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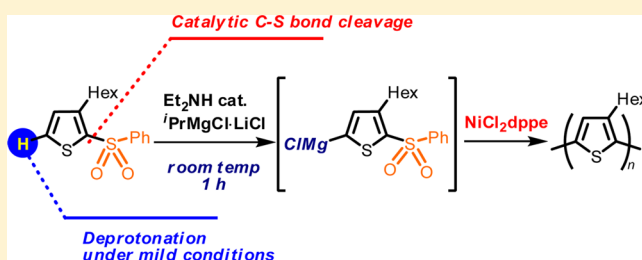
# Nickel(II)-Catalyzed Cross-Coupling Polycondensation of Thiophenes via C–S Bond Cleavage

Shunsuke Tamba, Kanta Fuji, Karin Nakamura, and Atsunori Mori\*

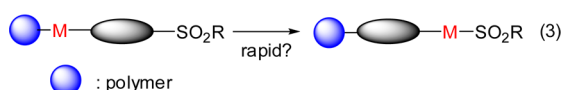
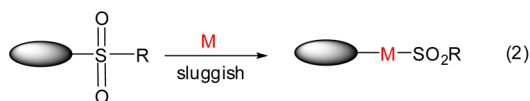
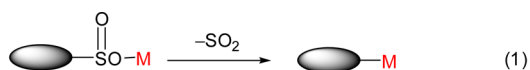
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**S** Supporting Information

**ABSTRACT:** Cross-coupling polycondensation of thiophene derivatives occurs via C–S bond cleavage in the presence of a nickel catalyst. Head to tail type (HT) regioregular poly(3-hexylthiophene) is obtained by a nickel(II)-catalyzed deprotonative C–H functionalization polycondensation of 2-(phenylsulfonyl)-3-hexylthiophene with stoichiometric TMPMgCl·LiCl or with the catalytic secondary amine/RMgX. Debrominative Grignard metathesis (GRIM) polymerization with 5-bromo-2-(phenylsulfonyl)-3-hexylthiophene also proceeds by the catalysis of the nickel(II) complex to afford the corresponding polythiophene.



Transition-metal-catalyzed cross coupling has attracted considerable attention in organic synthesis, and a wide range of organometallic reagents and organic electrophiles have been employed.<sup>1</sup> Among those, the coupling reaction with organic halides as an electrophile has been studied so far, whereas there has been fewer remarks on the use of an organic compound bearing a C–S bond as an electrophile for cross-coupling.<sup>2</sup> Recent advances in cross-coupling chemistry enabled the reaction of organic sulfinates through the oxidative cleavage of the C–S bond (eq 1)<sup>3</sup> and the thus formed organometallic



intermediate allowed the C–C bond formation. In contrast, there have been fewer studies on the direct oxidative cleavage of C–S bond of sulfoxides and sulfones by a transition-metal catalyst (eq 2)<sup>4</sup> due to the difficulties in the oxidative addition of low-valent metallic species to the C–S bond.

On the other hand, remarkable progress has recently been shown in cross-coupling polymerization of thiophene derivatives leading to conjugated polythiophenes, in which highly reactive nickel catalysts play a key role in successful polymerization.<sup>5–7</sup> Accordingly, we envisaged that such a coupling reaction may achieve C–S bond cleavage, as shown in eq 3. Herein, we describe that cross-coupling via C–S bond

cleavage with a transition-metal catalyst is shown to take place in the polymerization of thiophene derivatives.

