Cross-Coupling Polymerization of Organosodium for Polythiophene Synthesis

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Cross-coupling polymerization of organosodium for polythiophene synthesis

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ABSTRACT: Treatment of 2-chloro-3-hexylthiophene with sodium 2,2,6,6-tetramethylpiperidin-1-yl (TMPNa) in hexane underwent deprotonation at the 5-position to afford the thiophene–sodium species, which formation was confirmed by quenching with iodine leading to 2-chloro-3-hexyl-5-iodothiophene in 85% yield. Addition of nickel catalyst bearing N-heterocyclic carbene (NHC) to the thus formed thiophene–sodium species in cyclopentyl methyl ether induced the cross-coupling polymerization at −20 °C. After stirring for 24 h, poly(3-hexylthiophen-2,5-diyl) was obtained in 56% yield. The average molecular weight M_n was revealed to show 9700, which was close to the theoretical molecular weight (M = 8500) based on the ratio of the monomer feed/catalyst loading (2.0 mol %), and the molecular weight distribution was found to be 2.1.

INTRODUCTION

Polythiophene have attracted considerable attention as π-conjugated polymeric materials, which are widely employed as electronic devices including conductive materials, semiconductors, photovoltaic cells, electrodes, etc.[1–5] Development of facile and practical synthetic protocol for polythiophene is therefore a major concern in organic synthesis, organometallic chemistry, and transition metal catalysis as well as polymer synthesis. Cross-coupling polymerization of metallated halothiophene **1** by the catalysis of transition metal has been a method of choice to afford highly regioregular head-to-tail (HT) type polythiophene **2** along with controlled molecular weight through the catalyst-transfer-type cross-coupling polymerization.[6–9] Organomagnesium was first employed as an organometallic species as a monomer. Zinc and some other group II metallic species followed for the preparation of polythiophene to date.[10–12] Generation of such an organometallic species has been carried out by the regioselective halogen–metal exchange with 2,5-dihalo-3-substituted thiophene[6,7] when a certain alkyl metallic species is subjected to the dihalogenated precursor. Deprotonation of 2-halo-3-substituted thiophene at the 5-position with metal amide has also been alternatively employed to generate metallated halothiophene species **1**.[13–17] We have reported that the thiophene species of organolithium is available for polythiophene synthesis (Murahashi coupling polymerization), where it is worthy of note to control highly reactive organolithium as **1** (M = Li) for the cross coupling polymerization catalyzed by a nickel complex.[18,19] Polymerization proceeded in a highly regioregular manner with the controlled molecular weight with relatively narrow molecular weight distribution. We envisaged that *it is challenging to utilize much more reactive and less controllable but abundant sodium instead of other metallic species such as lithium, magnesium, zinc, etc. for polythiophene synthesis* in both fields of organometallic chemistry and polymer synthesis.[20–26] Herein we report that polythiophene synthesis can be achieved employing deptrotonative generation of metallated polythiophene **1** (M = Na) with a bulky sodium amide and that following nickel-catalyzed cross-coupling polymerization is tolerable in the use of the thus formed thiophene–sodium species as an organometallic monomer (Scheme 1).
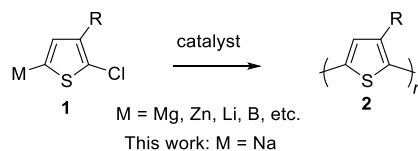
SCHEME 1. Cross-coupling polymerization of thiophene–metal species

We first examined the performance of the formation of thiophene–sodium species by the reaction of 2-chloro-3-hexylthiophene (**3a**) or 2-bromo-3-hexylthiophene (**3b**) as shown in Scheme 2 with sodium amide TMP–Na (sodium 2,2,6,6-tetramethylpiperidine-1-yl, **4**), which was prepared following the generation protocol reported by Takai et al.[27] with 2,2,6,6-tetramethylpiperidine and in situ-generated organosodium employing sodium dispersion.[28] The reaction of 2-chloro-3-hexylthiophene (**3a**) with **4** was examined in hexane at room temperature for 30 min and the progress of the reaction was confirmed by quenching with the

addition of iodine to afford 2-chloro-3-hexyl-5-iodothiophene (**5a**) to result in 85% yield of iodination. It was found that the carbon–chlorine bond of thiophene was intact by the addition of sodium amide **4** as well as the thus formed metallated chlorothiophene at the 5-position. By contrast, the reaction with the related bromide **3b** was ineffective to observe only 17% of the deprotonative metalation, which was also confirmed by the transformation to the corresponding iodide **5b**, accompanied by the formation of several unidentified side products probably because the deprotonated organometallic species itself may react at the carbon-bromine bond.

