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Nickel-catalyzed Dehydrobrominative Polycondensation for the Practical Preparation of Regioregular Poly(3-substituted thiophene)s

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Poly(3-hexylthiophene) was synthesized by the polycondensation of 2-bromo-3-hexylthiophene with a nickel catalyst and (2,2,6,6-tetramethylpiperidin-1-yl)magnesium. The polymerization proceeded at room temperature in a highly regioregular manner.

Oligothiophenes and polythiophenes attract considerable attention in materials science. Regioregular polythiophene, which involves head-to-tail (HT) repeating unit such as poly(3-hexylthiophene) (HT-P3HT) (**1**) (Chart 1) is of particular interest since the compound shows remarkable physical properties materials such as organic TFTs, thin-film organic solar cells, and conductive polymers.[1] Debrominative polycondensation of 2,5-dibromo-3-hexylthiophene (**2a**) with a Grignard reagent in the presence of a transition-metal catalyst is a method of choice for the preparation of **1**.[1d,2] A regiochemical error in the halogen–metal exchange causes incomplete conversion to the polymer **1**. Although use of the 5-iodinated derivative **2b** is a solution to such problem,[3] preparation of **2b** requires multistep procedures as well as inferior atom efficiency. On the other hand, the dehydrobrominative method to afford **1** with 2-bromo-3-hexylthiophene (**3**) is a potentially atom-economic pathway. Deprotonation of **3** with lithium amide and following metal exchange with zinc[1d] or magnesium[2a–2f,3] also gives **1** although extremely low temperature is necessary. A palladium-catalyzed direct polycondensation in the presence of an alkali metal carbonate has recently been shown to lead to polymer,[4] however, high temperature is necessary to afford the polythiophene in a reasonable yield with high degree of polymerization. It is thus highly intriguing to develop milder dehydrobrominative polymerization (around room temperature), which would be a goal for the efficient preparation of regioregular polythiophenes. We envisaged that our recent efforts on the development of transition-metal-catalyzed C–H functionalization of heteroaromatic compounds[5,6] can be applied to the synthesis of HT-P3HT (**1**) and herein disclose that the employment of Knochel-Hauser base[7] and a nickel-catalyst is a practical dehydrobrominative polycondensation method toward *highly regioregular poly(3-substituted thiophene)s at room temperature with high atom efficiency.*

We first examined palladium-catalyzed polymerizaton of **3a** in the presence of lithium *t*-butoxide.[8] The polymerization
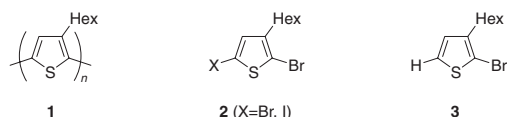
occurred at 50 °C to afford the corresponding polymer **1** with M_n of 7600. In contrast to the above undesired results, it was found that the use of (2,2,6,6-tetramethylpiperidin-1-yl)magnesium chloride·LiCl (**4**), which was developed by Knochel for the proton abstraction of various sp² C–H bonds,[7] induced polymerization highly efficiently. When the reaction was carried out with 0.5 mol % [NiCl₂(dppe)] as catalyst, the corresponding HT-P3HT (**1**) was obtained in quantitative yield in contrast to debrominative polymerization with a Grignard reagent which does not reach complete conversion due to regiochemical error in the halogen–metal exchange. The obtained polymer **1** exhibited extremely high HT selectivity. DPPP as a ligand of the nickel catalyst also was as effective as DPPE, while DPPB or tricyclohexylphosphine (PCy₃) was found less effective. The average molecular weight of the obtained polymer was found to be controlled by the amount of the employed nickel catalyst. The number of the polymer chain showed relatively good correspondence to the amount of nickel catalyst and the M_n value was found to increase by lowering the catalyst loading. The use of arylnickel complex as a catalyst also resulted in smooth polymerization with excellent HT selectivity and it was confirmed by ¹H NMR that the phenyl end group was at the terminal of the polymer chain.[2e] These results are summarized in Table 1.

It should be pointed out that the reaction proceeded at room temperature to afford the corresponding polymer in a quantitative yield. Comparing the preceding polymer syntheses with C–H functionalization conducted at elevated temperature[4] or at extremely low temperature for proton abstraction with lithium amide followed by lithium–magnesium exchange,[3] the present reaction conditions proceed at room temperature throughout the
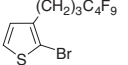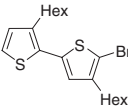

Chart 1.