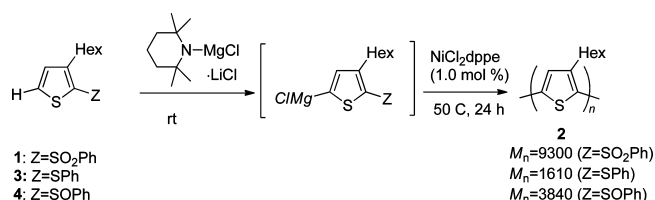
As a monomer precursor we have first chosen 2-(phenylsulfonyl)-3-hexylthiophene (**1**), and **1** was subjected to deprotonation with Knochel–Hauser base<sup>8</sup> at room temperature for 30 min. Addition of 1 mol % of NiCl<sub>2</sub>(dppe) as a catalyst to the reaction mixture and further stirring at 50 °C for 24 h induced polymerization to afford polythiophene **2** with  $M_n = 9300$  ( $M_w/M_n = 1.80$ ), although the reaction was slower than that of the related halothiophene that proceeded to completion within a few hours at room temperature.<sup>6a,10</sup> The head-to-tail (HT) regioregularity of the obtained polymer was confirmed by <sup>1</sup>H NMR analysis, showing 99% of the HT selectivity. Worth of note is that carbon–carbon bond formation by transition-metal catalysis occurred via C–S bond cleavage, which is a new class of cross-coupling polycondensation. On the other hand, polymerization with 3-hexylthiophen-2-yl phenyl sulfide (**3**) as a monomer was examined under similar conditions to afford P3HT (**2**) with much lower yield and molecular weight ( $M_n = 1610$ ). A sulfoxide, 2-phenylsulfinyl-3-hexylthiophene (**4**), also reacted in a similar manner to give the corresponding polymer with  $M_n = 3840$  ( $M_w/M_n = 1.56$ ) in 74% yield. The results show that phenyl sulfone serves as the most effective leaving group in the polymerization of thiophene (Scheme 1)

Polymerization with sulfonylthiophene **1** was examined under several conditions, as shown in Table 1. The reaction in the presence of 3 mol % of NiCl<sub>2</sub>(dppe) proceeded in THF, 1,4-dioxane, toluene, and cyclopentyl methyl ether (CPME) to afford the corresponding polymers in reasonable yields. Polythiophene **2** of a higher molecular weight was obtained by decreasing the catalyst loading of the nickel complex;

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**Scheme 1. Deprotonative Polymerization via C–S Bond Cleavage in the Presence of Ni Catalyst****Table 1. Nickel-Catalyzed Polymerization of Sulfonylthiophene 1 with Knochel–Hauser Base<sup>a</sup>**

NiCl <sub>2</sub> (dppe) amt (mol %)	solvent	temp (°C), time (h)	yield (%)	$M_n^b$	$M_w/M_n$
1	THF	50, 24	43	9300	1.80
3	THF	50, 24	74	3200	1.30
3	dioxane	60, 24	53	6800	1.94
3	toluene	60, 24	86	6300	2.26
3	CPME	60, 24	50	6500	1.81
2	THF	50, 24	79	7400	1.71
1.5	THF	50, 8	(79) <sup>c</sup>	15900	1.68
1.5	THF	50, 4	(22) <sup>c</sup>	6900	1.47
1.5	THF	50, 2	(8) <sup>c</sup>	2530	1.33

<sup>a</sup>The reaction was carried out with 1 and 1.0 equiv of TPMgCl·LiCl in THF for the metalation, and 1.0–3.0 mol % of nickel catalyst was employed for the polycondensation. <sup>b</sup> $M_n$  and  $M_w/M_n$  values were estimated by SEC analysis using CHCl<sub>3</sub> as an eluent. <sup>c</sup>Conversion of 1 was estimated by <sup>1</sup>H NMR analysis.

however, a nonlinear increase of the average molecular weight was observed over time (see Figure S2), indicating that the curve was slightly out of the theoretical line and suggesting that polymerization took place partially in a step-growth manner. Although the observed enhancement in the reactivity in cross-coupling via C–S bond cleavage is explained by the intramolecular catalyst transfer of nickel species,<sup>5</sup> a higher reaction temperature may have resulted in the partial step-growth polymerization.

