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# A Direct C–H Coupling Method for Preparing $\pi$ -Conjugated Functional Polymers with High Regioregularity

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# Supporting Information



ABSTRACT: Highly regionegular conducting polymers such as poly(3-substituted thiophene)s (rrP3STs) are an important class of  $\pi$ -conjugated polymers that can be used in plastic electronic devices such as solar cells and field-effect transistors. But the current state of the art syntheses of rrP3STs all involve transition-metal-catalyzed cross-coupling of a heteroaryl halide or pseudohalide with a heteroaryl organometallic reagent. In this work, an efficient and mild method was developed using direct cross-coupling of sp<sup>2</sup> C-H bonds. More importantly, the method not only gave generally high regioregularity (up to 99%) but also can be applied for a series of substrate compounds with various structures and substituted groups. This should provide a general and direct way for the easy access to many functional/conducting polymers.

# INTRODUCTION

 $\pi$ -Conjugated polymers have attracted extensive interest as important conducting or semiconducting materials for the next generation of electronic and optical devices<sup>1-3</sup> since the discovery of highly conductive polyacetylene by Shirakawa, MacDiarmid, and Heeger<sup>4</sup> over 40 years ago. Among these various (semi)conducting polymers, polythiophenes (PTs) are probably the most important and widely studied materials and have been studied for a variety of applications such as fieldeffect transistors (FETs),<sup>5–8</sup> polymer light-emitting diodes (PLEDs),<sup>9,10</sup> solar cells,<sup>3,11–14</sup> and chemical sensors.<sup>15</sup> While there are many parameters impacting the performance of these applications for even the same material with similar conjugation/polymerized length, one of the most important factors is probably the regioregularity<sup>16</sup> when the monomer unit has an unsymmetrical structure in most cases. This is because that the polymerization of unsymmetrical monomer often leads to mixture polymers due to multiple active linking sites.<sup>17</sup> For the case of polythiophene, the most used 3substituted thiophene monomer thus would lead to a mixture of polythiophene structures containing three region-chemical linkages between repeating units (2,2', 2,5'), and 5,5', namely, HH, HT, and TT).<sup>17,18</sup> The 2,2' and 5,5' couplings are usually considered as defects in the polymer structure since they diminish conjugation and hinder ideal solid-state packing, thus impairing the electronic and photonic properties of materials.<sup>16,19–23</sup> Therefore, great effort has been carried out on the development of new polymerization methods for regioregular, HT coupled poly(3-substituted thiophene)s (rrP3STs). The same is true for the polymers with other mono units.<sup>24</sup> Thus, easy and efficient methods for highly regioregular polymers are demanded and important for the applications of these conducting polymeric materials.

Indeed, great progress for such controlled polymerization has been made in the past few decades.<sup>16,17</sup> Most importantly, highly regioregular, HT coupled P3STs with alkyl groups or alkoxyl groups have been prepared by a variety of strategies, including the McCullough,  $^{25}$  GRIM,  $^{26}$  and Rieke method  $^{27,28}$ as well as the Stille and Suzuki cross-coupling reaction (Scheme 1).<sup>29-31</sup> Among these methods, the carbon-carbon bi-heteroaryl linkages are formed via transition-metal-catalyzed cross-coupling of a heteroaryl halide or pseudohalide with a heteroaryl organometallic reagent. While great success has been achieved for these methods, the biggest issue for these methods is that they all require the monomers in the form of either having metal or halide containing functional groups. Thus, these approaches not only make the synthesis having a longer route thus less efficient; more importantly, in many cases the acquirement of such intermediate materials is a great challenge if not possible.