Table 1. Polycondensation of 2-bromo-3-hexylthiophene (**3**) with various catalysts[a]

Catalyst (mol %)	M_n[b]	M_w/M_n[b]	%HT[c]	Yield/%
[NiCl₂(dppe)] (0.5)	44900	1.32	>98	>99
[NiCl₂(dppp)] (0.5)	23200	1.35	97	73
[NiCl₂(dppb)] (0.5)	4500	1.78	76	87
[NiCl₂(PCy₃)₂] (0.5)	10100	1.93	90	20
[NiCl₂(dppe)] (1.0)	15400	1.48	95	70
[NiCl₂(dppe)] (2.0)	8380	1.33	95	>99
[PhNiBr(dppp)] (2.0)	9900	1.11	>99	48

[a]The reaction was carried out with 1.0 mmol of **3** in 10 mL of THF at room temperature for 24 h. [b]Estimated by SEC analysis based on polystyrene standards. [c]Estimated by ¹H NMR.

**Table 2.** Nickel-catalyzed polycondensation of 3-substituted thiophene[a]

Monomer		M_n[b]	M_w/M_n[b]	%HT[c]	Yield/%
(structure)	(5)[d]	2700	1.12	84	35
3:5 = 1:1		19300	1.25	—	55
(structure)	(6)[e]	22000	1.75	97	83

[a]Unless noted, the reaction was performed with monomer (1.0 mmol), TMPMgCl·LiCl (1.0 mmol), and [NiCl₂(dppp)] (1.0 mol %) in 10 mL of THF at room temperature for 24 h. [b]Estimated by SEC analysis using CHCl₃ as an eluent. [c]Estimated by ¹H NMR. [d]With 5 mol % of [NiCl₂(dppp)]. [e]With 2 mol % of [NiCl₂(dppp)].
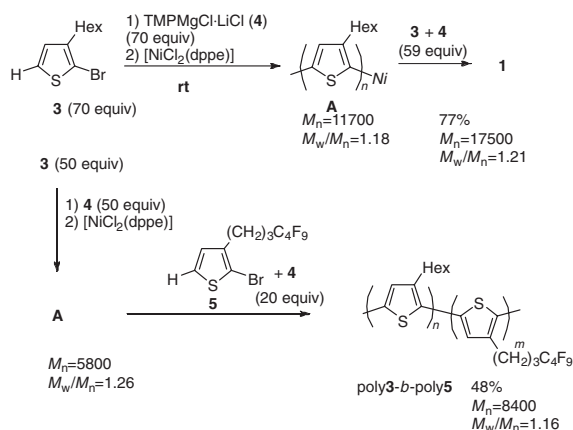
Scheme 1.

overall process. In addition, the atom efficiency of the formal C–H functionalization polycondensation is much superior to the existing dehalogenative polymerization. Accordingly, the reaction is a remarkably simple and practical synthetic protocol for HT polythiophenes.

Table 2 summarizes the polymerization of other monomers involving 3-substituted thiophenes. Polymerization of fluoroalkyl-substituted bromothiophene **5**[9] took place in a similar manner. Although the insoluble polymer was obtained by reaction under similar conditions (1.0 mol % catalyst loading), reaction with 5 mol % of the catalyst afforded the corresponding oligomer with M_n of 2700 ($M_w/M_n = 1.12$). Copolymerization with a mixture of **3** and **5** occurred to afford the corresponding copolymer, in which comonomers were incorporated in a ratio of 1.4:1, respectively. It was found that polymerization of bromobithiophene **6** also proceeded.

The polymerization was found to proceed in a living manner. As summarized in Scheme 1, addition of monomer **3** to reaction mixture **A** ($M_n = 11700$) induced further polymerization to afford the extended polymer ($M_n = 17500$, $M_w/M_n = 1.21$). In addition, block copolymerization was found to occur with the first polymerization product **A** and following addition

of 3-substituted 2-bromothiophene **5** bearing a $-(CH_2)_3C_4F_9$ group to afford the copolymer.

In summary, we have shown that nickel-catalyzed polymerization of 2-bromo-3-hexylthiophene via C–H functionalization polycondensation, which involves superior atom efficiency, with high reactivity to proceed at room temperature, and to achieve excellent head-to-tail (HT) regioregularity.[10]

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.