It was also found that deprotonation of 1 was achieved with the combination of a Grignard reagent and a catalytic amount of Et<sub>2</sub>NH, which resulted in catalytic in situ generation of magnesium amide. Such deprotonation has been achieved in unsubstituted 3-hexylthiophene and 2-chloro-3-hexylthiophene, whereas that of bromothiophene has been unsuccessful, due to undesired bromine–magnesium exchange with a Grignard reagent.<sup>6b,9</sup> Deprotonation reactions of 1 and several related derivatives were studied as summarized in Table 2. The result was confirmed by quenching the generated anion with iodine, leading to 5-iodo-3-hexyl-2-(phenylsulfonyl)thiophene. The use of EtMgCl and 10 mol % of Et<sub>2</sub>NH was found to result in a reasonable metalation efficiency to afford the iodide in 65% yield. In contrast, deprotonation of 3-hexylthiophene or 2-chloro-3-hexylthiophene under similar conditions hardly took place, although these reactions have been achieved under more harsh conditions.<sup>10</sup> Better deprotonation efficiency was achieved with <sup>i</sup>PrMgCl·LiCl and 10 mol % Et<sub>2</sub>NH to afford the iodide in 86% yield. It should be pointed out that deprotonation with a decreased amount of Et<sub>2</sub>NH to only 1 mol % also resulted in giving metalated thiophene in 50% yield in 1 h. Switching the secondary amine to *cis*-2,6-dimethylpiperidine (DMP) improved the yield dramatically. Metalation in the presence of 1 mol % of DMP smoothly proceeded to give

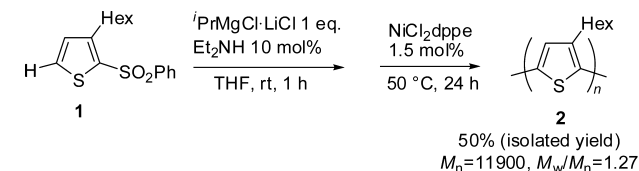
**Table 2. Generation of Thienyl Magnesium Species with a Grignard Reagent and a Catalytic Amount of Amine<sup>a</sup>**

X	amine (amt (mol %))	RMgCl	temp (°C)	time (h)	yield <sup>b</sup> (%)
–SO <sub>2</sub> Ph	Et <sub>2</sub> NH (10)	EtMgCl	room temp	1	65
–H	Et <sub>2</sub> NH (10)	EtMgCl	room temp	1	1
–Cl	Et <sub>2</sub> NH (10)	EtMgCl	room temp	1	9
–SO <sub>2</sub> Ph	Et <sub>2</sub> NH (10)	<sup>i</sup> PrMgCl·LiCl	room temp	1	86
–SO <sub>2</sub> Ph	Et <sub>2</sub> NH (1)	<sup>i</sup> PrMgCl·LiCl	60	1	50
–SO <sub>2</sub> Ph	DMP <sup>c</sup> (1)	<sup>i</sup> PrMgCl·LiCl	60	1	95
–SO <sub>2</sub> Ph	none	<sup>i</sup> PrMgCl·LiCl	60	1	13

<sup>a</sup>The reaction was carried out with 2-substituted 3-hexylthiophene (0.2 mmol), Grignard reagent (0.2 mmol), and amine (0.02 or 0.002 mmol) in 0.4 mL of THF at room temperature. <sup>b</sup>The conversion was estimated by <sup>1</sup>H NMR analysis after quenching the reaction mixture with iodine. <sup>c</sup>DMP = *cis*-2,6-dimethylpiperidine.

iodinated thiophene in 95% yield, whereas the reaction in the absence of amine under similar conditions resulted in poor deprotonation (13% yield).

With the method for catalytic generation of metallic species with 10 mol % of Et<sub>2</sub>NH and <sup>i</sup>PrMgCl·LiCl at room temperature for 1 h, polymerization in the presence of 1.5 mol % of NiCl<sub>2</sub>(dppe) was indeed carried out at 50 °C for 24 h. P3HT (2) was obtained in 50% isolated yield with  $M_n$  = 11900 ( $M_w/M_n$  = 1.27), as shown in Scheme 2.