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Scheme 1. Methods for the Preparation of HT Regioregular Polythiophenes $^a$ 



Partially solving the challenge by removing the requirement of organometallic intermediate, direct (hetero)arylation processes (DHAP) via the dehydrohalogenative cross-coupling reaction of heteroarenes with aryl halides has been achieved.  $3^{32-34}$  In addition to the same requirement to obtain the halides, this strategy still needs to solve the end functional group issue after polymerization, particularly in the cases for application for optoelectronic devices, where the material performance is very sensitive to the end group.<sup>34</sup> Thus, it would be ideal to achieve direct carbon-carbon coupling starting from C-H bond directly and polymerization with high regioselectivity and avoiding the use of such preactivated functional (organometallic or halide) groups. But unfortunately, not only the investigation of such an ideal strategy has been very limited,<sup>35-42</sup> but also no success with high regioselectivity and mild condition (temperature) process has been achieved so far. This is rather contrary to the great success of direct C-H/C-H coupling from (hetero)arenes for small molecule preparation,  $^{40-42}$  which includes many reports using such as Ag- and Pd-based catalysts for the preparation of bithiopehens and other bi(hetero)arenes via homocoupling reaction.  $^{43}$ 

Using this direct coupling of C-H bond strategy, indeed, some pioneering works for preparation of polymers have been reported.<sup>35-42</sup> Among these limited investigations, homopolymerization in most cases, the polymerizations give reasonable yield and molecular weight, but in all cases, the C-C coupling has generally very low regioselectivity and thus gave the products with low regioregularity.<sup>40,42</sup> Thus, their application for preparing the materials used in optoelectronics is very limited. More importantly, the monomer substrates are symmetrical and do not have the regioselectivity issue since there is possibly only one C–H position to couple each other.  $^{35-39}$  Recently, Tsuchiya reported the direct C–H coupling polymerization of alkylthiophene, but unfortunately, it offers rather low regioregularity.<sup>42</sup> Also, these methods generally need temperatures higher than 100 °C, which could cause more side reaction/products-again a big issue for optoelectronic applications. Furthermore, so far, no alternating copolymerization with two different monomers using this strategy has been reported, which have been severely limiting the choice of the monomers.

In this work, a general and mild method has been developed for the preparation of conjugated polymers by direct C–H coupling with high yield (up to quantitative) using various monomer substrates via both homopolymerization and copolymerization methods. More importantly, this approach generally gave high regioselectivity and thus regioregularity (up to 99%) and was performed even at a temperature of 60 °C. The mechanism and theoretical studies indicate that regioselectivity originated from the synergy of the electronic

Table 1. Screening of the Reaction Conditions for the Polymerization of Poly(3-octylsulfonylthiophene) (P3OST, 2a) by Pd-Catalyzed Oxidative C-H Coupling<sup>a</sup>

entry	catalyst	oxidant	additive	$T(^{\circ}C)$	solvent	yield (%) <sup>b</sup>	$M_{\rm n}~({\rm kDa})^c$	$M_{\rm w}/M_{\rm n}^{\ c}$	HT $(\%)^d$
1	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	110	DMAc	68	3.9	1.25	89
2	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	90	DMAc	96	6.9	1.78	99
3	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	60	DMAc	94	5.5	1.42	99
4	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	50	DMAc	23	5.4	1.02	81
5	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	110	THF	70	4.0	1.25	99
6	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	90	THF	98	9.6	1.71	99
7	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	60	THF	28	6.4	1.15	76
8	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	50	THF	trace			
9	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	110	toluene	24	4.3	1.23	74
10	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	110	DMAc/THF	89	4.8	1.35	92
11	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	110	DMAc/toluene	62	4.4	1.29	93
12	$Pd(OAc)_2$	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	110	DMAc/xylene	73	4.0	1.23	89
13	$Pd(OAc)_2$	AgOAc	KOAc	110	THF	30	4.5	1.23	77
14	$Pd(OAc)_2$	$Cu(OAc)_2$	KOAc	110	THF	trace			
15	$Pd(OAc)_2$	$Cu(OAc)_2$	K <sub>2</sub> CO <sub>3</sub>	110	DMAc	84	4.0	1.38	83
16	$Pd(OAc)_2$	PivOH <sup>e</sup>	K <sub>2</sub> CO <sub>3</sub>	110	DMAc	51	3.7	1.01	63
17	Pd(dppf)Cl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	90	DMAc	97	7.5	1.93	99
18	Pd(dppf)Cl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	60	DMAc	97	6.2	1.29	99
19	Herrmann's catalyst	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	90	DMAc	98	7.3	1.90	99
20	Herrmann's catalyst	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	60	DMAc	58	6.7	1.41	99
21	Herrmann's catalyst	Ag <sub>2</sub> CO <sub>3</sub>	KOAc	50	DMAc	14	5.2	1.02	75

