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Inoue, Tomoki
Kuwayama, Aika
Okano, Kentaro
Horie, Masaki
Mori, Atsunori

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RESEARCH ARTICLE

Generation of sodium–thiophene species with metal amide-free approach toward polythiophene synthesis by cross-coupling polymerization

Tomoki Inoue,[a] Aika Kuwayama,[a] Kentaro Okano,[a] Masaki Horie,[b] and Atsunori Mori[a,c]*

Dedication ((optional))

[a] T. Inoue, A. Kuwayama, Dr. Kentaro Okano, Dr. Atsunori Mori
Department of Chemical Science and Engineering
Kobe university
1-1 Rokkodai, Nada, Kobe 657-8501, Japan
E-mail: amori@kobe-u.ac.jp
[b] Dr. M. Horie
Department of Chemical Engineering
National Tsing-Hua University
101, Sec. 2, Kuang-Fu Road, Hsinchu 30013, Taiwan
[c] Dr. Atsunori Mori
Research Center for Membrane and Film Technology
Kobe university
1-1 Rokkodai, Nada, Kobe 657-8501, Japan

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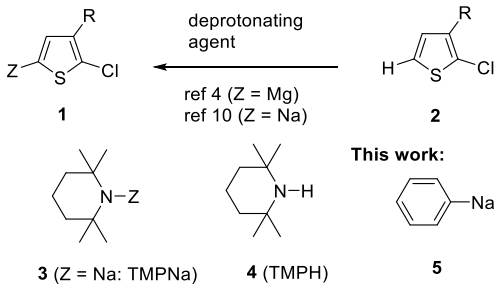
Abstract: Deprotonative metalation of 2-halo-3-substituted thiophene in a metal amide-free manner takes place at the 5-position smoothly in the presence of additive *N*,*N*,*N*',*N*'-teteramethylethylenediamine (TMEDA) at room temperature in a hexane solution. Following addition of nickel catalyst to the thus formed thiophene–sodium species promotes cross-coupling polymerization. When toluene was employed as a solvent in the polymerization reaction of 2-chloro-3-hexylthiophene in the presence of 2 mol% of nickel catalyst bearing N-heterocylcic carbene ligand, polythiophene was obtained in up to 86% yield with M_n of 23700 (M_w/M_n = 1.98) suggesting that ca. 30% of the catalyst participated in the polymerization.

Introduction

Thiophene, which is recognized as a heteroaromatic molecule bearing a sulfur atom, is widely employed as a series of electronic materials and found in a variety of biologically active compounds as pharmaceuticals and agrochemicals.[1–3] We have been engaged in the development of practical protocols for the bond formation at a carbon atom on the thiophene ring by transition metal catalysis. In particular, our recent concern has been centered to the synthesis of polythiophene, which proceeds through the cross-coupling polymerization catalyzed by nickel(II).[4–10] We have recently reported that the use of thiophene–sodium species **1** as an organometallic monomer for the polythiophene synthesis,[11] which involves deprotonative metalation of thiophene **2** with sodium amide composed of the metalated 2,2,6,6-tetramethylpiperidine (TMPNa: **3**).[12] The major drawback of such a process is the in-situ formation of the corresponding secondary amine **4** in the polymerization mixture[13,14] as well as the preparation of sodium amide with metallic sodium species through several steps. Accordingly, it is intriguing to develop a more simplified and straightforward protocol for the formation of metallothiophene monomer **1** (Z = Na). (Scheme 1) Herein, we describe that deprotonative metalation of 2-chloro-3-hexylthiophene (**2a**) proceeds with phenyl sodium (**5**) in hexane as an aprotic solvent in the presence of a small amount of an additive and the thus formed organometallic thiophene is successfully employed for the polythiophene synthesis.

