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Remarkable Reactivity Differences of Chlorothiophene and Chlorinated Oligothiophenes in $NiCl_2(PPh_3)_2$-catalyzed Polymerization

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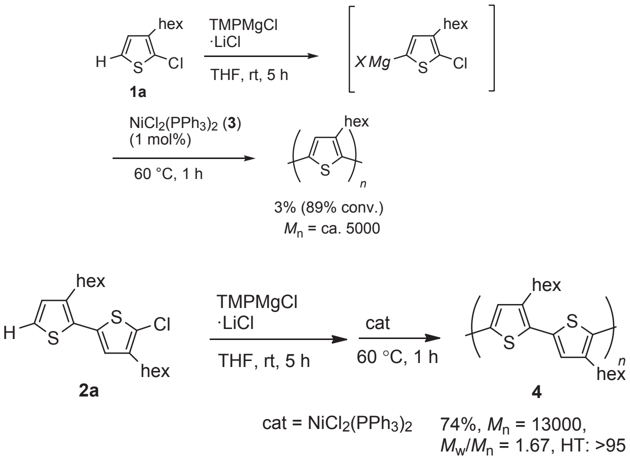
A simple and ubiquitous nickel(II) complex $NiCl_2(PPh_3)_2$ catalyzes polymerization of oligothiophenes. Treatment of chlorobithiophene with chloromagnesium 2,2,6,6-tetramethylpiperidin-1-yl lithium chloride salt (TMPMgCl•LiCl) followed by addition of 2.0 mol % $NiCl_2(PPh_3)_2$ undergoes deprotonative polymerization leading to poly(3-hexylthiophene) (P3HT) with $M_n = 13000$ and $M_w/M_n = 1.67$ (74% yield). The related terthiophene and quaterthiophene also polymerize to afford the corresponding polythiophene while little polymerization takes place with 2-chloro-3-hexylthiophene under similar conditions.

Keywords: Poly(3-hexylthiophene) (P3HT) | $NiCl_2(PPh_3)_2$ | Chlorinated oligothiophene

Development of a preparation method for polythiophenes attracts considerable attention since highly regioregular poly(3-substituted thiophene)s are widely employed as electronic materials.[1] Polythiophenes are synthesized utilizing polymerization of 2-halo-5-metalated thiophene with a transition-metal catalyst. A frequently employed protocol in polythiophene synthesis is the Grignard metathesis (GRIM): the reaction of 2,5-dihalothiophene with a Grignard reagent to induce a halogen–metal exchange reaction.[2] We have also shown recently that deprotonative metalation with a bulky magnesium amide TMPMgCl•LiCl (TMP: 2,2,6,6-tetramethylpiperidin-1-yl)[3] or the combination of a Grignard reagent with a catalytic amount of secondary amine serves as an effective polythiophene synthesis.[4] In particular, the reaction was revealed to allow the use of chlorothiophene, which involves superior atom efficiency to the related bromide, leading to highly regioregular polythiophenes.[4b] In polythiophene synthesis, use of a nickel(II) or palladium(II) catalyst bearing bidentate diphosphines[2] or *N*-heterocyclic carbene (NHC)[4b,5] as a ligand has shown to give polythiophene highly efficiently, whereas use of a ubiquitous ligand PPh_3 resulted in much less effective polymerization. During the course of our studies on the development of preparation protocol of oligo- and polythiophenes, we have shown that regioselective deprotonation of 3-substituted thiophene achieves stepwise synthesis of regioregular head-to-tail-type oligothiophenes with well-defined structures.[4,6] Accordingly, we have been interested in the employment of thus chlorinated oligothiophenes as a monomer of polythiophene synthesis, in which the reactivity of thiophene oligomers toward the nickel catalyst is our particular concern. We herein report that the use of triphenylphosphine as a ligand of a nickel catalyst allows polymerization of *chlorinated oligothiophenes*, whereas little polymerization of the related 2-chlorothiophenes composed of a single thiophene ring takes place.

