

New Synthetic Pathways to Well-Defined Oligothiophenes and Polythiophenes *via* C-H Coupling Reactions

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1. Introduction

π -Conjugated aromatic and heteroaromatic compounds have been utilized as a wide variety of advanced organic materials. In particular, oligothiophenes and polythiophenes, which are composed of multiple linkage of sulfur-containing five-membered heteroaromatic compounds, involve potential utilization for conductive,¹⁾ organic-semiconductive,²⁾ and liquid crystalline materials.³⁾

Cross coupling, which is a carbon-carbon bond-forming reaction with organometallic compounds and organic electrophiles in the presence of a transition metal catalyst, is a highly effective method for the synthesis of such π -conjugated organic materials,⁴⁾ however, the major drawback of cross coupling strategy is the preparation of the organometallic reagent prior to the transition metal-catalyzed reaction as well as the formation of metal salt waste accompanied by the desired cross-coupling product. If the related coupling product is formed by the direct reaction at the C-H bond of an organic compound,⁵⁾ the process is remarkably simplified. In recent years, extensive studies to synthesize π -conjugated organic compounds with C-H coupling are carried out.⁶⁾ We herein describe our recent studies on the synthesis of oligo- and polythiophenes using C-H coupling reactions.

2. Oligothiophenes

Oligothiophenes have recently attracted considerable attention in materials science as advanced organic materials with electronic and optoelectronic characteristics. These are employed as various materials such as thin-film organic transistors,⁷⁾ liquid crystalline compounds,⁸⁾ and dye-sensitized organic photovoltaic cells⁹⁾ as representative in Figure 1.

Oligothiophenes composed of a thiophene unit bearing a substituent at the 3-position form three type of possible regioisomers, head-to-head (HH), tail-to-tail (TT), and head-to-tail (HT) as shown in Figure 2. Among these, the HT isomer generally shows a superior performance as materials due to the least steric congestion and thus occurring extended π -conjugation.^{2c, 7d, 9d)} Development of a concise preparative method of HT-type oligothiophenes is therefore an important issue in organic synthesis.

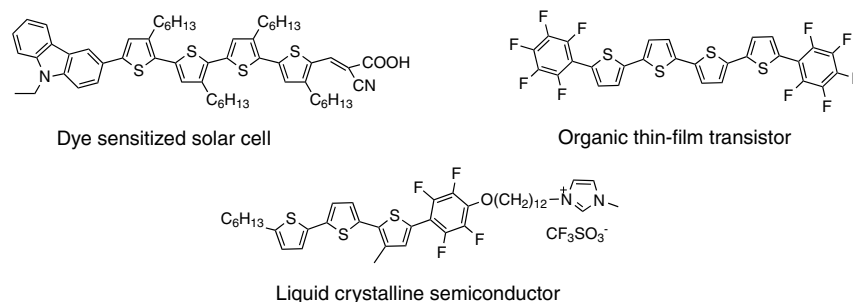


Figure 1. Oligothiophene derivatives as advanced materials.

2-1. Previous synthetic methodologies of HT type oligothiophenes

Transition metal catalyzed cross coupling reaction of thiophene and thiophene to form bithiophene would be an effective synthetic method for HT type oligothiophenes. Suzuki-Miyaura coupling with organoboranes and Migita-Kosugi-Stille coupling with organostannanes have actually been employed for the oligothiophene synthesis.^{10,11)} When halogenation of the bithiophene, which is formed by the thiophene-thiophene cross coupling, is conducted, the halogenated thiophene, again, can be a substrate for the reaction of further metallated thiophene thus allowing stepwise extension of the thiophene unit. Hence, oligothiophene with a certain number of thiophene unit would

be formed by repeating the cross coupling and halogenation sequence as shown in Scheme 1.¹²⁻¹⁴⁾

We have also reported iterative extension of thiophene unit leading to HT-oligothiophenes using palladium catalyzed C-H coupling.¹⁵⁾ We have previously shown that C-H arylation of thiophenes with AgNO₃/KF as an activator only takes place with aryl iodide whereas no reaction occurs with the corresponding bromides.¹⁶⁾ Stepwise extension of a thiophene unit would be possible by combining C-H arylation of thiophene bearing carbon-bromine bond with iodothiophene affording the bithiophene and a halogen exchange reaction of thus formed bithiophene bromide to give the bithiophene iodide (Scheme 2).