"Reaction conditions: substrate (1 equiv), Pd catalyst (0.05 equiv), oxidant (2.0 equiv), additive (2.0 equiv) for 48 h. <sup>b</sup>Isolated yield after purification. <sup>c</sup>Estimated by GPC measurements (eluent: THF; standard: polystyrene). <sup>d</sup>Estimated by <sup>1</sup>H NMR. <sup>e</sup>PivOH is used as coadditive, but not on behalf of an oxidant.

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effect and steric effect of the 3-position substituted group on the thiophene substrate.

# RESULTS AND DISCUSSION

**Optimization of Reaction Conditions.** Recently, the ester group has been investigated to direct the coupling for preparation of polythiophenes,<sup>40,41</sup> but it gave low regiose-lectivity. As high regioregularity is important for functional polymer materials particularly for the cases of optoelectronic application such as OPV and OLED,<sup>16,44</sup> direct C–H coupling for polymerization with high regioselectivity is highly demanded. On the basis of previous works,<sup>40–42,45–48</sup> including ours,<sup>38,39</sup> it is thought that a stronger electron-withdrawing group might be able to solve the low regioselectivity observed before. Thus, the thiophene monomer with sulfonyl group as the directing group was investigated for its homopolymerization under various conditions using Pd(II) as the catalyst.

As illustrated in Table 1, the effects of the type of catalysts, the polarity of solvent, and reaction temperature and other additives on the regioregularity, yield, and average molecular weight were systematically investigated. Under the optimized conditions, poly(3-octylsulfonylthiophene) (P3OST, 2a) could be obtained with the HT regioregularity as high as 99% (entries 2-3, 5-6, and 17-20) and  $M_n$  of 9.6 × 10<sup>3</sup> (PDI: 1.71, entry 6) in a nearly quantitative yield (98%, entries 6 and 19). Initial testing using the previous conditions  $^{43,44}$  for the substrate with a carbonyl group as the directing group only offers moderate regioregularity (89%, entry 1). The reaction was then investigated under the same conditions for different temperatures (entries 1-4), and it was found that the reaction gave the best results with 96% yield and 99% regioregularity at 90 °C (entry 2). Based on these results, more screening was investigated using different solvents, since it has been found that different polarity of solvents has a great impact on the reactivity.<sup>49</sup> Thus, different solvents have been applied for the reactions under the same conditions (entries 1-12). The results indicate that when the temperature was 90 °C, THF gave the best results (entry 6). Finally, different Pd catalysts (entries 17-21) were investigated, and the results indicated the reactions generally all gave very good results in terms of both regioselectivity and yields for various Pd catalysts such as Pd(OAc)<sub>2</sub>, Pd(dppf)Cl<sub>2</sub>, and Herrmann's catalysts. Overall, compared with previous works,<sup>38,39</sup> this catalyst system generally gave both high regioselectivity and yield at mild temperature (90 °C or even lower 60 °C). After thoroughly optimizing the reaction conditions, reaction with 0.05 equiv of  $Pd(OAc)_2$  in THF at 90 °C was found to produce highest yield and best HT regioregularity.

Note the molecular weights in general are in the range of a few to tens of kDa in the present work. While these molecular weights are moderate, they are rather comparable with that of polythiophenes obtained from the conventional and widely used methods such as the McCullough, Rieke, GRIM, Stille, and Suzuki reactions.<sup>16,17,22,30,50,51</sup> It is expected that the molecular weights should be improved after optimization as other methods.