We first compared the reaction of 2-chloro-3-hexylthiophene (**1a**) vs. the corresponding chlorobithiophene **2a**. When the reaction of **1a** was attempted to polymerize with $NiCl_2(PPh_3)_2$ (**3**) as a catalyst, the corresponding polythiophene was obtained in only 3% yield (M_n = ca. 5000) after stirring at 60 °C for 1 h whereas 89% of **1a** was consumed to afford homocoupled dichlorobithiophene as a major product, suggesting that catalyst **3** is less active compared with $NiCl_2(PPh_3)IPr$, with which polymerization of **1a** is complete within 1 h at room temperature.[4b] By contrast, it was found that polymerization of chlorobithiophene **2a** proceeded with nickel catalyst **3** (2.0 mol %) at 60 °C for 1 h to afford polymer **4** in 74% yield with $M_n = 13000$ ($M_w/M_n = 1.67$) and head-to-tail (HT) regioregularity of >95%. The results show that chlorobithiophene **2a** is a highly reactive monomer precursor for the preparation of polythiophene as shown in Scheme 1.



Scheme 1. Polymerization of chlorobithiophene **2a** catalyzed by $NiCl_2(PPh_3)_2$ (**3**).

Although several halogenated oligothiophenes have been employed as a monomer for polythiophene synthesis to date, there have been little studies to compare the reactivity of oligothiophene vs. 2-halo-3-substituted thiophenes.[7] To our surprise, polymerization of chlorobithiophene **2a** shows higher reactivity and takes place with a nickel catalyst bearing the ubiquitous ligand PPh_3, which has been recognized much less efficient in polythiophene synthesis. Although the use of an arylnickel(II) catalyst bearing PPh_3 as a ligand is shown to undergo polymerization of 2-bromo-3-hexylthiophene (**1b**),[8] attempted polymerization with $NiCl_2(PPh_3)_2$ (**3**) was found to be unsuccessful to afford the polymer in a considerably poor yield. By contrast, bromobithiophene **2b** also showed superior reactivity to **1b** with **3** as a catalyst to afford 77% of **4** ($M_n = 17300$; $M_w/M_n = 1.65$) as shown in Chart 1.

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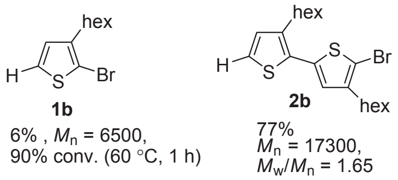


Chart 1. Polymerization of bromothiophene derivatives catalyzed by $NiCl_2(PPh_3)_2$.

Table 1. Deprotonative polymerization of chlorobithiophene **2a** with TMPMgCl•LiCl and a nickel catalyst[a]

Ni cat	Ligand[b]	Yield /%	$M_n \times 10^{-3}$	M_w/M_n
$NiCl_2(PPh_3)_2$[c]		69	13.0	1.42
$NiCl_2(dppe)$		93	32.0	2.09
$NiCl_2(dppp)$		81	17.2	1.48
$NiCl_2(PCy_3)_2$		86	19.1	1.55
$Ni(acac)_2$	2 PPh_3	70	14.7	1.74
$PdCl_2(PPh_3)_2$		<1	—	—
$PdCl_2(dppe)$		<1	8.9	1.49
Pd-PEPPSI-SIPr[d]		28	5.7	1.15

[a]Unless otherwise specified, **2a** (0.30 mmol) was treated with TMPMgCl•LiCl (1.5 equiv) at rt for 5 h and polymerization was performed at 60 °C for 1 h with 2 mol % of catalyst. [b]DPPE: 1,2-diphenylphosphinoethane; DPPP: 1,3-diphenylphosphinopropane; SIPr: 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene; PCy_3: tricyclohexylphosphine. [c]The polymerization was carried out at rt for 3 h. [d]See ref 9.