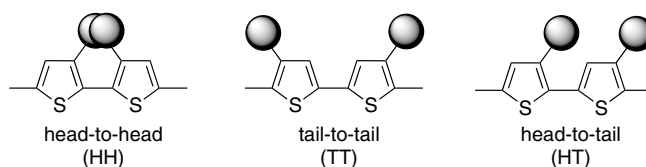
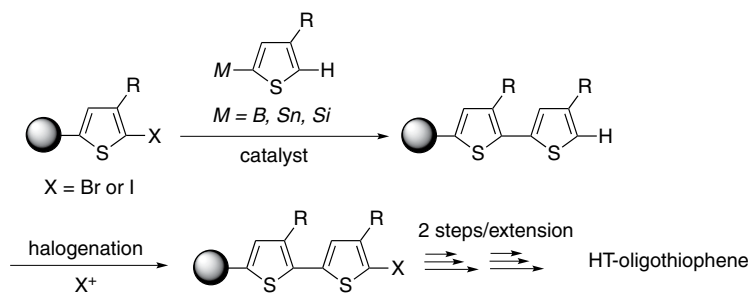
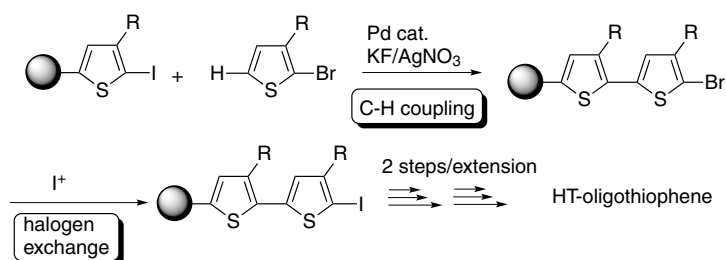


Figure 2. Regioregularity of oligothiophenes.



Scheme 1. Synthetic strategy for the stepwise preparation of HT-oligothiophene.



Scheme 2. Iterative synthesis of oligothiophene by C-H functionalization and halogen exchange.

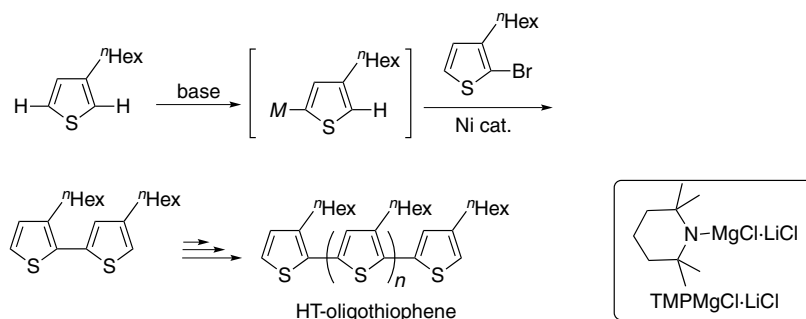
2-2. Synthetic method of HT type oligothiophenes with regioselective C–H coupling reaction ¹⁷⁾

A simpler synthesis of HT-type oligothiophenes is available by employing the regioselective C–H coupling of 3-hexylthiophene. We envisaged developing regioselective metalation of 3-substituted thiophene by hydrogen abstraction to generate a coupling precursor for the reaction of 2-bromo-3-hexylthiophene leading to the corresponding HT connected bithiophene. The bithiophene thus formed would be employed directly as a substrate for further extension without any transformation. Hence, this synthetic strategy would require only a single step per extension of the thiophene unit, which contrasts with the previous stepwise oligothiophene syntheses performed in the two steps sequence for extension of one thiophene unit.

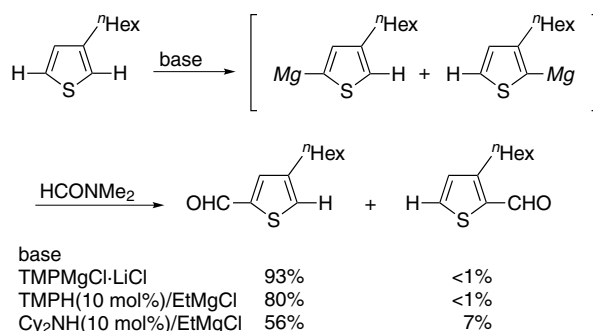
Such strategy was achieved by the use of $\text{TMPMgCl}\cdot\text{LiCl}$ (Knochel-Hauser base)^{18,19)} and a nickel-catalyzed cross

coupling. The single step extension of a thiophene unit leading to well-defined HT-oligothiophene was shown to take place highly efficiently. $\text{TMPMgCl}\cdot\text{LiCl}$ was indeed found to extract the C–H bond of 5-position of 3-hexylthiophene regioselectively. Treatment of 3-hexylthiophene with $\text{TMPMgCl}\cdot\text{LiCl}$ was carried out at room temperature for 3 h in THF probably forming 5-metalated thiophene, which was confirmed by treatment of *N,N*-dimethylformamide (DMF) to afford the corresponding aldehyde, exclusively, in 93% yield. We also found that regioselective metalation of 3-hexylthiophene took place by using ethyl magnesium chloride (EtMgCl) and a catalytic amount of 2,2,6,6-tetramethylpiperidine (TMPH) instead of stoichiometric $\text{TMPMgCl}\cdot\text{LiCl}$. (Scheme 4)

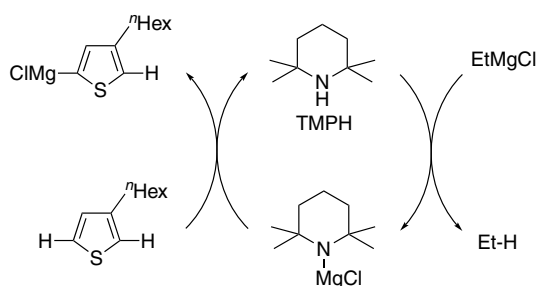
Asselin reports that treatment of 3-methylthiophene with 10 mol% of TMPH and EtMgCl and following addition of an aldehydes result in giving the corresponding secondary alcohol.²⁰⁾ We also confirmed the regioselective metalation of 3-hexylthiophene by the reaction of 10 mol% of TMPH and the



Scheme 3. Oligothiophene synthesis by regioselective metalation.