**Determination of Homocoupling Product Regioregularity.** The structures and regioregularity of the polymer products have been first systematically investigated and characterized, including the most direct and widely used NMR technique. The following is given for the product 2a as an example (Figure 1). Note particularly, this method has been widely used for the cases of alkyl, alkoxyl, and ester group substituted polythiophenes.  $^{18,40,41}$ 



**Figure 1.** Comparison for the <sup>1</sup>H NMR spectra of (a) HT-coupling P3OST (**2a**) obtained in this work via the direct C–H coupling polymerization shown in Table 1, entry 6; (b) reference HT coupling P3OST (**2a**\*) obtained via the DHAP method; and (c) reference HH–TT coupling P3OST (**2a**#) obtained via the DHAP method. The inset in the enlarged spectrum in the range of 3.00-3.30 ppm for (a) for determination of the regioregularity of product **2a**. All spectra were collected in CDCl<sub>3</sub>.

First, a reference polymer  $(2a^*)$  with specific and known HT regioregularity was obtained by the DHAP method<sup>32,33</sup> but using 2-bromo-3-(octylsulfonyl)thiophene as the monomer (Scheme 2). The <sup>1</sup>H NMR of this standard HT regioregular

Scheme 2. Synthesis of Reference Polymer 2a\* via the DHAP Method



polymer (2a\*) is shown as Figure 1b (also shown as Figure S2 in the Supporting Information). As can be seen, the chemical shift of the  $\alpha$ -methylene signals of the side 3-octylsulfonyl groups is in the range of 3.13–3.17 ppm. The NMR of another possible type coupling polymer product (2a#) but with specific HH–TT regioregularity was also used for the comparison. This polymer was obtained by the copolymerization of 5,5'dibromo-3,3'-bis(octylsulfonyl)-2,2'-bithiophene with 3,3'-bis-(octylsulfonyl)-2,2'-bithiophene via the same DHAP method (Scheme 3). In the NMR of this HH–TT regioregular product (Figure 1c and Figure S3), the chemical shift of the  $\alpha$ methylene signals of the side 3-octylsulfonyl groups is in the range of 3.03–3.07 ppm.

In terms of the chemical shifts and patterns of the main peaks (the peaks at 7.87 and 3.14 ppm), comparing the <sup>1</sup>H NMR spectra of our product (2a) with the two reference polymers (2a\* and 2a#) with known regioregularity (Figure 1b,c), at least qualitatively, it is safe to say that our product 2a should have the same type of regioregularity as that of the reference polymer  $2a^*$  (Figure 1b) with the HT regioregu-

# Scheme 3. Synthesis of Reference Polymer 2a# via the DHAP Method



larity, but not the regioregularity as that of the reference HH– TT type polymer **2a#** (Figure 1c).

Note the NMR (Figure 1a) of our product (2a) has a strong multiple peak at 3.13-3.16 ppm, corresponding the same CH<sub>2</sub> peak at the same position for the NMR (Figure 1b) of the reference HT coupling product 2a\*. A weak multiple peak around 3.04-3.08 ppm (inset, Figure 1) is also present. Note the reference polymer HH–TT type polymer 2a# has a similar peak at the same position. So it is clear that this peak should come from other type coupling, which might give the HH–TT type product as the reference polymer 2a#. With these assignments, then the regioregularity of product 2a could be estimated by the integral area ratio of such NMR peaks as ~2.00/0.02, that is, ~99% (inset, Figure 1).

Note all other NMR peaks are consistent with the structure, too. Especially, in the aromatic region (Figure 2a), only one sharp singlet for the proton in the 4-position of the thiophene



Figure 2. <sup>1</sup>H NMR spectra in the aromatic region of (a) our HTcoupling product 2a, (b) the reference polymer  $2a^*$  obtained via the DHAP method, and (c) the monomer 3-(octylsulfonyl)thiophene.