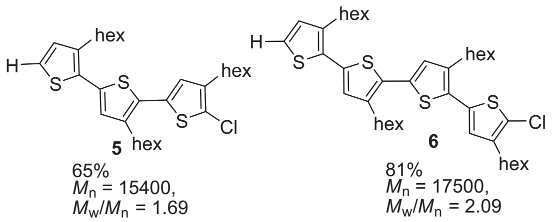
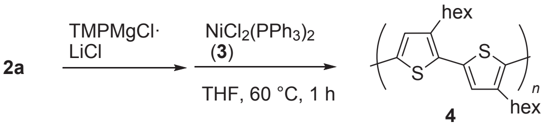


Chart 2. Polymerization of oligothiophenes with $NiCl_2(PPh_3)_2$ as a catalyst.



76%, M_n = 12400; M_w/M_n = 1.51 (**3**: 5.0 mol %)
74%, M_n = 13000; M_w/M_n = 1.67 (**3**: 2.0 mol %)
64%, M_n = 11000; M_w/M_n = 1.39 (**3**: 2.0 mol % at rt, 30 min)
22%, M_n = 7100 ; M_w/M_n = 1.23 (**3**: 2.0 mol % at rt, 5 min)

Scheme 2. Studies on living characteristics of polymerization **2a** catalyzed by $NiCl_2(PPh_3)_2$.

Table 1 summarizes the results of the polymerization of chlorobithiophene **2a** with several catalysts. It was found that polymerization with $NiCl_2(PPh_3)_2$ proceeded at room temperature to afford polythiophene **4** (69% yield) within 1 h. The reaction with bidentate ligands DPPE, DPPP, and tricyclohexylphosphine PCy_3, with which polymerization of chlorothiophene **1a** composed of a single thiophene ring was shown to proceed less efficiently in our previous report,[4a,4b] similarly affected the polymerization of bithiophene **2a**. In situ formation of a nickel triphenylphosphine complex with $Ni(acac)_2$ with PPh_3 (2 equivalents to Ni) also afforded polymer **4**. On the other hand, polymer **4** was hardly obtained with the related palladium catalysts $PdCl_2(PPh_3)_2$ and $PdCl_2(dppe)$. Although polymerization with Pd-PEPPSI-SIPr[9] took place, the yield of polymer **4** was considerably inferior to the case with a nickel catalyst.

Chloroterthiophene **5** with catalyst loading of 3.3 mol % under similar conditions also reacted to afford polythiophene in 65% yield with $M_n = 15400$ ($M_w/M_n = 1.69$). The polymerization of chlorinated quaterthiophene **6** (catalyst loading: 4.0 mol %) also proceeded to afford the corresponding polymer in 81% yield ($M_n = 17500$, $M_w/M_n = 2.09$).[7,10] These results suggest that enhanced reactivity is observed in oligothiophene tri- and tetramer as well as bithiophene. Accordingly, the reactivity enhancement would not be concerned with the odd–even effect in the number of oligothiophene (Chart 2).

The reaction of the bithiophene **2a** with a different amount of catalyst loading (5.0 mol %) resulted in giving the M_n value as 12400 (theor. M = 6600) with M_w/M_n = ca. 1.5 as represented in Scheme 2. The result suggests that nonlinear relationship of the molecular weight with the ratio of monomer feed vs. catalyst loading as compared with the result shown in Scheme 1 ($M_n = 13000$ with 2.0 mol % of **3**). Nevertheless, we consider that polymerization with $NiCl_2(PPh_3)_2$ (**3**) proceeds partly in a catalyst transfer manner,[2c,11] which migrates the nickel species along the polymer chain to result in rapid polymerization in a living manner. Accordingly, the reaction was found to proceed within a few minutes (22% conversion at room temperature for 5 min) to afford polythiophene **4** with $M_n = 7100$.

