3-hexylthiophene)

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The oxidative insertion of readily available zinc dust into the carbon-bromine bond of 2,5-dibromo-3-hexylthiophene was efficiently achieved to provide 2-bromo-3-hexylthien-5-ylzinc bromide (I), which was utilized for the preparation of highly regioregular poly(3-hexylthiophene) (P3HT) in the presence of catalytic amounts of Ni-catalyst.

1. Introduction

Due to its unique chemical properties, P3HT has been employed in a wide range of chemical devices such as photovoltaics, electrochromic devices, optical sensors, organic light-emitting diodes, and field-effect transistors [1–6]. Therefore, many procedures have been developed and utilized for its production. Of the various protocols, chemical synthesis with 2,5-dihalo-3-hexylthiophene has been extensively used because this approach efficiently provides the desired polymer with high regioregularity and excellent yield [7–13].

To accomplish the chemical synthesis of P3HT, organo-metallic intermediates such as thienylzinc halides and thienylmagnesium halides have most frequently been employed [14–16], along with a few other reagents, such as Suzuki [17, 18] and Stille [19] reagents. As depicted in Scheme 1, thienylmagnesium halides have been generally prepared by Grignard metathesis (Method A, McCullough method) [15]. Chen and coworker also demonstrated the preparation of thienylzinc bromide intermediates using the direct insertion of highly active zinc (Zn^*) to 2,5-dibromo-3-alkylthiophenes (Method B) [14]. The subsequent polymerization provided the corresponding polymer with good qualities, even though the benefits of the previously mentioned procedures for

the P3HT, somewhat harsh reaction conditions such as cold temperature, oxygen-free environment, transmetallation, and a specially prepared active metal (Zn^*), were employed throughout those routes.

In our continuing studies on the development of synthetic methodologies of P3HT, we focused on more practical synthetic procedures, especially utilizing a thienylzinc monomer intermediate. For this aim, our main goal in the preparation of thienylzinc intermediate was to avoid the use of specially prepared zinc metal (Zn^*) and a tedious transmetallation step with zinc salts. Therefore, we considered using zinc dust, which is readily available. We would like to report the first results obtained from utilizing zinc dust and 2,5-dibromo-3-hexylthiophene (Method C in Scheme 1).

2. Experimental

2.1. Materials. 3-Bromothiophene, *n*-hexylmagnesium bromide, zinc dust, NBS, $Ni(dppe)Cl_2$, and all of the solvents were purchased from Fisher or Aldrich and used without any further purification.

2.2. General. All the reactions were carried out under Ar-gas pressure. 1H NMR spectra were recorded using a Varian

SCHEME 1: Representative synthetic routes for P3HT.

SCHEME 2: Preparation of 2,5-dibromo-3-hexylthiophene.

SCHEME 3: Preparation of thienylzinc bromide (I) and its polymerization.

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.

2.3. Preparation of 2-Bromo-3-hexylthien-5-ylzinc Bromide (I) and Its Polymerization. An oven-dried 50 mL round-bottomed flask was charged with zinc dust (0.98 g, 15 mmol), iodine (0.13 g, 5.0 mol%), and LiBr (0.86 g, 10.0 mmol), and then 15.0 mL of N,N-dimethylacetamide (DMA) was added. Next, 2,5-dibromo-3-hexylthiophene (3.20 g, 10.0 mmol) was added to the flask. The resulting mixture was stirred at 80 ~ 90°C for 24 h and then cooled down to room temperature and settled down. The top layer was then cannulated into the flask containing Ni(dppe)Cl₂ (0.02 g, 0.3 mol%, based on I) in 5.0 mL of DMA at room temperature and the resulting mixture was allowed to stir at ambient temperature for 24 h. The whole mixture was then poured into 50 mL 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 and then was used for Soxhlet extraction.

2.4. 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 0.85 g of a dark black P3HT in 51% isolated yield.

3. Results and Discussion

Since 2,5-dibromo-3-alkylthiophene compounds have been intensively used as a monomer for the synthesis of poly(3-alkylthiophene) derivatives in most of the previous works, it has been selected as a suitable candidate for the preparation of thienylzinc intermediate (I) in our study. 2,5-Dibromo-3-hexylthiophene was readily prepared by a literature procedure: coupling of n-hexyl Grignard reagent with 3-bromothiophene in the presence of Ni(dppe)Cl₂, followed by bromination with NBS [14] (Scheme 2).

As described in Scheme 3, the intermediate 2-bromo-3-hexylthien-5-ylzinc bromide (I) should be generated first for the successful completion of the following polymerization. To obtain the intermediate I, the direct oxidative addition of zinc metal into the carbon-bromine bond of 2,5-dibromo-3-hexylthiophene can be employed as described in Method B in Scheme 1. However, since the commercially available zinc dust itself is not so active for obtaining the desired thienylzinc reagent, it should be activated prior to use in this study. Therefore, we have decided to examine the direct oxidative insertion of zinc dust into the carbon-bromine bond in conjunction with lithium bromide in the presence of a small amount of iodine as activating agents [20, 21].