ring was observed at  $\delta$  7.87 for our product 2a. The rather same peak positions and patterns in the aromatic region in the <sup>1</sup>H NMR spectrum for the reference polymer  $2a^*$  (Figure 2b) indicate these two polymers (2a and 2a\*) should have the same HT-HT structure and regioregularity. It should be also pointed out that the NMR spectrum of 2a should be much more complicated than that we obtained if any type coupling such as HH-TT, etc., inside the main chain happened in any significant amount. In addition, the three weak peaks at  $\delta$  8.21  $(H_a)$ , 7.80  $(H_b)$ , and 7.65  $(H_c)$  in the aromatic region in <sup>1</sup>H NMR spectrum of the product polymer 2a are assigned as the terminal ring protons H<sub>a</sub>, H<sub>b</sub>, and H<sub>c</sub> in the polymer chain, respectively, by the comparison for NMR in aromatic region of 2a with that of its monomer (Figure 2a,c). The slight difference of chemical shifts between that in the terminal units with the monomer should be due to the formation of the polymer chain, as widely observed in polymers. Based on these results, the formation of highly regioregular HT-poly(3octylsulfonylthiophene) containing at least 99% HT linkage in the polymer chain should be clearly evidenced. The regioregularity of other homopolymer products was determined in the same way.

To further support the regioregularity of product 2a, the UV-vis absorption spectra of 2a (entry 6, Table 1) and reference  $2a^*$  and 2a# obtained by the DHAP method were compared. 2a and  $2a^*$  exhibit rather similar spectra (Figure 3) with an absorption peak at about 396 nm in chloroform solution. However, because of the different regioregularity compared with 2a and  $2a^*$ , the absorption of 2a# is different and has a blue-shift.



Figure 3. UV–vis absorption spectra of 2a (entry 6, Table 1), 2a<sup>\*</sup>, and 2a<sup>#</sup> obtained via the DHAP method in a chloroform solution with the same concentration  $(10^{-5} \text{ mol/L})$ .

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Scheme 6. Synthesis of Various Conjugated Copolymers via the Direct C-H Coupling Method



**Substrates Scope for Direct C–H Homocoupling.** Having established the structure and regioregularity of the products, the generality of this catalyst system was investigated for other more complicated monomers using homopolymerization (Scheme 4). Under optimized conditions discussed above, a variety of thiophenes bearing various functional groups, including ester, sulfone, sulfoxide, and oxadiazole, gave a generally medium to good isolated yield and more



Figure 4. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> of (a) 9a synthesized by our direct C–H cross-coupling polymerization and (b) 9a\* obtained by the Stille coupling method.





importantly the same excellent regioselectivity (2a-2d). Notably, other heteroaromatic substrates such as furan and selenophene substrates were also successfully employed to yield the corresponding polymerized products with high HT (2e, 2f). Generally, it was observed strong electron-withdrawing groups and small size groups provided higher HT regioregularity (up to 99% HT). The HT regioregularity could be affected by the electronic properties and steric hindrance of the 3-substituent groups as will be discussed below.

Since the polymers with alkyl ester functional groups have been explored for various applications such as solar cells,<sup>52–55</sup> polymer light-emitting diodes (PLEDs),<sup>56,57</sup> and field-effect transistors (FETs),<sup>58</sup> the optimization of the reaction conditions for **2b** with alkyl ester functional groups has been also carried out (Table S1). The moderate HT regioregularity (~90%, entries 2 and 4, Table S1) was obtained under the optimized conditions. The HT regioregularity of **2b** in the present work was determined in the same way and also compared with previous data reported for the same polymer.<sup>40,41</sup>

As the homopolymerization of bi- or coupled aromatics with high regioselectivity is both more challenging and more important, such substrates were studied also under the same conditions (Scheme 5). Impressively, the reactions also worked well and gave high HT products (4a-4c). Note the high selectivity comes from the direct C-H coupling of two defined C-H sites on two different ring units, indicating the high selectivity of the reaction, as there are multiple possibilities of coupling sites ( $H_a-H_a$ ,  $H_a-H_b$ ,  $H_a-H_c$ , etc.).