3a (X=Cl)
**3b** (X=Br)

5a (X=Cl), 85%
5b (X=Br), 17%
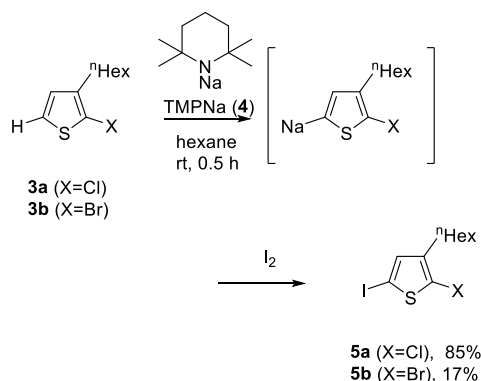
SCHEME 2. Deprotonative metalation of halothiophene **3** with TMPNa **4**

Encouraged by the smooth formation of sodiated chlorothiophene **1** (M = Na) in hexane at room temperature, the organometallic species was subjected to the polymerization reaction by the catalysis of the nickel complex bearing N-heterocyclic carbene as a ligand **6**, which was shown to be highly effective for the polymerization with chlorothiophene **3a**.[29,30] When the reaction was carried out in hexane in the presence of 2 mol % of nickel catalyst **6**, the polymerization indeed proceeded at room temperature to confirm immediate color change to dark purple and subsequent formation of precipitates of polythiophene **2**. Accordingly, the polymer was obtained in 47% yield after stirring at room temperature for 2 h with M_n of 25000 (M_w/M_n = ca. 3.0). The use of 1,4-dioxane as a solvent further lowered the yield to 22% and the molecular weight distribution was much inferior. (M_n =23800; M_w/M_n = 5.2). The reaction in a polar solvent THF at room temperature did not improve the yield despite improved solubility of the formed polymer to afford **2** in 41% yield. The use of cyclopentyl methyl ether (CPME) at room temperature was also ineffective to afford polymer **2** in only 23% yield and the molecular weight was inferior. However, when the reaction temperature was lowered to 0 °C in THF, the yield of polythiophene **2** was remarkably improved to 71%. The reaction of 4-methyl-tetrahydropyran (4-MeTHP) at 0 °C also resulted to give polythiophene in 48% yield whereas the molecular weights M_n in THF and 4-MeTHP were yet marginal to the theoretical one based on the monomer feed/catalyst loading ratio (M = 8500). The molecular weight distribution values (M_w/M_n = 4.2–4.7) were also extremely broad, which was unlike in our previous polymerization with the lithiated analog.[18] Further improved yield and narrower M_w/M_n at 0 °C were achieved when the reaction was carried out in cyclopentyl methyl ether (CPME) or toluene as a solvent. The reaction of CPME afforded polymer **2** in 65% yield (M_n = 23500; M_w/M_n = 2.3) and that in toluene resulted in 62% yield (M_n =21600, M_w/M_n = 2.1). These results are summarized in Table 1.

Table 1. Solvent effect of the deprotonative polymerization of 2-chloro-3-hexylthiophene (3a)[a]
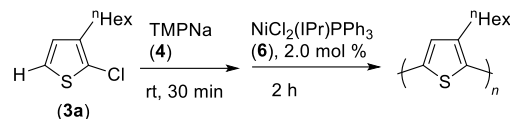
| Solvent	Temp[b]	Yield[c]	M_n x 10^{-3} [d]	M_w/M_n [d]
hexane	rt	47	25.0	3.0
1,4-dioxane	rt	22	23.8	5.2
THF	rt	41	20.9	2.4
CPME	rt	23	7.5	1.8
THF	0 °C	71	19.4	4.2
4-MeTHP	0 °C	48	12.3	4.7
CPME	0 °C	65	23.5	2.3
toluene	0 °C	62	21.6	2.1

[a] The deprotonation was performed with chlorothiophene **3a** (0.3 mmol) and NaTMP (**4**) (0.3 mmol) in 0.6 mL of hexane at room temperature. Polymerization followed by the addition of nickel catalyst **6** (2.0 mol %) in 3 mL of the solvent. [b] The reaction temperature for the polymerization. [c] Isolated yield. [d] The molecular weight was estimated by the measurement by SEC based on polystyrene standards.

