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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-tetramethyl-piperidin-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
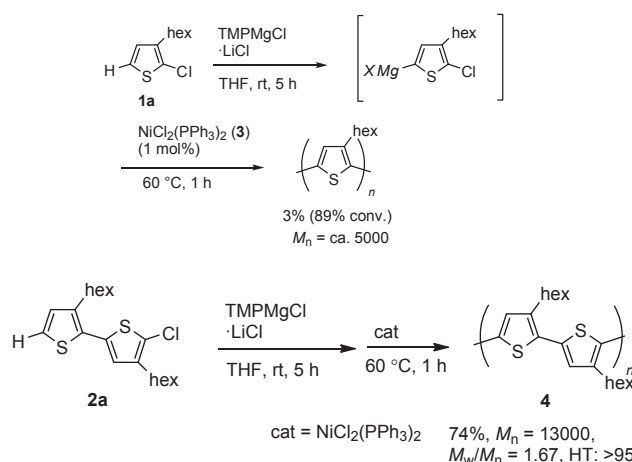
Scheme 1. Polymerization of chlorobithiophene **2a** catalyzed by NiCl$_2$(PPh$_3$)$_2$ (**3**).

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.

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.

1b
6%, $M_n = 6500$,
90% conv. (60 °C, 1 h)

2b
77%
$M_n = 17300$,
$M_w/M_n = 1.65$
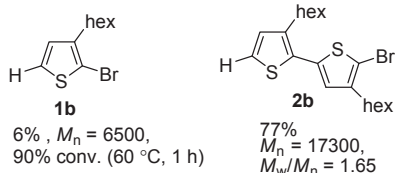
Chart 1. Polymerization of bromothiophene derivatives catalyzed by $NiCl_2(PPh_3)_2$.

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.
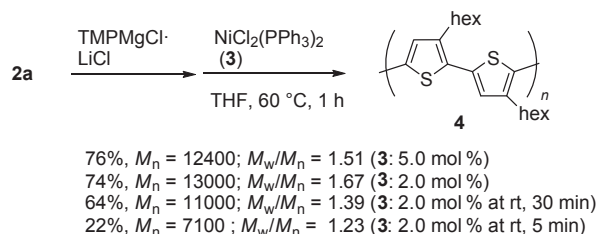
Table 1 summarizes the results of the polymerization of chlorobithiophene **2a** with several catalysts. It was found that polymerization with $NiCl_2(PPh_3)_2$ proceeded at room temperature to afford polythiophene **4** (69% yield) within 1 h. The reaction with bidentate ligands DPPE, DPPP, and tricyclohexylphosphine 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

5
65%
$M_n = 15400$,
$M_w/M_n = 1.69$

6
81%
$M_n = 17500$,
$M_w/M_n = 2.09$
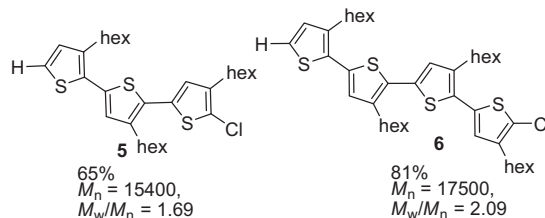
Chart 2. Polymerization of oligothiophenes with $NiCl_2(PPh_3)_2$ as a catalyst.

2a → TMPMgCl·LiCl, $NiCl_2(PPh_3)_2$ **(3)**, THF, 60 °C, 1 h → **4**

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 $NiCl_2(PPh_3)_2$.

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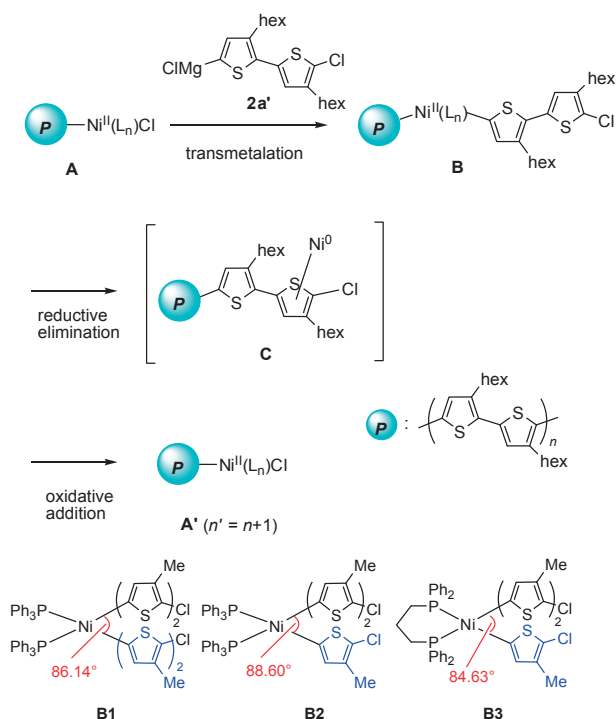
Scheme 3. Plausible polymerization pathway and calculated structure of nickel(II) species.

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.

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

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