Substrate Scope for the Direct C–H Cross-Coupling (Copolymerization). As copolymerization with two different monomers A and B can offer much more choices of polymer

products and used more widely, the same reaction was also studied for copolymerization. Obviously, it is more challenging to achieve high regularity for the copolymerized product (AB) from two different monomers as there are many different polymerizing patterns. And even if there is only one type of reactive site on A and B, it will require high regioselectivity to just achieve one product of  $-(A-B)_n-$  among the possible multiple products such as  $-(A-B)_n-$ ,  $-(A-A)_n-$ ,  $-(B-B)_n-$ ,  $-(A-A-B)_n-$ , and so on. Note that all previous studies<sup>35-40,42,59</sup> on the preparation of P3ST by direct C–H coupling are based on homopolymerization. Remarkably, even with multiple ring systems with possible multiple coupling sites, the copolymerization with our approach still worked well and gave high regioselective alternative polymerized products (9a–9b and 10a–10b, Scheme 6).

Structural Regularity Determination of Cross-Coupling Polymer Products. The structural regularity of cross-coupling copolymers was validated by comparing the product NMR with that of the polymer products obtained by using the Stille coupling reactions (Figure 4), which is supposed to give  $\sim$ 100% regularity in theory.

As seen from Figure 4, the <sup>1</sup>H NMR spectra of our copolymer 9a (Figure 4a) exhibit the same features (positions and patterns) as that (Figure 4b) of the reference polymer 9a\* synthesized by the Stille method (Scheme 7). In addition, heteronuclear multiple quantum correlation (HMQC) NMR spectroscopy (Figure S7) and heteronuclear multiple bond correlation (HMBC) NMR spectroscopy (Figure S8) were collected to further prove the linking sites of two monomers in 9a. These results indicate that the alternative A/B cross-coupling copolymer with high selectivity was successfully obtained via our direct C-H coupling method. This





Scheme 9. Proposed Mechanism for Direct C-H Coupling Homopolymerization



conclusion is also based on the two reasons below: (1) The  ${}^{1}$ H NMR for the possible  $-(A-A)_n$ ,  $-(B-B)_n$ ,  $-(A-A-B)_n$ , etc., products with other coupling manners should have more (and more complicated) peaks for the characteristic methylene group on the sulfonyl side group around 3.11 ppm. But our product clearly has one main peak in this region (Figure 4a). (2) For the <sup>13</sup>C NMR, the total number of the <sup>13</sup>C peaks in aromatic region matches the structure of the alternative crosscoupling product (Figure S5). If a significant amount of homocoupling (as either an individual product or just some coupling inside the main chain of the main alternative A/B type product) happened in any manner, it is easily understood that the number of <sup>13</sup>C peaks should be much more due to the product highly unsymmetrical structure. In short, both the <sup>1</sup>H and <sup>13</sup>C NMR spectra should be much more complicated than we obtained if homocoupling happened in any significant amount.

Furthermore, more experiments were carried out to support the above conclusion. Each of the three monomers (5, 6, and 8, Scheme 6) for reaction of 9b (5 + 8) and 10b (6 + 8) was treated under the same conditions separately. No reaction was observed, and almost all the starting materials were recovered for all the three cases (see I-3.14-3.16, Figures S9-S11 for the details). Not any polymer product was observed for all the cases either. This clearly indicates that at least no homocoupling has played a major role for the copolymerization.

The fact that no polymerization could happen for either monomer 5 or 8 used in the copolymerization might appear rather puzzling when considering the fact that copolymerization could move forward with high yield when 5 and 8 coexist under the same conditions (entry 9b in Scheme 6). For the 6 and 8 copolymerization system (entry 10b in Scheme 6), the case is the same. To confirm the reactive site for the copolymerization, a model coupling reaction was designed and performed for two monomers 5 and 11 (Scheme 8). The <sup>1</sup>H NMR, <sup>13</sup>C NMR, and FT-MS results (Figures S13-S15) indicated that the 2-methylthiophene (11) was linked to the monomer 5 via the 5- and 5'-position in monomer 5, and only one product 12 was obtained with the yield of 90%. Neither self 5–5 nor 11–11 homocoupling products from monomer 5 or 11 were observed. This clearly indicated that the 5- or 5'position hydrogen atom on monomer 5 was first activated to form the IM1-like intermediate (Scheme 9 and discussion below) and then coupled with the second monomer 11 at the 5-H site to form the final product.