Scheme 4. Regiochemical study on the metalation of 3-hexylthiophene with $\text{TMPMgCl}\cdot\text{LiCl}$ or cat. $\text{TMPH}/\text{EtMgCl}$.



Scheme 5. Mechanism of metalation of thiophene with cat. $\text{TMPH}/\text{EtMgCl}$.

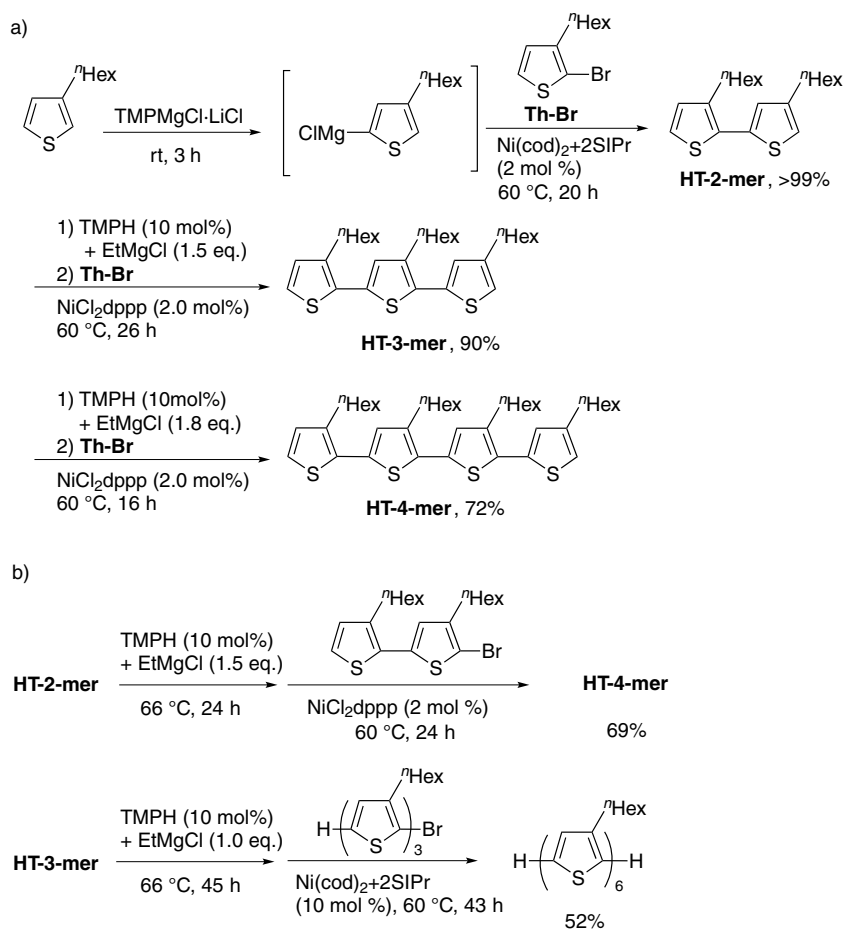
ethyl Grignard reagent, whereas the use of dicyclohexylamine instead of TMPH induced inferior regioselectivity.

Scheme 5 shows the reaction mechanism of the metalation at the C–H bond of thiophene. The reaction of TMPH with EtMgCl forms magnesium amide TMPMgCl. The formed TMPMgCl abstracts the 5-position of 3-hexylthiophene accompanied by TMPH, thus, allowing the metalation with catalytic use of secondary amine.

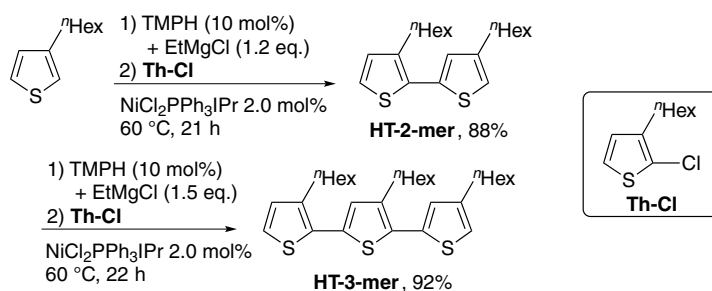
Scheme 6. summarizes the synthesis of HT-type oligomers of 3-hexylthiophene using TMPMgCl·LiCl or a combination of EtMgCl and 10 mol% of TMPH. The regioselective coupling of 3-hexylthiophene was found to proceed with 2-bromo-3-hexylthiophene (**Th-Br**) in the presence of 2.0 mol% of nickel catalyst bearing a N-heterocyclic carbene (NHC) ligand SIPr,

1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene, to afford **HT-2-mer** in >99% yield at 60 °C, whereas HH isomer was not observed at all. The obtained **HT-2-mer** was subjected to the further reaction with **Th-Br** with 10 mol% of TMPH and 1.5 equiv of EtMgCl in a similar manner furnishing terthiophene in 90% yield. Treatment of **HT-3-mer** with TMPH (10 mol%) and EtMgCl (1.8 equiv) and the reaction with **Th-Br** lead to quaterthiophene (**HT-4-mer**) in 72% yield. (a) It was also found that formation of **HT-4-mer** was also performed by the reaction of **HT-2-mer** with mono-brominated bithiophene to afford **HT-4-mer** in 69% yield. In addition, **HT-3-mer** reacted with brominated terthiophene to give the corresponding sexithiophene. The results are represented in Scheme 6. (b)

We also found that the reaction with 2-chloro-3-



Scheme 6. Stepwise synthesis of head-to-tail type oligothiophene.



