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Synthesis of High-molecular-weight Head-to-tail-type Poly(3-substituted-thiophene)s by Cross-coupling Polycondensation with [CpNiCl(NHC)] as a Catalyst

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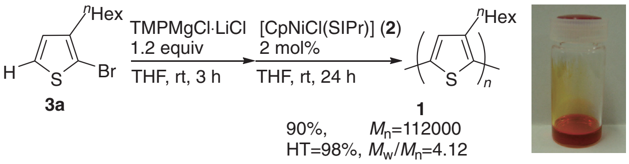
High-molecular-weight head-to-tail-type regioregular polythiophenes are synthesized by [CpNiCl(SIPr)]-catalyzed dehydrobrominative polycondensation. Polycondensation of 2-bromo-3-hexylthiophene at the C–H bond proceeds with an equimolar amount of TMPMgCl•LiCl and a catalytic amount of [CpNiCl(SIPr)] to afford the regioregular poly(3-hexylthiophene) (HT-P3HT) with up to $M_w = 815000$. A self-standing HT-P3HT film is obtained with the regioregular HT-P3HT of $M_w = 414000$, while the attempted formation of the corresponding film with lower-molecular-weight HT-P3HT ($M_w = 38000$) is unsuccessful.

Polythiophenes have attracted considerable attention recently because of their remarkable physical properties as electronic materials.[1] The formation of head-to-tail (HT)-type polythiophenes such as poly(3-hexylthiophene) (P3HT) (**1**) has been particularly important, since superior material performances have been generally found in HT-P3HT materials because of their highly planer and π-conjugation-extended characteristics.[2] In contrast with the extensive spectroscopic and electronic characterizations of HT-type polythiophenes, the mechanical performance of HT-polythiophene as a self-standing film has rarely been studied owing to the preparative difficulties involved in the synthesis of high-molecular-weight HT-P3HT.[3] Although regioregular HT-P3HT was shown to be prepared by nickel-catalyzed polycondensation of the corresponding dibromothiophene with a Grignard reagent (the GRIM method),[4] it had been difficult to obtain HT-P3HT with a molecular weight as high as 100000.[5] Very recently, Seferos and co-workers revealed that the synthesis of higher-molecular-weight P3HT could be achieved with [(*o*-tolyl)NiCl(dppp)] as an initiator, affording polythiophene with a molecular weight up to ca. 200000.[6] This prompted us to report our separate findings on the development of a new class of nickel catalysts bearing a cyclopentadienyl (Cp) ligand for the polymerization of thiophene derivatives to yield high-molecular-weight HT-P3HT. We have reported recently that nickel-catalyzed dehydrobrominative or dehydrochlorinative polycondensation is also a powerful tool (in addition to the GRIM method) for the synthesis of HT-type polythiophenes using the Knochel–Hauser base, chloromagnesium 2,2,6,6-tetramethylpiperidide lithium chloride salt (TMPMgCl•LiCl),[7] in the presence of a nickel(II) catalyst.[8] The method allows polymerization at a lower reaction temperature within a shorter polymerization period with high atom efficiency. In our studies on the dehydrobrominative synthesis as well as the aforementioned GRIM method,[9,10] it is remarkable that the average molecular weight of HT-P3HT is controllable by the ratio of monomer feed and catalyst loading, because of the characteristics of living polymerization. In the course of our studies on the synthesis of HT-P3HT, we found unexpectedly that P3HT of an extremely high molecular weight (>100000) was obtained irrespective of the catalyst loading when a nickel catalyst bearing a cyclopentadienyl (Cp) and an *N*-heterocyclic carbene ligand (NHC: SIPr) [CpNiCl(SIPr)][11,12] (**2**) was employed. This finding may open extensive characterizations of the mechanical properties of HT-P3HT as a self-standing film,[13] which, to the best of our knowledge, have rarely been studied owing to the lack of a methodology to afford high-molecular-weight polymers. Herein, we report the synthesis of high-molecular-weight HT-P3HT with [CpNiCl(SIPr)] as a catalyst.