**Scheme 2. Polymerization of 1 with a Nickel Catalyst after Deprotonation with Catalytic Amine and Grignard Reagent**

Concerning the polymerization mechanism of halothiophenes, it has been considered that the initiation reaction in the polymerization is reductive tail to tail homocoupling of metalated sulfonylthiophene and oxidative addition of Ni(0) species into the C(thiophene)–S bond.<sup>11</sup> As shown in Scheme 3, a propagation reaction thus occurs, after initial homocoupling with the metalated monomer A to give B, by the incorporation of monomer B at the terminal C–S bond. Accordingly, an end group of C is the terminal thiophene bearing an SO<sub>2</sub>Ph group. ESI-MS analysis of the reaction mixture revealed the formation of Ph-SO<sub>2</sub><sup>–</sup> ( $[M_{\text{found}}] = 141.0012$ ), suggesting that the phenylsulfonyl group served as a leaving group, forming Ph-SO<sub>2</sub>MgCl(LiCl) species.

An end group of the polymer 2 was also found by measurement of the <sup>1</sup>H NMR spectrum to be SO<sub>2</sub>Ph, as shown in Figure 1a.<sup>12</sup> A proton signal corresponding to the terminal thiophene ring H<sub>b</sub> was observed at 6.95 ppm by the

### Scheme 3. Proposed Mechanism of the Cross-Coupling Polymerization via C–S Bond Cleavage

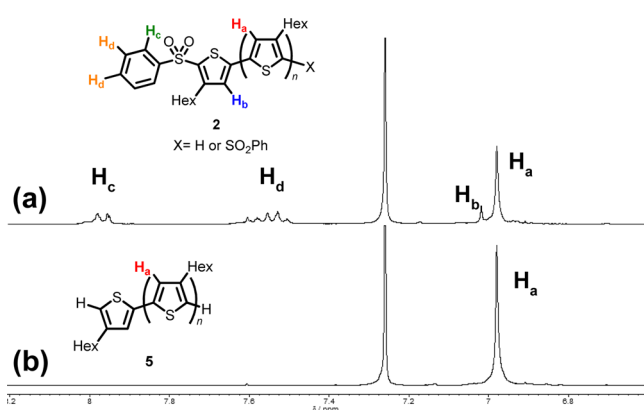
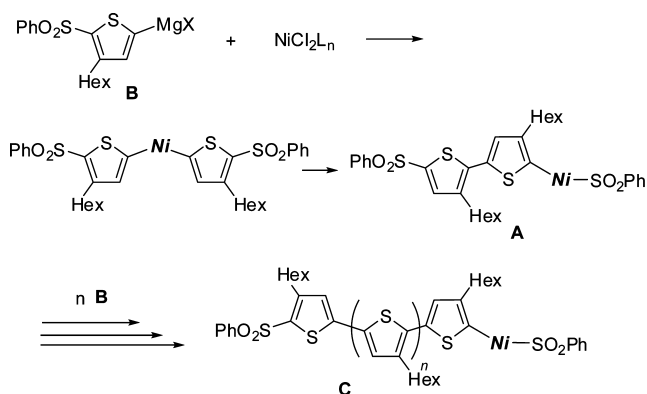
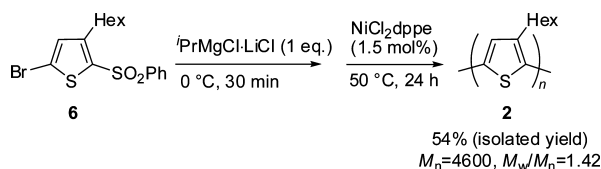


Figure 1.  $^1\text{H}$  NMR spectra of **2** (a) and desulfonylated polymer **5** (b).