Scheme 7. Oligothiophene synthesis with 2-chloro-3-hexylthiophene.

hexylthiophene (**Th-Cl**) instead of **Th-Br** took place successfully by using 2.0 mol% of $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$ as a nickel catalyst to give **HT-2-mer** and **HT-3-mer** in excellent yield, respectively (Scheme 7).

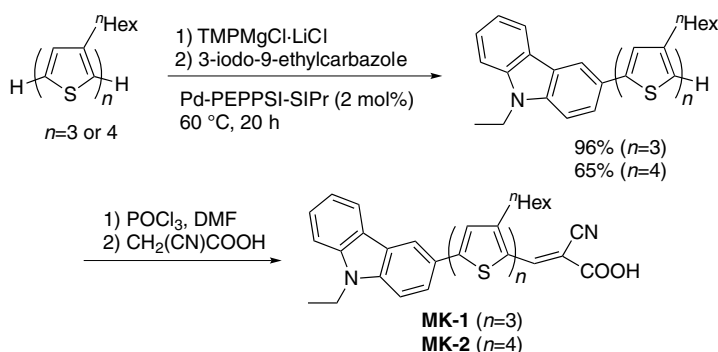
This simple iterative extension of the thiophene ring is applied to the short formal synthesis of **MK-1** and **MK-2**, which are organic dye molecules for the dye-sensitized organic photovoltaic cell showing excellent energy-conversion efficiency.^{9b,9d} As shown in Scheme 8, the reaction of terthiophene (**HT-3-mer**) and quaterthiophene (**HT-4-mer**) with $\text{TMPMgCl}\cdot\text{LiCl}$ and following addition of 3-iodo-9-ethylcarbazole in the presence of palladium catalyst PEPPSI-SIPr²¹⁻²³ (2.0 mol%) led to incorporation of the carbazole moiety. The obtained products are identical with the reported intermediates and following sequential Vilsmeier formylation and Knoevenagel reaction to introduce the cyanoacrylic acid moiety into the terminal thiophene ring would be performed by the literature method leading to **MK-1** and **MK-2**.⁹

It was also found to be possible to undergo cross coupling between different 3-substituted thiophenes. The reaction proceeded in a similar manner to afford bithiophenes bearing various substituent in good yields as summarized in Scheme 9. Bithiophene obtained in this way was transformed into terthiophene bearing three different substituent.

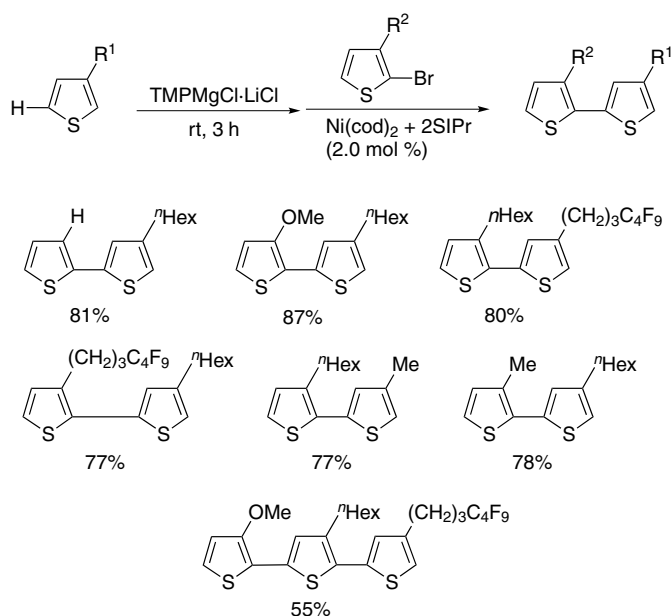
3. Polythiophene synthesis with bromothiophene derivatives as a monomer

Synthesis of HT-type-poly(3-hexylthiophene)s (P3HT) has been carried out with 2,5-dibromo-3-substituted-thiophene by the reaction of zinc or a Grignard reagent to induce metalation at the 5-position of thiophene ring in a regioselective manner and thus occurring cross coupling polycondensation with the remaining C-Br bond by Kumada-Tamao coupling (Mg) or Negishi coupling (Zn). In 1992, Rieke reported synthesis of HT-type P3HT by the reaction of 2,5-dibromot-3-hexylthiophene with Rieke zinc, which is the activated zinc, at low temperature leading to the corresponding organozinc and the following addition of palladium or nickel catalyst induced the cross-coupling polymerization.²⁴ McCullough also showed that formation of the corresponding thiophene-magnesium species was achieved by the reaction of an alkyl Grignard reagent to undergo magnesium-halogen exchange and the nickel-catalyzed polymerization.²⁵ Yokozawa improved the selective metalation by switching the exchanging bromine to iodine and discussed the possibility of living polymerization.²⁶

Concerning polythiophene synthesis utilizing the metalation at the C-H bond of thiophene, McCullough employed lithium amide to undergo proton abstraction at the 5-position



Scheme 8. Short formal synthesis of MK-1 and MK-2.