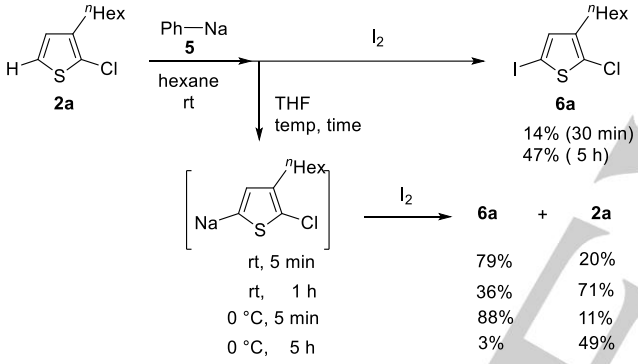


Scheme 1. Deprotonative metalation of chlorothiophene **2** and the deprotonating agents derived from sodium

Results and Discussion

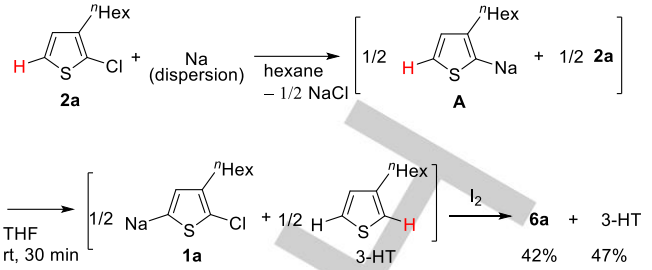
We first examined the performance of the formation of thiophene-sodium species by the reaction of 2-chloro-3-hexylthiophene (**2a**) with phenyl sodium (**5**)[15,16] in hexane, which was prepared by the reaction of chlorobenzene with sodium dispersion.[17–22] The initial attempt of the formation of thiophene–sodium species was performed by the addition of chlorothiophene to a solution of in-situ formed phenyl sodium in hexane. After

stirring for 30 min at room temperature, it was found that little reaction took place to undergo only 14% of metalation, which was monitored by the transformation into the corresponding iodide **6a** by quenching with iodine.[23] Recovery of 2-chloro-3-hexylthiophene (**2a**) accompanied in 81% yield was also confirmed, accordingly. Although the prolonged reaction period was attempted, it was found to observe slightly improved conversion to **6a** (47%) after 5 h. We next performed the metalation reaction by switching the solvent to a mixture of THF and hexane. It was revealed to afford iodothiophene **6a** in 79% yield after 5 min. However, the longer reaction period significantly decreased the yield of **6a** to 36% in 1 h probably because of the decomposition of the metalated thiophene through the ring opening of THF[19,24] to result in forming the protonated thiophene **2a**, while iodination at the methylene of the hexyl group adjacent to the thiophene ring was not confirmed at all by ^{1}H NMR analysis (See Supporting Information Figure s1). Although lowering the reaction temperature to 0 °C employing THF as a cosolvent was also examined to afford 88% of **6a** after 5 min, the similar decomposition of the metalated thiophene could not be avoided to give **6a** in only 3% yield under further continuous stirring for 5 h. (Scheme 2)



Scheme 2. Deprotonative metalation of chlorothiophene **2a** with phenyl sodium (**5**)

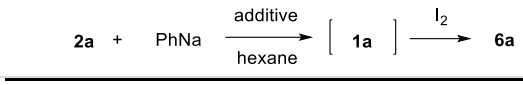
We also carried out the reaction of 2-chloro-3-hexylthiophene (**2a**) with an equimolar amount of sodium dispersion in hexane followed by the addition of THF. After being stirred for 30 min, it was confirmed to afford 47% of 3-hexylthiophene and 42% of iodothiophene **6a** after treatment with iodine as shown in Scheme 3. During the reaction a half amount of 2-metalated thiophene **A** was generated in hexane with the formation of NaCl. The recovery of a half amount of **2a** accompanied. When THF was added to the reaction mixture, deprotonation of remaining **2a** by the intermediate **A** efficiently proceeded. The result shows that thiophene–sodium species **A** also serves as an effective deprotonating agent in a polar solvent in a similar manner to the use of phenyl sodium **5** whereas a half amount of chlorothiophene **2a** must be sacrificed to undergo the successful formation of **1a**.[25]