TABLE 1: Summary of the study.

Entry	Oxidative addition ^a			Polymerization ^b				
	Solvent	Additive ^c	Conversion ^d	Solvent	Yield ^e	NMR ^f	Mw ^g	PDI ^g
1	THF	I ₂	No insertion			— ^h		
2	DMSO	I ₂	No insertion			— ^h		
3	NMP	I ₂	96% (80 : 20)	NMP		No polymerization		
4	DMA	I ₂	94% (82 : 18)	DMA	50%	>97%	10,000	1.4
5	DMA	I ₂ /LiBr	99% (85 : 15)	DMA	51%	>97%	12,000	1.5
6	DMA	I ₂ /LiBr	98% (85 : 15)	DMA/THF (1 : 1)	62%	>97%	13,000	1.5
7	DMF	I ₂ /LiBr	96% (84 : 16)	DMF		No polymerization		
8	DMF	I ₂ /LiBr	96% (84 : 16)	DMF/THF (1 : 1)	40%	>96%	5,000	1.3

^aCarried out at refluxing temperature for 24 h, ^b0.3 mol % Ni(dppe)Cl₂ used, ^c5.0 mol % I₂/1.0 eq LiBr used, ^dcalculated by GC, ^eisolated yield based on monomer, ^fregioregularity: calculated by the integration of 2-methylene proton in ¹H NMR spectrum, ^gdetermined by GPC analysis (eluent: THF; calibration: polystyrene standards), and ^hnot available to perform.

FIGURE 1: ¹H NMR ((a), in CDCl₃) and UV spectra ((b), in CHCl₃).

The results of the oxidative addition and subsequent polymerization are summarized in Table 1. Owing to the popularity of THF as a solvent in the literatures, we first tried the oxidative addition of zinc dust in THF. Unfortunately, it turned out to be an inefficient solvent for the addition. No reaction took place even with prolonged reaction time (entry 1, Table 1). A similar unsatisfactory result in the insertion step was observed using DMSO (entry 2, Table 1).

Interestingly, a successful insertion was accomplished by a simple change in solvent to NMP under the same conditions. With the resulting thienylzinc bromide, the subsequent polymerization was carried out using Ni(dppe)Cl₂-catalyst, which was superior over other catalysts, especially in terms of regioregularity in the resultant polymer. The expected polymerization, however, did not proceed even at refluxing temperature (entry 3, Table 1).

The next attempt was executed using a different solvent, DMA, under the same conditions. As shown in Table 1, the oxidative addition went easily to completion within 24 h. The subsequent condensation was also smoothly performed in the same solvent, giving rise to the desired polymer in moderate yield (entry 4, Table 1). An improvement in the oxidative addition procedure was observed when using iodine along with 1.0 equivalent of lithium bromide. After stirring at 80 ~ 90 °C for 24 h, 2,5-dibromo-3-hexylthiophene was totally converted to the corresponding organozinc reagent intermediate (I), which consisted of an 85 : 15 ratio of regioisomers. This ratio is similar to the result observed in previous works [14]. The resulting thienylzinc bromide (I) was then polymerized in DMA providing the P3HT with slightly higher molecular weight (entry 5, Table 1). The analytical data of the resulting polymer obtained from this procedure are shown in Figure 1.

The formation of the desired regioregular P3HT was confirmed by ^1H NMR data. This evidence is further supported by optical measurement. The UV-vis absorption spectra of the polymers are similar to that of P3HT gained from Method B in Scheme 1, indicating the possession of the same optical properties.

Since THF was the most frequently used solvent in the preparation of P3HT, a mixed solvent system (DMA/THF, 1:1 v/v) was employed in anticipation of better results. It worked fine and led to the corresponding polymer in a slightly higher yield (entry 6, Table 1). Unfortunately, no huge improvement in the molecular weight or PDI was achieved. In addition, another aprotic polar solvent DMF turned out to be a good solvent in the oxidative addition step. Surprisingly, however, no polymer was obtained using DMF only in the subsequent condensation procedure (entry 7, Table 1). To complete the polymerization, a mixed solvent system (DMF/THF, 1:1, v/v) was required, which resulted in the formation of the title polymer with lower molecular weight (entry 8, Table 1). This result clearly indicated that THF played a role in some way during the polymerization procedure. At this point, no concrete evidence of the role of THF was available.

4. Conclusions

In conclusion, we developed a facile and reliable protocol for the preparation of well-defined high regioregular poly(3-hexylthiophene). It is of great importance that the preparation of the monomer, 2-bromo-3-hexylthien-5-ylzinc bromide (**I**), has been easily accomplished utilizing readily available zinc dust under mild conditions. Also, the subsequent polymerization took place successfully affording the desired regioregular polymer P3HT. Moreover, it should be emphasized that a tedious procedure of the preparation of highly active zinc and/or transmetallation can be avoided using this protocol.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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