Scheme 9. Differently-substituted oligothiophenes.

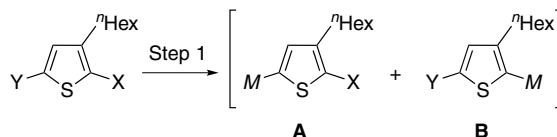
of thiophene, the following metal exchange by the addition of $ZnCl_2$ to afford the similar organometallic species, and nickel or palladium-catalyzed polymerization.²⁷⁾ The method had to be carried out with low-temperature process ($-78\text{ }^\circ\text{C}$) and complicated procedures. We envisaged to develop much simpler and practical C-H coupling polymerization and the use of Knochel-Hauser base (TMPMgCl·LiCl), which was highly effective for oligothiophene synthesis, was examined. The reaction of 2-bromo-3-hexylthiophene with TMPMgCl·LiCl was found to proceed at room temperature within 30 min to afford the corresponding organometallic species. (Table 1)

When the polymerization of bromothiophene was carried out with TMPMgCl·LiCl, polymerization took place highly efficiently with $NiCl_2dpppe$ or $NiCl_2dppp$ as a catalyst to afford P3HT in good yield with high HT selectivity as shown in Scheme 10.²⁸⁾ The reaction proceeded in a quantitative yield

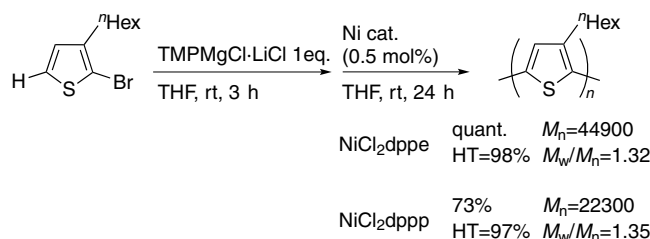
and the molecular weight showed good correspondence with the ratio of monomer/nickel catalyst. Polythiophene with molecular weight of higher than 40000 was obtained in the presence of 0.5 mol% of the catalyst with relatively narrow molecular weight distribution and high HT selectivity ($>98\%$).

It is also an interesting issue as a facile synthetic protocol to achieve 'one-shot' polymerization, which is the addition of substrate, reagent, and catalyst in one portion. In terms of the GRIM method, debrominative polymerization of 2,5-dibromo-3-thiophene, complete conversion of the dibromothiophene with a Grignard reagent to the corresponding metalated thiophene and the following nickel-catalyzed cross-coupling polymerization is a requisite, otherwise, no polymer would be obtained because of the termination reaction of Thieryl-Ni-Br, which is the reactive propagation end, with a remaining alkyl Grignard reagent.²⁹⁾ On the other hand, Knochel-Hauser base, sterically congested

Table 1. Generation of metalated thiophen as polythiophene precursor.



Method	X	Y	Step1	ratio A/B (M)
Rieke	Br	Br	Zn^* , $-78\text{ }^\circ\text{C}$ to rt, 4 h	97 : 3 (ZnBr)
GRIM	Br	Br	RMgX, rt, 30 min	~85 : ~15 (MgX)
Yokozawa	Br	I	iPrMgCl , $0\text{ }^\circ\text{C}$, 30 min	~99 : ~1 (MgCl)
McCullough	Br	H	1) LDA, $-40\text{ }^\circ\text{C}$, 40 min 2) $ZnCl_2$, -60 to $-40\text{ }^\circ\text{C}$, 40 min	~98 : ~2 (ZnCl)
Our group	Br	H	TMPMgCl·LiCl , rt, 30 min	~99 : ~1 (MgCl·LiCl)



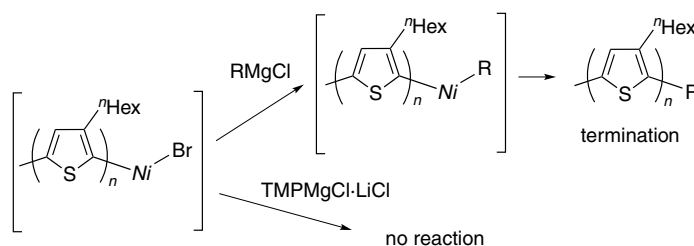
Scheme 10. Synthesis of HT-P3HT with 2-bromo-3-hexylthiophene and Knochel-Hauser base.

magnesium amide, would not cause any undesired side reactions such as termination of polymerization, thus one-shot addition would be plausible for the dehydrobrominative polymerization with 2-bromo-3-hexylthiophene with TMPMgCl. (Scheme 11)