Scheme 3. The metalation reaction with sodium dispersion

To solve the dilemma between solvent polarity in deprotonative metalation and unexpected E2-type cleavage of an ethereal solvent by the formed carbanion species[19] we next examined the effect of additive. Compared with much less deprotonation in hexane accompanied by the recovery of unreacted chlorothiophene **2a**, the use of two equivalents of HMPA as an additive revealed to undergo the effective deprotonation reaction, which was confirmed by the addition of iodine, to form **6a** in 50% yield after the reaction period of 5 min. However, the prolonged deprotonation period to 30 min caused significant decrease of the yield of **6a** to 0% suggesting that HMPA assisted the decomposition of anionic species **1a** (R = ^{n}Hex; Z = Na). The reaction in the presence of crown ether 15-crown-5 was also found to be ineffective (**6a**: 0%). The effective metalation to afford the organometallic monomer **1a** was found to take place efficiently when only twice equivalents of THF toward thiophene **2a** was employed. The reaction of phenyl sodium (**5**) with chlorothiophene **2a** in hexane in the presence of two equivalents of THF was carried out at 0 °C for 15 and 30 min. It was shown that 61% and 67% of **6a** was obtained along with the formation of 24% and 18% **2a**, respectively. Further longer reaction period 1 h significantly decreased the yield of **6a** to 18% as observed in the use of excess THF as a cosolvent of hexane. Several other additives were also examined in a similar manner and the results are summarized in Table 1. Ethereal additive DME (1,2-dimethoxyethane) was found to undergo the metalation reaction to afford **6a** in 44% yield at 0 °C, whereas the reaction at room temperature resulted to decrease the yield to 18%. The most effective deprotonative metalation was achieved in the use of 1.0 equivalent of TMEDA (*N*,*N*,*N*',*N*'-teteramethylethanediamine) to afford iodothiophene **6a** in 72% yield (with 13% of **2a**). It is remarkable to observe little decrease of the yield of **6a** (71% yield) under prolonged reaction period to 5 h. Although the deprotonation reaction proceeded with a decreased amount of TMEDA (10 mol%), slightly inferior conversion resulted (27% of **2a** remained). Tertiary amines such as Et_3N and $^iPr_2NEt$ were shown to be less effective to give **6a** in 38% and 39% yields, respectively. These results suggest that the basicity of tertiary amine and the chelating characteristics of diamine is the requisite of the successful deprotonative metalation. The most effective additive for the deprotonative metalation by PhNa (**5**) as a surrogate of TMPNa at this stage has been the use of TMEDA, which should have been achieved by any of ethereal derivatives. However, it is worthy of note that TMEDA is much inexpensive compared with TMPH.

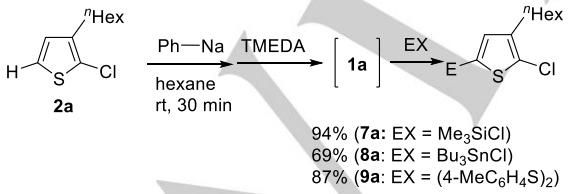
Table 1. Deprotonative metalation of 2-chloro-3-hexylthiophene (**2a**) with phenyl sodium (**5**) in hexane employing additives [a]



Addotve (equiv)	Temp	Time[b]	**6a**[c]	**2a**[c]
none	rt	30 min	14%	81%
HMPA (2)	rt	5 min	50%	31%
HMPA (2)	rt	30 min	0%	11%
15-crown-5 (1)	0 °C	30 min	0%	41%
THF (2)	0 °C	15 min	61%	24%
THF (2)	0 °C	30 min	67%	18%
THF (2)	0 °C	1 h	18%	53%
THF (2)	–20 °C	1 h	40%	53%
DME (2)	0 °C	30 min	44%	52%
DME (2)	rt	30 min	18%	60%
TMEDA (1)	rt	30 min	72%	13%
TMEDA (1)	rt	5 h	71%	9%
TMEDA (0.1)	rt	30 min	60%	27%
NEt_3 (2)	rt	30 min	38%	36%
*i*PrNEt (2)	rt	30 min	39%	57%