Inferior yields in the use of hexane and 1,4-dioxane would be the effect of the poor solubility of the formed polythiophene. The formation of precipitates along with the increase of the degree of polymerization might have terminated the propagation reaction. On the other hand, a low yield at room temperature in THF would be ascribed to the consumption of active organometallic monomer **1** (M = Na) by the ring opening of the five-membered cyclic ether.[31] Such a similar deprotonative cleavage of the solvent would also proceed in the use of CPME and 1,4-dioxane and consumption of monomer **1** caused the decrease of the yield of polymer **2**. When the polymerization reaction was carried out at 0 °C, such undesired reaction of **1** was suppressed and the improved yield was achieved.

The obtained polythiophene **2** was found to show high head-to-tail regioregularity of 96:4 similar to the reaction with other metallic species (Li, Mg, etc.). Measurement of ^{1}H NMR spectrum revealed that the methylene signals adjacent to the thiophene ring (δ = 2.80 and 2.58 for head-to-tail/tail-to-tail, respectively) showed the high regioregularity of the obtained polythiophene **2**. The measurement of MALDI-TOF mass spectrum of polythiophene **2** showed the clear increment of the molecular weight as 166.4 Da, which observation was derived from the repeating unit of 3-hexylthiophen-2,5-diyl segment (166.1 mass) in polymer **2**. (Figure 1) These results suggest that the cross-coupling polymerization with organosodium also proceeds in a chain-growth

manner as the propagation reaction in the employment of thiophene–magnesium species as an organometallic monomer.[6] Although the polymerization with thiophene–sodium species remains the room to be improved for the control of the molecular weight and the molecular weight distribution toward the practical living-like polymerization, it should be pointed out that such a chain-growth polymerization is achieved in the use of highly reactive and less controllable organosodium.
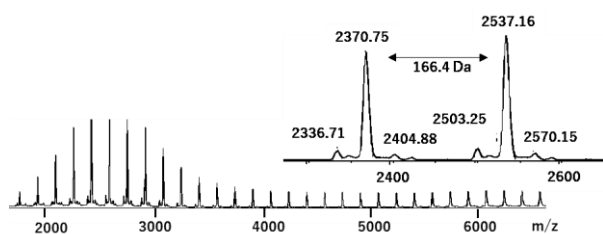
a)
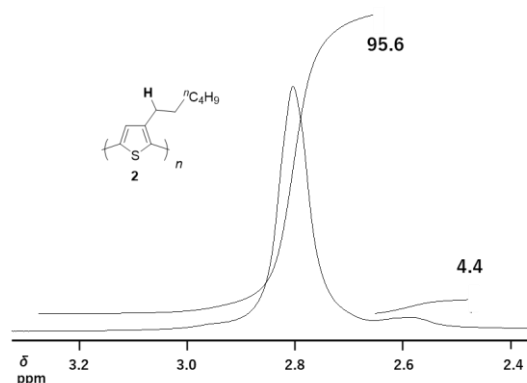
(b)

Figure 1. (a) ^{1}H NMR spectrum of polythiophene **2** for the analysis of regioregularity and (b) MALDI-TOF mass spectrum of **2**

We next studied the effect of the polymerization temperature with CPME and hexane as a mixed solvent system as shown in Table 2. Polymerization was found to take place until the temperature was lowered to −20 °C whereas further lower temperature resulted in an insufficient yield. The reaction at −25 °C significantly lowered the yield of polymer **2** to 20% and polymerization was found to hardly proceed at −30 °C (9% yield). Worthy of note is that the polymerization at −20 °C afforded **2** with M_n = 9700, which reached to further close to the theoretical molecular weight based on the monomer/catalyst feed ratio (M = 8500). When the polymerization reaction with a lower catalyst loading of **6/3a** at 0.01 was carried out at −20 °C, polythiophene **2** of higher M_n of ca. 25000 was obtained. Polythiophene **2** of lower molecular weight was obtained of a higher **6/3a** catalyst loading/monomer feed ratio (0.03) at 0 °C whereas the molecular weight distribution (M_w/M_n) of the obtained **2** was insufficient because several unexpected side reactions caused by highly reactive and uncontrollable thiophene–sodium, which brought about still slightly broader molecular weight distribution compared with that in the use of other counter ions (M_w/M_n = <2.0).