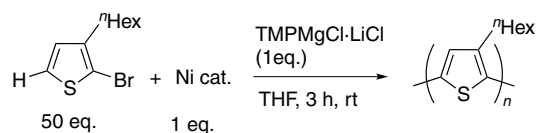
When NiCl₂dppp was employed as a nickel catalyst for one-shot polymerization of 2-bromo-3-hexylthiophene, the corresponding P3HT was obtained in excellent yield and high HT-regioregularity. Although the molecular weight distribution of the polymer was relatively broad, this value was improved when a nickel complex bearing 2-methylphenyl (*o*-tol) group NiCl(*o*-tol)dppp³⁰ was employed. (Scheme 12) This simple protocol allows to avoid preparation of metalated species prior to the polymerization, thus, a remarkable advantage of C-H coupling polymerization compared with the GRIM method.

4. Polythiophene synthesis of extremely high molecular weight

A nickel catalyst bearing *N*-heterocyclic carbene (SIPr) and cyclopentadienyl (Cp) group as ligands, which was developed by Nolan,³¹ was found to give the corresponding P3HT with the molecular weight of higher than 100,000. When the reaction was carried out with 2.0 mol% of CpNiCl(SIPr) at room temperature for 24 h, HT-type P3HT with Mw of higher than 400,000 was obtained. (Scheme 13) It has not been shown to give HT-type polythiophene with the molecular weight of higher than 100,000 and the molecular weight of commercially available polythiophene is as high as 50,000, therefore, novel characteristics of thus obtained extremely high HT-polythiophene may be interesting.

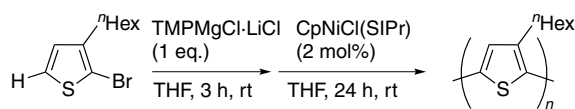


Scheme 11. Proposed mechanism for termination reaction with alkyl Grignard reagent.

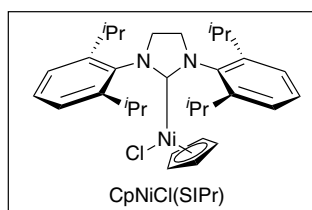


NiCl ₂ dppp	90%	M _n =10500
	HT=98%	M _w /M _n =1.84
NiCl(<i>o</i> -tol)(PPh ₃) ₂	70%	M _n =9500
+DPPP	HT=99%	M _w /M _n =1.14

Scheme 12. One-shot polymerization using Knochel-Hauser base.



81%
M_n=220,000
M_w/M_n=1.85



Scheme 13. Polymerization of 2-bromo-3-hexylthiophene using CpNiCl(SIPr).

5. Polymerization of chlorothiophene

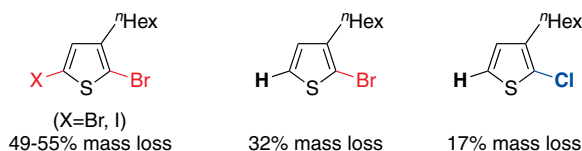
It is an important issue to consider atom efficiency particularly when a larger scale preparation is conducted. In the GRIM method with 2,5-dihalothiophene, the obtained P3HT would be as high as 50 g by employing 100 g of the starting material. On the other hand, 100 g of monobromothiophene can afford ca. 70 g of P3HT. Accordingly, we envisaged the P3HT synthesis with 2-chloro-3-hexylthiophene for the purpose of further improvement of the atom efficiency, which brings about the mass loss of only 17%. (Scheme 14) However, it is well known that the reactivity of cross coupling with aryl chloride is much lower than that of the corresponding iodide or bromide.

Indeed, when the polymerization of 2-chloro-3-hexylthiophene was conducted with $\text{TMPMgCl}\cdot\text{LiCl}$ and 0.5

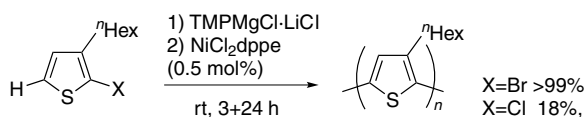
mol% of NiCl_2dpe at 25 °C for 24 h, which is the conditions to undergo the polymerization of bromothiophene highly efficiently, only afforded P3HT in 18% with the molecular weight of 4200. (Scheme 15)

Although the yield and the molecular weight was improved by the use of NiCl_2dppp , it is still unsatisfactory, it was found that a commercially available nickel(II) chloride complex bearing triphenylphosphine and *N*-heterocyclic carbene (NHC) ligands $\text{NiCl}_2(\text{PPh}_3)\text{IPr}^{32}$ dramatically improved the polymerization efficiency to afford P3HT with the molecular weight of 29200 with relatively narrow molecular weight distribution ($M_w/M_n = 1.29$).³³ (Scheme 16)

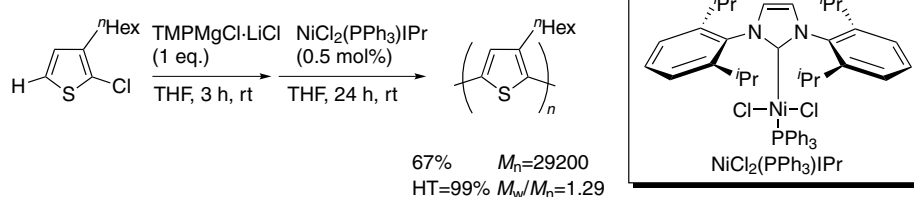
Figure 3(a) shows the relationship of the ratio of the consumed monomer/nickel catalyst with the molecular weight (M_n) of the obtained polymer indicating linear increasing of



Scheme 14. Atom efficiency in the polythiophene synthesis.