[a] The reaction was carried out with chlorothiophene **2a** (0.3 mmol) and PhNa (**5**, 0.6 mmol) in 0.6 mL of hexane and the reaction was terminated by the addition of iodine (0.6 mmol) dissolved in 1.2 mL of diethyl ether. Id based on ^{1}H NMR analysis. [b] The reaction period of the deprotonation reaction. [c] The yield based on ^{1}H NMR analysis.

The metalated thiophene with phenyl sodium in hexane in the presence of TMEDA was found to be transformed into other thiophene derivatives employing several electrophiles as summarized in Scheme 4. Trimethlysilylated **7a**, tributylstannylated **8a**, and thiolated **9a** were obtained in 94%, 69%, and 87% yields, respectively.

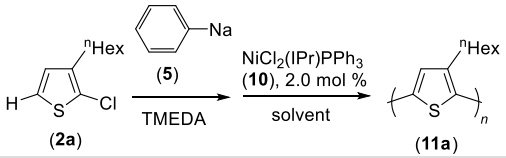


Scheme 4. Transformation of thiophene–sodium species with electrophiles

Encouraged by the smooth formation of sodiated chlorothiophene **1a**, the organometallic species was subjected to the polymerization reaction by the catalysis of the nickel complex $NiCl_2(PPh_3)IPr$ (**10**) bearing N-heterocyclic carbene as a ligand,[26,27] which was shown to be highly effective for the deprotonative polymerization with chlorothiophene **2a** and magnesium amide **3** (Z = MgCl·LiCl).[28,29] Table 2 summarizes the results. When the reaction was carried out in cyclopentyl methyl ether (CPME)[30] in the presence of 2 mol % of nickel catalyst **10**, the polymerization proceeded at room temperature to confirm color change gradually to dark purple and subsequent formation of precipitates of polythiophene **2** was observed. Polythiophene **11a** was obtained after stirring at –20 °C for 24 h in only 31% yield with M_n of 9200 (M_w/M_n = 1.96). The polymerization reaction at an elevated temperature (0 °C) in CPME slightly improved the yield to afford 34% of **11a** with higher M_n of 14200 and M_w/M_n of 1.77. The use of THF as a solvent and the reaction at –20 °C resulted in an improved yield (51%) with M_n of 15900 and M_w/M_n of 2.40. It was found that the smooth polymerization reaction took place when toluene was employed as a solvent. The reaction at 0 °C and room temperature resulted in giving polythiophene in 55% (M_n =15600; M_w/M_n =1.94) and 69% (M_n =23800; M_w/M_n =1.74) yields, respectively. Higher yields were shown to be observed in the polymerization reaction with a slightly increased amount of phenyl sodium (**5**) as a deprotonating agent. The yield of **11a** was improved to 86% with M_n of 23700 (M_w/M_n =1.74) when 1.2 equivalents of phenyl sodium was employed, while the use of further excess amounts of phenyl sodium decreased the yield to 72% (1.25 equiv) and 66% (1.50 equiv), respectively, which would be caused by the inhibition of the polymer propagation by the remaining phenyl sodium (**5**). Although termination of the polymerization is less likely in the use of TMPNa (**3**) than that of PhNa (**5**), such an unexpected side reaction could be avoided to some extent by complete consumption of **5**.