**Polymerization Mechanism.** On the basis of previous results,  $^{45,46,60,61}$  it is believed that the first step of the polymerization comes from the Pd metalation at the sulfonyl neighboring C–H site (Scheme 9). For monosubstituted thiophene ring substrates, there are two possible initial Pd

insertion paths (2 and 5 sites), and the 2-H site Pd insertion is not only electronically favored due to the electron withdrawing of SO<sub>2</sub>R, the formed five-member ring is also obviously more stable and thus favored.<sup>45,52</sup> Importantly, one of the possible major immediates, IM1", was confirmed directly using HRMS from the reaction mixture when Hermann's catalyst was used (Figure S17). The next step is the similar Pd insertion into the C-H bond of next substrate molecule. Obviously, there are two possible ways for this step, at 2 or 5 site, respectively, and the two possible corresponding intermediates are shown as IM2' and IM2. The selectivity of this step should come mainly from the steric effect. This proposed catalytic cycle is also supported by the DFT calculation (Figure S18). The ratedetermining step should be the step from IM1 to IM2 (IM2'), and the overall regioselectivity should depend on the stability difference of TS2 and TS2'. Since the energy difference of these two transition states is ~60 kJ/mol (Table S2 and Figure \$18), this large stability difference should make the intermediate IM2' hardly formed and make the intermediate IM2 the dominant one, leading to high regioselectivity. Thus, the overall high selectivity should come from the synergy effect of both the initial Pd insertion due to mainly electronic effect in the first step and the steric effect in the second Pd insertion step. Note the DFT calculation results gave the same conclusion for both the cases when AcOH or the basic form AcO<sup>-</sup> was used as ligands (Table S2).

For copolymerization with A and B two substrates, the mechanism should be similar (Scheme S1). The first step of the copolymerization comes from the Pd metalation at the sulfonyl neighboring C-H site of monomer molecule A to generate similar intermediate IM1 due to mainly electronic effect. The next step is the Pd insertion into the C-H bond of substrate molecule B to have intermediate IM2. Importantly, note intermediate IM1 should be formed with favor from monomer molecule A due to its electronic activation compared with monomer molecule B, and intermediate IM2 should be formed in favor from monomer molecule B due to its less steric effect. This strategy using the combination and synergy electronic and steric effect from two substrate molecules A and B individually and in sequence might be used for other types of reactions. This is strongly supported by the two experimental results discussed above: (1) no polymerization could happen when either of the two monomers used in the copolymerization was treated individually under the same conditions (Figures S9-S11) and (2) the results from the modeling reaction shown in Scheme 8. Obviously, to clearly understand the mechanism in full, further studies are needed.

## CONCLUSION

In conclusion, a mild and general method was developed using direct C–H coupling without any metal or halide reagents required, which not only gave high selectivity and yields more importantly but also can be applied for both homopolymerization and copolymerization and a wide range of substrates even for multiply ring systems. The high selectivity comes from the synergy of both electronic effect in the first step and steric effect in the second step. Considering the high importance of substituted polythiophene and other conducting polymers with high HT for optoelectronic devices, this new method could work as a direct and easy access for a variety of HT coupled conducting and other functional polymers. Note the directing group used in this investigation could be easily converted to other groups or removed using many widely available methods. Also, while most of this study focused on polythiophenes, it is believed that the same strategy could be applied for other aromatic systems when high HT is required.

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.7b02390.

General experimental methods; <sup>1</sup>H and <sup>13</sup>C NMR spectra of all polymers; UV-vis absorption spectra, CV and TGA data of the polymers **2a**-**2b**, **9a**-**9b**, and **10a**-**10b**; proposed mechanism; computational details (PDF)

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#### Notes

The authors declare no competing financial interest.

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