Table 2. Polymerization of 2-chloro-3-hexylthiophene (3a) by deprotonative metallation with sodium amide 4 followed by nickel-catalyzed cross coupling polymerization with 6

Temp[b]	**6/3b**	yield[c]	M_n x10^{-3} [d]	M_w/M_n [d]
0 °C	0.02	68	22.5	2.5
−10 °C	0.02	75	14.9	2.5
−20 °C	0.02	56	9.7	2.1
−25 °C	0.02	20	8.5	2.5
−30 °C	0.02	9	--	--
−20 °C	0.01	37	24.8	2.0
0 °C	0.04	34	9.3	2.4

[a] The deprotonation reaction was carried out with chlorothiophene **3a** (0.3 mmol) and NaTMP (**4**) (0.3 mmol) at room temperature in 0.6 mL of hexane. Polymerization was performed with nickel catalyst **6** in CPME (3.0 mL) for 24 h. [b] Bath temp during the polymerization reaction. [c] Isolated yield. [d] The molecular weight was estimated by the measurement by SEC based on polystyrene standards.

The reaction was also found to take place with several thiophene derivatives bearing a different alkyl substituent at the 3-position. As represented in Scheme 3, octylthiophene **7a** and dodecylthiophene **7b** similarly afforded the corresponding polythiophenes **8** in good yield with an agreement of the molecular weight with the ratio of monomer feed/catalyst loading.

R = $^nC_8H_{17}$, 51%, M_n = 11000; PDI = 2.9 (**8a**)
R = $^nC_{12}H_{25}$, 51%, M_n = 12000; PDI = 2.8 (**8b**)
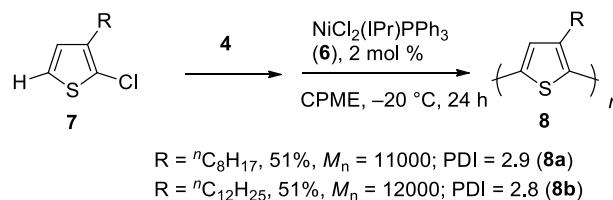
SCHEME 3. Polymerization of 2-chloro-3-substituted thiophenes

In summary, cross coupling of polymerization of organosodium was achieved by employing the nickel catalyst. The present polymerization serves as a new class of cross coupling of organosodium by transition metal catalysis in addition to the recent report by Asako, Takai, and coworkers, in which the formation of organosodium was shown to take place smoothly when metallic sodium dispersed in a mineral oil (SD) is employed and the formed carbanion was shown to undergo reaction with variety of organic electrophiles.[20–25] Although several arylated sodium species were shown to be employed for transition metal-catalyzed cross coupling, such an example is only shown to take place in a rather limited substrate. Coupling reactions have been performed after the transformation into such a more stable metallic species as zinc, boron, etc. Thus, worthy to mention is

that the direct cross coupling with organosodium itself was revealed to proceed in nickel-catalyzed cross-coupling polymerization with sodiated chlorothiophene **1** (M = Na) without a metal exchange protocol. Although polymerization proceeded in a regioregular manner in moderate to good yield, undesired side reaction of thiophene–sodium could not be avoided completely and thus the broadening of the molecular weight distribution resulted. Further improvement needs to be studied for the control of the molecular weight distribution.

ASSOCIATED CONTENT

Supporting Information

Experimental details. Spectroscopic and analytical data. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

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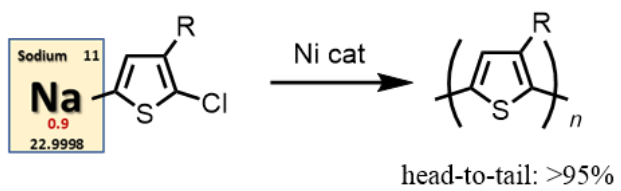
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head-to-tail: >95%

cross-coupling polymerization
with **organosodium**