Compared with the polymerization with TMPNa (**3**) as a deprotonating agent, which we previously reported, smooth polymerization would be expected by the employment of PhNa (**5**) because the reaction of **5** only forms PhH (benzene) accompanied by the formation of metalated thiophene **1a**. Meanwhile, the reaction with sodium amide **3** furnishes a basic TMPH (**4**), which may react unexpectedly with polymer end bearing thiphene–nickel species. However, remarkable improvement has not been achieved whereas the molecular weight distribution was slightly improved in the deprotonation with **5** compared with that of **3**. Because highly reactive organometallic **1a** is still present in the polymerization system, further controlled polymerization has been difficult at this stage.

Table 2. Deprotonative polymerization of thiophene **2a** by the treatment with PhNa (**5**) followed by the addition of nickel catalyst **10**[a]



Solvent	PhNa (equiv)	Temp[b]	Yield[c]	M_n x 10^3 (M_w/M_n)[d]
CPME	1.0	–20 °C	31%	9.2 (1.96)
CPME	1.0	0 °C	34%	14.2 (1.77)
THF	1.0	–20 °C	51%	15.9 (2.40)

Toluene	1.0	–20 °C	35%	19.8 (1.78)
Toluene	1.0	0 °C	55%	15.6 (1.94)
Toluene	1.2	rt	86%	23.7 (1.98)
Toluene	1.25	rt	72%	28.0 (1.97)
Toluene	1.5	rt	66%	25.0 (2.03)
Toluene	1.5	rt	66%	25.0 (2.03)

[a] The deprotonation reaction was carried out with **2a** (0.3 mmol) and TMEDA (0.3 mmol) in 0.6 mL of hexane and polymerization was performed by the addition of nickel catalyst **10** (2.0 mol%) in 3.0 mL of toluene for 24 h. [b] The reaction temperature for the polymerization reaction. [c] Isolated yield. [d] Based on SEC (size exclusion chromatography) analysis.

Although the molecular weight distribution M_w/M_n is still broad from that in the ideal living polymerization, it was revealed that the ratio of catalyst loading/monomer feed showed a linearity shown as a solid line of Figure 1. The results of polymerization with several ratios of the monomer feed/catalyst loading are also summarized in Table 3. The use of the decreased amount of the nickel catalyst improved the molecular weight M_n. Despite marginal M_ns from the theoretical molecular weights shown as the dotted line of Figure 1, each M_n value was revealed to fit the solid line suggesting linear relationship. Considered that ca. 30% of the employed nickel catalyst participates in the polymerization of the metalated thiophene monomer, the number average molecular weight M_n would be rather close to the theoretical value for the catalyst transfer-type polymerization.[31,32] Because of the high reactivity of organosodium species toward nickel catalyst, deactivation of nickel that is inactive to initiation and propagation reactions would occur at the early stage of the polymerization.[8,33] Nevertheless, the survived polymer chain end bearing thiophene–nickel species might undergo smooth incorporation of the organometallic monomer.

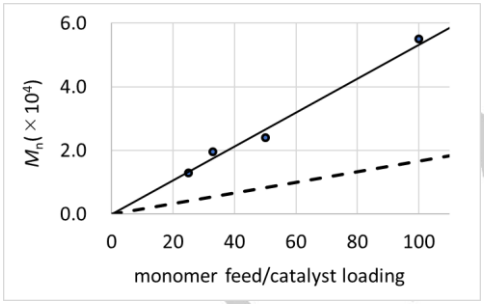


Figure 1. The relationship of catalyst loading vs molecular weight of polythiophene **11a**. Dotted line: Theoretical molecular weight based on monomer **2a**/catalyst **10**; solid line: Normalized theoretical molecular weight based on the survived catalyst **10** as 30%.