When the polymerization of 2-bromo-3-hexylthiophene (**3a**) was carried out with 1.2 equiv of TMPMgCl•LiCl and 2.0 mol % of [CpNiCl(SIPr)] (**2**) at 25 °C for 24 h, P3HT (**1**) was obtained in 90% yield, as shown in Scheme 1. To our surprise, it was found that the obtained high-molecular-weight polymer **1** dissolved reasonably in chloroform (4.2 mg mL^{-1} at 60 °C) and 1,2-dichlorobenzene (12.5 mg mL^{-1} at 80 °C). These polymers were dissolved after cooling to room temperature, as shown in the picture of Scheme 1 (a chloroform solution). Thus, the HT regioregularity can be confirmed to be 98% by measurement of the ^{1}H NMR spectrum as a $CDCl_3$ solution, and SEC analysis revealed that the average molecular weight M_n was 112000 ($M_w/M_n = 4.12$).

Table 1 summarizes the [CpNiCl(SIPr)]-catalyzed polymerization to afford **1** under several conditions. The reaction was found to take place with an equimolar amount of TMPMgCl•LiCl to afford P3HT. When the reaction was performed with 3 mol % of [CpNiCl(SIPr)] as a catalyst, HT-P3HT was obtained in a lower yield, with $M_n = 103000$ (Entry 1). The reaction in the presence of 2 and 1 mol % of the catalyst in THF (0.1 M) afforded **1** in excellent yield with $M_n = 224000$ and 174000, respectively ($M_w/M_n = 1.85$ and 1.98: Entries 2 and 3). The polymerization with a higher concentration (0.33 M) was found to have a different optimum catalyst loading to obtain the high-molecular-weight polymer. The reaction with 0.75 mol % of catalyst loading led to the



Scheme 1.

Table 1. Polymerization of **3a** with [CpNiCl(SIPr)][a]

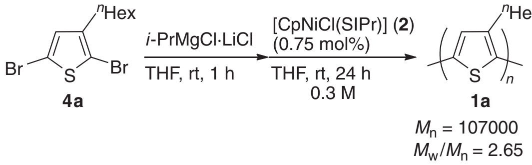
Entry	Ni cat. /mol %	Temp /°C	%yield[b]	M_n[c]	M_w[c]	M_w/M_n[c]
1	3	rt	27	103000	214000	2.08
2	2	rt	81	224000	414000	1.85
3	1	rt	65	174000	345000	1.98
4[d]	0.75	rt	74	233500	815000	3.49
5[d]	0.5	rt	85	172600	630000	3.65
6	2	40	54	10700	21600	2.02
7[e]	2	0	33	126000	295000	2.34

[a]Unless otherwise noted, the reaction was carried out with 1.0 mmol of **3a** and 1.0 equiv of TMPMgCl•LiCl in 10 mL of THF for 3 h (metalation) and for 24 h (polymerization). [b]Isolated yield. HT regularity of the obtained polymer (except Entry 6) was confirmed to be >99% by ^{1}H NMR analysis. [c]M_n and M_w/M_n values were estimated by SEC analysis using $CHCl_3$ as an eluent. [d]The reaction was carried out with 20 mmol of **3a** in 60 mL of THF. [e]Polymerization time: 72 h.

polymer with an extremely high molecular weight, $M_w = 815000$ (Entry 4). The use of an elevated temperature (40 °C) afforded **1** with a much lower molecular weight of $M_n = 10700$ ($M_w/M_n = 2.02$: Entry 6). When the polymerization was carried out at 0 °C, the corresponding polymer was afforded in a considerably inferior yield with $M_n = 126000$ (Entry 7). These results suggest that the optimum conditions for the formation of **1** with high molecular weight are room temperature and a catalyst loading of 0.5–2.0 mol %.

With the obtained polymerization conditions of 2-bromo-3-hexylthiophene (**3a**) in the presence of [CpNiCl(SIPr)], other 3-substituted bromothiophenes were also converted to high-molecular-weight polythiophenes, as shown in Table 2. The polymerization of these monomers, prepared in a similar manner to that of **3a**, proceeded highly efficiently to afford the corresponding polymers.

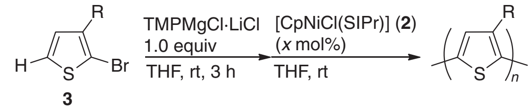
It was also found that GRIM polymerization with 2,5-dibromo-3-hexylthiophene (**4a**), with [CpNiCl(SIPr)] (**2**) as a catalyst, also proceeded as shown in eq 1. After treatment of **4a** with *i*-PrMgCl•LiCl at room temperature for 1 h in THF, the addition of the nickel catalyst **2** initiated the polymerization, and further stirring at room temperature for 24 h afforded the corresponding polymer **1a** with $M_n = 107000$ ($M_w/M_n = 2.65$).