Scheme 15. Effect of halogen atom in the Ni-catalyzed P3HT synthesis.



Scheme 16. Polymerization of 2-chloro-3-hexylthiophene using $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$.

M_n by decreasing the catalyst loading. It was also found that the molecular weight showed linear increase corresponding to the monomer conversion and the molecular weight distribution was constantly narrow as shown in Figure 3(b). These results suggest that the polymerization of 2-chloro-3-hexylthiophene with $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$ as a catalyst proceeds in a living manner.

6. Polymerization with Grignard reagent and catalytic amine

As shown in the oligothiophene synthesis, metalation of 2-chloro-3-hexylthiophene was also examined with a Grignard reagent and a catalytic amount of secondary amine. Treatment of 2-chloro-3-hexylthiophene with EtMgCl (1.0 eq) and 10 mol% of TMPH at 60 °C for 10 h induced metalation at the 5-position, which was confirmed by treatment with iodine to

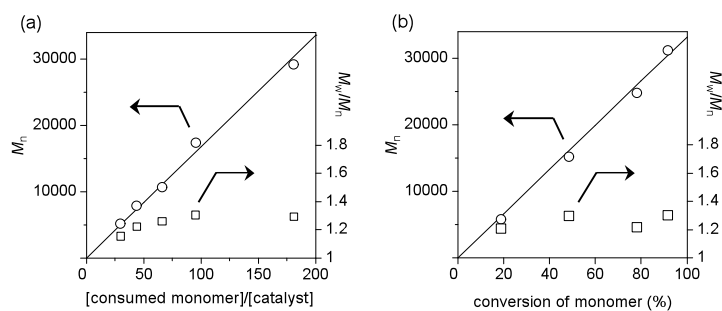
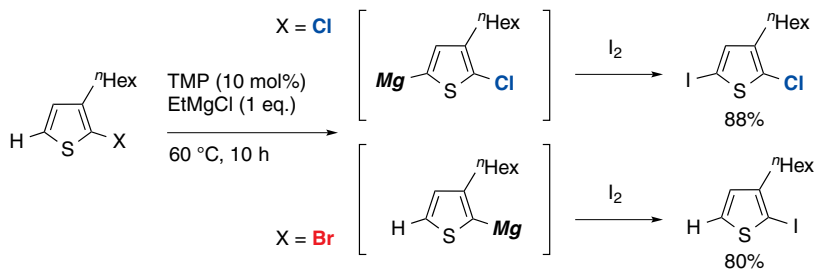


Figure 3. (a) Relationship of the monomer/catalyst feed ratio toward M_n and M_w/M_n . (b) Relationship of monomer conversion vs M_n .



Scheme 17. Metalation of 2-halothiophene with Grignard reagent and a catalytic amount of amine.

Table 2. Generation of thienyl magnesium species with a Grignard reagent and a catalytic amount of amine.

Grignard reagent	amine	time, h	conversion (%)
EtMgCl	none	10	26
	Et_2NH	2	73
	$i\text{Pr}_2\text{NH}$	10	85
	Cy_2NH	1	85
	TMP	10	88
$i\text{PrMgBr}$	none	10	21
	Et_2NH	10	85
	$i\text{Pr}_2\text{NH}$	5	73
	Cy_2NH	2	83
	TMP	10	35
$t\text{BuMgCl}$	none	10	6
	Et_2NH	10	71
	$i\text{Pr}_2\text{NH}$	10	90
	Cy_2NH	10	95
	TMP	10	5

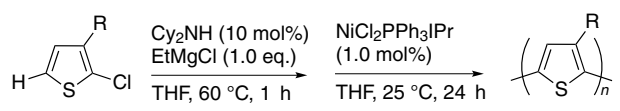
result in giving 5-iodinated product in 88% yield. By contrast, metalation at the 5-position was not observed in the similar reaction of 2-bromo-3-hexylthiophene but to afford bromine-iodine exchange at the 2-position. (Scheme 17) We then examined several combination of Grignard reagent and amine. Since regiochemical control was not necessary in this case, less bulky amines was found to be available in the deprotonation of 2-chloro-3-hexylthiophene. It should be pointed out that the reaction with EtMgCl and dicyclohexylamine (Cy₂NH) was found to complete the metalation within 1 h at 60 °C as shown in Table 2.