Table 3. The relationship of catalyst loading vs. molecular weight of polythiophene **11a**.[a]

feed ratio	Yield (%)[b]	M_n x 10^3 [c]	M_w/M_n[c]	catalyst survived[d]
25	70	12.9	1.70	30%
33	76	19.6	1.85	35%
50	86	23.7	1.98	28%
100	68	56.1	1.74	32%

[a] The deprotonation reaction was carried out with **2a** (0.3 mmol), PhNa (1.2 equiv), and TMEDA (1.0 equiv) in 0.6 mL of hexane and polymerization was performed by the addition of nickel catalyst **10** (1–4 mol%) in 3.0 mL of toluene at room temperature for 1 h. [b] Isolated yield. [c] Based on SEC analysis. [d] The calculated value of the survived catalyst by comparing the M_n with the theoretical molecular weight based on the ratio of monomer feed/catalyst loading.

Conclusion

In summary, we have shown that phenyl sodium serves as a deprotonating agent of 2-chloro-3-hexylthiophene (**2a**) for the in-situ generation of the organometallic monomer **1a** for the polythiophene synthesis. The process is recognized as metal amide-free deprotonation thus allows step-efficient generation of organometallic thiophene and avoids the use of costly 2,2,6,6-tetramethylpiperidine as an amide source whereas further developments in the reaction efficiency is required to take the advantage of the step efficiency through the deprotonation by PhNa/TMEDA. It is remarkable that all the procedures are conducted at room temperature thereby the process is free from the temperature control. Although the highly reactive organosodium is still uncontrolled for the smooth living polymerization catalyzed by nickel, the development of optimum conditions may improve the catalyst efficiency. Further studies are in progress for the practical polymerization employing sodium as an abundant element.

Experimental Section

General procedure for the synthesis of poly(3-hexylthiopene-2,5-diyl) (11a): To a solution of chlorobenzene (0.037 mL, 0.36 mmol) in hexane, was added sodium dispersion (66.2 mg, 25 w/w% in mineral oil, 0.72 mmol) at room temperature under nitrogen atmosphere. After stirring for 30 min, 2-chloro-3-hexylthiophene (0.045 mL, 0.3 mmol) and TMEDA (0.045 mL, 0.3 mmol) were added. To the resulting mixture was added 3.0 mL of toluene and the addition of nickel catalyst $NiCl_2(PPh_3)IPr$ (**10**, 4.7 mg, 0.006 mmol) followed. Stirring was continued at room temperature for 1 h. Polymerization was terminated by the addition of 1 M HCl to form dark purple precipitates, which was filtered off to leave a crude solid. The residue was washed with methanol and hexanes repeatedly to afford 43.0 mg of **11a** in 86% yield. The molecular weight and the molecular weight distribution was measured by SEC (size exclusion chromatography) analyses to show M_n = 23700 (M_w/M_n = 1.98). Measurement of ^{1}H NMR showed the regioregularity of 96:4 based on the methylene signals adjacent to the thiophene ring δ 2.81 (head to tail) and 2.61 (tail-to-tail). Spectroscopic properties were identical with those of the authentic polythiophene.[28]

Supporting Information

Experimental details, SEC profiles of polythiophene **11a**, Copies of NMR spectra.

Acknowledgements

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Keywords: Chlorothiophene • Nickel catalyst • Phenyl sodium •Polythiophene • TMEDA

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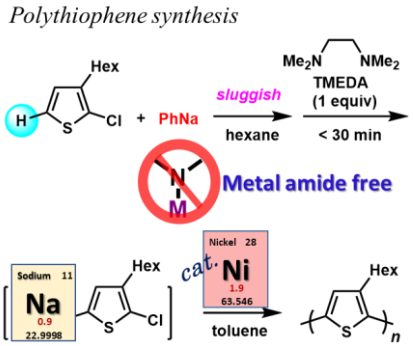

Phenyl sodium, which is prepared by the reaction of chlorobenzene and sodium dispersion, deprotonates 2-chloro-3-hexylthiophene in hexane as a solvent in the presence of an equimolar amount of *N,N,N′,N′*-tetramethylehtylenediamine (TMEDA) leading to thiophene–sodium species, which smoothly reacts to polymerize by the addition of nickel (II) catalyst through cross-coupling polymerization in a highly regioregular manner.

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