(1)

It should be pointed out that the synthetic protocol for high-molecular-weight P3RTs can be performed similarly to the reaction with dehydrobrominative and debrominative (GRIM) procedures with the usual organometallic technique, although lowering the catalyst loading generally requires greater care with regard to moisture and oxygen.[6,14] HT-P3HT with extremely high molecular weight would be formed by the polymerization irrespective of the monomer/catalyst feed ratio, suggesting nonliving polymerization character in spite of the fact that the reaction proceeds in a highly HT-regioregular manner via chain-growth polymerization.[15] Indeed, an increase in the molecular weight was observed with the progress of the monomer conversion, albeit in nonlinear increments (9%, M_n (M_w/M_n) = 3100 (1.40); 25%, 6500 (2.20); 66%, 28800 (3.77)), suggesting that the formation of the high-molecular-weight polymer was not caused by the initial consumption of monomers in the early stage and the subsequent coupling between small polymers, as is representative of step-growth polymerization (Figure S1 in the Supporting Information).[16] The reaction may thus occur with relatively slow formation of a small amount of initiating species toward the propagation rate to result in a broad M_w/M_n value, although the detailed mechanism has not yet been clarified.

Table 2. [CpNiCl(SIPr)]-catalyzed polymerization of 2-bromo-3-substituted thiophenes[a]



–R	Time/h, *x*	Yield /%	M_n[b]	M_w[b]	M_w/M_n[b]	HT[c] /%
–Octyl (**3b**)	96, 1.5	47	87000	288000	3.31	98
$–C_{12}H_{25}$ (**3c**)	48, 2.0	85	70400	276000	3.92	99

[a]The reaction was performed with monomer (0.5 mmol), TMPMgCl•LiCl (0.5 mmol) and [CpNiCl(SIPr)] in 5 mL of THF at room temperature for 3 h (metalation) and at room temperature (polymerization). [b]Estimated by SEC analysis using $CHCl_3$ as an eluent. [c]Estimated by ^{1}H NMR.

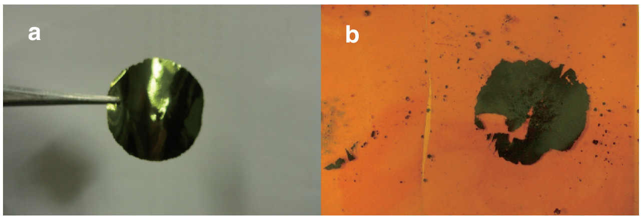


Figure 1. (a) Self-standing film of regioregular HT-P3HT (**1**) with $M_n = 224000$. (b) Attempted formation of thin-film of **1** ($M_n = 24000$) with the melt and hot press process on a polyimide film.

The obtained high-molecular-weight HT-P3HT showed a similar λ_{max} value[9a] (451–454 nm) in the UV–vis absorption spectra compared to HT-P3HT with $M_w = 40000$, while the melting point of the higher-molecular-weight polymer was found to be slightly higher by DSC analysis (208–244 °C). Notably, the self-standing film can be formed with the HT-P3HT of extremely high molecular weight. HT-P3HT (**1**) with $M_n = 224000$ was compression-molded between polyimide films at 290 °C and 6 MPa, then quenched in ice-water. A dark purple film with a thickness of 55 µm was obtained, as shown in Figure 1a.[5a] By contrast, attempted film formation with HT-P3HT of regular molecular weight ($M_w = 24000$, $M_w/M_n = 1.60$) under similar conditions failed to afford a fragile and non-self-standing polymer (Figure 1b). Preliminary studies showed that the film had an outstanding elastic modulus compared to other polymers. Further studies on the details of the mechanical and spectroscopic properties of the self-standing P3HT film will be discussed in due course.

In conclusion, we have revealed that the polycondensation of 2-bromo-3-substituted or 2,5-dibromo-3-substituted-thiophenes with the [CpNiCl(SIPr)] complex as a catalyst afforded HT-P3HT with extremely high molecular weight (up to $M_w = 815000$). The obtained polymer formed a self-standing film successfully, which had not been achieved with HT-P3HT of lower molecular weight. Accordingly, the mechanical characteristics of the thus obtained self-standing HT-P3HT film are of significant interest in terms of the relationship of its physical properties with its mechanical treatment as a high-performance material instead of as a substance on a supporting substrate.[16]

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