electron-withdrawing effect of the  $\text{PhSO}_2$  group. The phenylsulfonyl group was efficiently removed by nickel-catalyzed reductive desulfonylation with  $^i\text{BuMgCl}$  to give polythiophene **5**. Desulfonylation with **2** was carried out by excess amounts of  $^i\text{BuMgCl}$  and  $\text{NiCl}_2(\text{dppe})$  as a catalyst at  $60^\circ\text{C}$  for 16 h to afford poly(3-hexylthiophene) (**5**).<sup>13</sup> The  $^1\text{H}$  NMR spectrum of Figure 1b shows that signals corresponding to the phenylsulfonyl group observed in Figure 1a at 7.98, 7.60, and 7.52 ppm, respectively, assigned as para, ortho, and meta positions ( $\text{H}_c$  and  $\text{H}_d$ ), disappeared after the reaction and the proton signal  $\text{H}_b$  of terminal thiophene ring in **2** shifted to be merged with  $\text{H}_a$ . Thus, the obtained  $^1\text{H}$  NMR spectrum of desulfonylated polymer **5** was confirmed to be identical with that of authentic HT-P3HT.<sup>6</sup>

Similar to the case of debrominative GRIM metalation of 2,5-dibromothiophene,<sup>14</sup> the reaction of 5-bromo-2-phenylsulfonyl-3-hexylthiophene (**6**) was also found to take place, leading to an organometallic monomer similar to that in the deprotonative case. As shown in Scheme 4, treatment of **6** with  $^i\text{PrMgCl}\cdot\text{LiCl}$  at  $0^\circ\text{C}$  for 30 min and the following nickel-catalyzed reaction

### Scheme 4. GRIM Polymerization through C–S Bond Cleavage



with 1.5 mol % of  $\text{NiCl}_2(\text{dppe})$  afforded the corresponding polymer **2** in 54% isolated yield<sup>15</sup> ( $M_n = 4600$ ;  $M_w/M_n = 1.42$ ).

In conclusion, we have shown nickel-catalyzed polymerization with sulfonylthiophene, which occurs via unprecedented C–S bond cleavage, when  $\text{NiCl}_2(\text{dppe})$  was employed as a catalyst. Generation of the polymerizable organometallic species was performed in a deprotonative manner with **1** by the use of stoichiometrically or catalytically generated magnesium amide. The deprotonation reaction of thiophene was revealed to occur under conditions milder than those for the related halothiophenes due to its improved acidity by the effect of an electron-withdrawing sulfonyl group. The GRIM-type halogen–metal exchange was also found to furnish a similar metalated monomer species, and the following nickel-(II)-catalyzed polymerization led to the polymer **2**.

## ■ ASSOCIATED CONTENT

### Supporting Information

Text and figures giving experimental details and spectroscopic characterization data of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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(10) The reaction of 2-chloro-3-hexylthiophene at 60 °C for 3 h resulted in 73% metalation,<sup>6b</sup> and the reaction of 3-hexylthiophene required conditions at 60 °C for 24 h for >99% conversion with EtMgCl and 10 mol % of 2,2,6,6-tetramethylpiperidine. See: Tanaka, S.; Tamba, S.; Tanaka, D.; Sugie, A.; Mori, A. *J. Am. Chem. Soc.* **2011**, *133*, 16734.

(11) The reaction of **1** with a thienyl Grignard reagent produced bithiophene in 62% yield as the sole product, whereas the phenylated cross-coupling product was not observed at all. See the Supporting Information.

(12) The results of the <sup>1</sup>H NMR spectrum and SEC analysis suggested that polymer **2** possessed a PhSO<sub>2</sub> group at the end. While end group analysis is qualitatively valuable, its quantitative accuracy is limited by the impact of low polymer mobility on relaxation times. See Figure S1 in the Supporting Information.

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(15) Considering technical loss during isolation, the actual yield and the average molecular weight might be different.