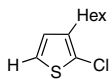
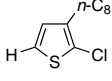
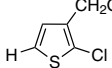
Several 3-substituted chlorothiophenes were subjected to the polymerization with the above optimized metalation protocol and following nickel-catalyzed cross coupling. Substituents bearing *n*-octyl group and ether functionality were successfully applied to the polymerization to afford the corresponding poly(3-substituted thiophene)s in excellent yield, high HT-selectivity, and narrow molecular weight distribution as shown in Table 3.³³⁾

7. Practical head-to-tail-type polythiophene synthesis

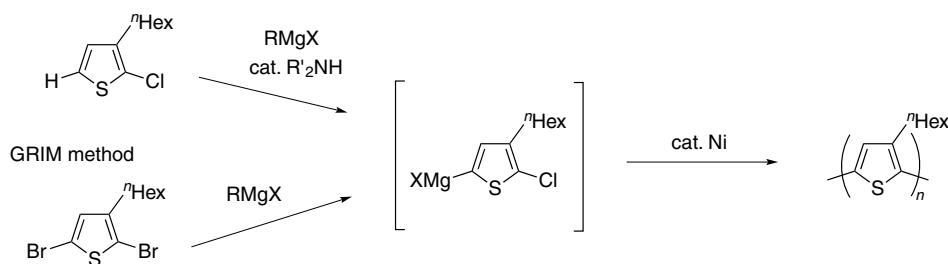
The following scheme represents comparison of our C-H coupling polymerization and the GRIM method. In addition to the difference of the starting monomer precursor, there is a difference in only the use of a catalytic amount of secondary amine. In considering the atom efficiency, the process with chlorothiophene by C-H coupling polymerization involves potentially practical advantage after further scale-up studies have been subjected. (Scheme 18)

Table 3. Polycondensation of chlorothiophene using Grignard reagent and catalytic amine.



Chlorothiophene	<i>M_n</i>	<i>M_w/M_n</i>	%HT	Yield (%)
	14900	1.21	98	82
	23100	1.29	99	76
	17000	1.31	99	84

C-H coupling polymerization



Scheme 18. Synthesis of HT-P3HT by C-H coupling polymerization/GRIM method.

8. Conclusion

We have described that thiophene-thiophene bond formation is successfully performed by the formation of thiophene organometallic species by the reaction of thiophene C-H bond with magnesium amide or the combined use of Grignard reagent and catalytic amine. The method efficiently leads to the formation of head-to-tail-type thiophene-thiophene bond to afford well-defined oligothiophenes and polythiophenes. The method can be applied to the synthesis of a variety of thiophene derivatives as advanced materials.

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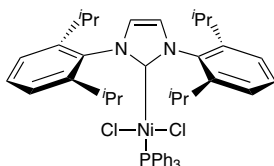
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Atsunori Mori received his Ph.D. from Nagoya University in 1987. He became a postdoctoral fellow at department of Chemistry University of California, Berkeley in 1987. He joined at The University of Tokyo as a research associate in 1988, and moved to JAIST (Japan Advanced Institute of Science and Technology) in 1993. He became an associate professor at Chemical Resources Laboratory, Tokyo Institute of Technology in 1995. In 2005, he was appointed to his current position as a full professor of Kobe University. His major field is organic synthesis, organometallic chemistry, and materials science.

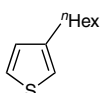
TCI Related Products

Nickel Catalyst

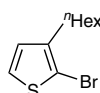


NiCl₂(PPh₃)IPr
200mg, 1g [B3235]

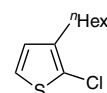
3-Alkylthiophene



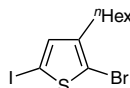
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1g, 5g, 25g [H0756]



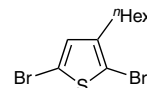
2-Bromo-3-hexylthiophene
5g, 25g [B3507]



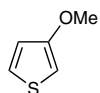
2-Chloro-3-hexylthiophene
5g [C2613]



2-Bromo-3-hexyl-5-iodothiophene
(stabilized with Copper chip)
1g, 5g [B3865]



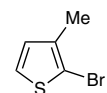
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3-Methoxythiophene
1g, 5g [M1093]

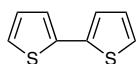


3-Methylthiophene
25g, 500g [M0440]

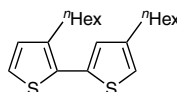


2-Bromo-3-methylthiophene
5g, 25g [B1025]

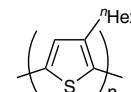
Bithiophene



2,2'-Bithiophene
1g, 10g, 25g [B1276]



3,4'-Dihexyl-2,2'-bithiophene
1g, 5g [D3928]



P3HT (regioregular)
200mg, 1g [P2018]

Others

B3691	2-Bromo-3-dodecylthiophene		5g
D4053	2,5-Dibromo-3- <i>n</i> -octylthiophene		5g
D4031	2,5-Dibromo-3-dodecylthiophene		5g
E0378	3-Ethylthiophene		5mL 25mL
P1128	3-Propylthiophene		1g 5g
B1458	3-Butylthiophene		1g 5g
P1127	3-Pentylthiophene		1g 5g
H0722	3-Heptylthiophene		1g 5g
O0213	3- <i>n</i> -Octylthiophene	1g	5g 25g
E0973	3-(2-Ethylhexyl)thiophene	200mg	1g
N0533	3-Nonylthiophene		1g 5g
D2098	3-Decylthiophene		1g 5g
U0056	3-Undecylthiophene		1g 5g
D2016	3-Dodecylthiophene	1g	5g 25g
O0245	3-Octadecylthiophene		1g 5g