The catalyst-transfer polymerization of thiophene derivatives is recognized to proceed as summarized in Scheme 3[12] via transmetalation of **A** with thienylmagnesium **2a′** to give **B**. The following reductive elimination and oxidative addition lead to **A′** with propagation of the bithiophene unit through the intermediate **C**. Our concern turns to account for the enhanced reactivity of oligothiophenes that allow polymerization with $NiCl_2(PPh_3)_2$ (**3**). Since oxidative addition of nickel(0) species in **C** to the terminal carbon–chlorine bond at the polymer chain end to give **A′** is the reaction at the carbon–chlorine bond at the polymer end, there would be regardless of the monomer structure (thiophene vs. bithiophene). Therefore, enhancement of the oxidative addition in **C** can be ruled out. Rate difference in transmetalation of chloronickel(II) **A** with thienyl Grignard reagent **2a′** vs. the related species of monothiophene would also be unlikely. In considering possible enhancement in the reductive elimination of **B** to give **C**, calculation of nickel(II) bistriphenylphosphine complexes bearing two bithiophene **B1**, which serves as a model for the reductive elimination at the polymer end using bithiophene **2a′** as a monomer, was carried out. The bond angle of C–Ni–C indicated as 86.10° while that of bithiophene and thiophene (complex **B2**) as a model of the polymerization of **1a** composed of a single thiophene ring showed the larger angle 88.60°. The results suggest that reductive elimination of **B1** would be preferable to that of **B2**.[13] The angle of **B1** is indeed close to the value of the related nickel DPPP complex **B3** (84.63°), which is the catalyst to undergo smooth polymerization. Ozawa and co-workers also

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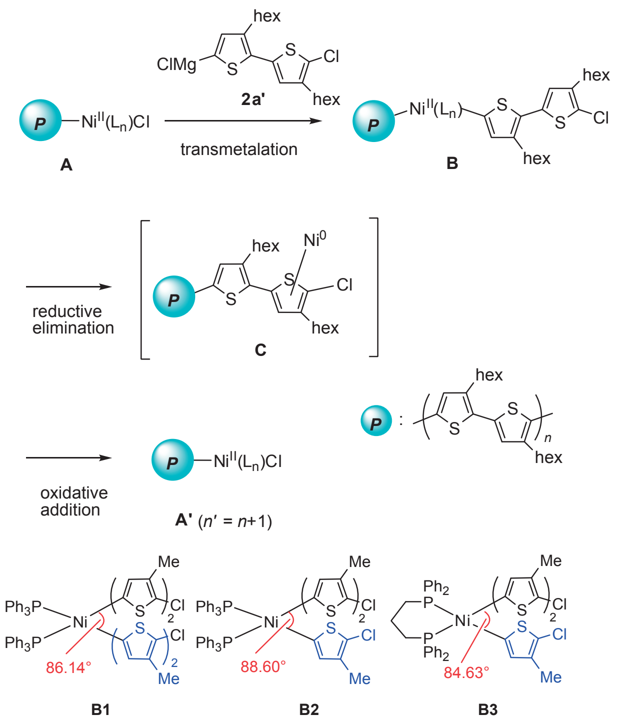

Scheme 3. Plausible polymerization pathway and calculated structure of nickel(II) species.

showed that the competing arylation of thiophene and bithiophene mediated by palladium,[14,15] in which bithiophene reacted much faster, is due to the enhanced reactivity in the reductive elimination step by DFT calculation. Although the detailed mechanism of chloro-oligothiophenes using $NiCl_2(PPh_3)_2$ is still unclear, enhanced reductive elimination may result in smooth polymerization.

In summary, we have shown that chlorinated oligothiophenes are highly reactive in the transition-metal-catalyzed polymerization compared to the related species composed of a single thiophene ring. The polymerization was revealed to take place with a ubiquitous and inexpensive nickel complex $NiCl_2(PPh_3)_2$ (**3**), which had been shown as a less reactive catalyst for the polymerization of monochlorothiophenes.[4b] Thiophene derivatives composed of 2–4 thiophene units **2a**, **5**, and **6** were found to polymerize with catalyst **3** to afford P3HT with different repeating unit sizes.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.161180.

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