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A Rational Design of Highly Controlled Suzuki-Miyaura Catalyst-Transfer Polycondensation for Precision Synthesis of Polythiophenes and their Block Copolymers: Marriage of Palladacycle Precatalysts with MIDA-boronates

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ABSTRACT: Herein, we report a highly efficient Suzuki-Miyaura catalyst-transfer polycondensation (SCTP) of 3-alkylthiophenes using bench-stable but highly active Buchwald dialkylbiarylphospine Pd G3 precatalysts and *N*-methylimidodiacetic (MIDA)-boronate monomers. Initially, the feasibility of the catalyst-transfer process was examined by screening various dialkylbiarylphospine-Pd(0) species. After optimizing a small molecule model reaction, we identified both RuPhos and SPhos Pd G3 precatalysts as excellent catalyst systems for this purpose. Based on these model studies, SCTP was tested using either RuPhos or SPhos Pd G3 precatalyst, and 5-bromo-4-*n*-hexylthien-2-yl-pinacol-boronate. Poly(3-hexylthiophene) (P3HT) was produced with controlled molecular weight and narrow dispersity for a low degree of polymerization (DP) only, while attempts to synthesize P3HT having a higher DP with good control were unsuccessful. To improve the control, slowly hydrolyzed 5-bromo-4-*n*-hexylthien-2-yl-MIDA-boronate was introduced as a new monomer. As a result, P3HT and P3EHT (up to 17.6 kg/mol) were prepared with excellent control, narrow dispersity, and excellent yield (>90%). Detailed mechanistic investigation using ^{31}P NMR and MALDI-TOF spectroscopy revealed that both fast initiation using Buchwald precatalysts and the suppression of protodeboronation due to the protected MIDA-boronate were crucial to achieve successful living polymerization of P3HT. In addition, a block copolymer of P3HT-*b*-P3EHT was prepared via SCTP by sequential addition of each MIDA-boronate monomer. Furthermore, the same block copolymer was synthesized by one-shot copolymerization for the first time by using fast propagating pinacol-boronate and slow propagating MIDA-boronate.

INTRODUCTION

Conjugated polymers have attracted much attention amongst chemists because their intriguing applications to optoelectronic devices have provided promising technological advantages such as solution processibility, flexibility, low cost, and tunability of optoelectronic properties.[1] For example, poly(3-hexylthiophene) (P3HT) is one of the most extensively studied conjugated polymers in polymer electronics due to its good solubility, excellent thermal stability, and high hole mobility.[2] In line with an increasing interest in polymer electronics, the importance of developing new synthetic methodologies to prepare novel conjugated polymers has also grown over the past two decades. Conventionally, most of these conjugated polymers were prepared by a step-growth polymerization method using coupling reactions such as the Suzuki, Stille, and Heck reactions.[3] While these methods produced conjugated polymers with well-defined conjugated backbones, the precise control of their molecular weights, polydispersity indices (PDIs), and chain-ends was virtually impossible. In contrast to step-growth polymerization, controlled chain-growth polymerization methods provide conjugated polymers with precise control, thereby allowing facile access to various functional materials such as block copolymers, complex macromolecular architectures (e.g. graft copolymers), and hybrid nanomaterials modified with conjugated polymers.[4] Therefore, developing new controlled chain-growth polymerization methods for the synthesis of conjugated polymers has been one of the main focuses in polymer chemistry. For example, pioneering works on the Kumada catalyst-transfer polycondensation (KCTP) method, the most widely used CTP method, provided a breakthrough in the synthesis of various conjugated polymers including P3HT and their corresponding block copolymers.[5] However, despite the versatility of KCTP, the use of stoichiometric amounts of moisture-sensitive and reactive Grignard reagents often limited the molecular weight control, yield, potential monomer scope, and synthetic applications (Figure 1a). Moreover, preparation of externally initiated nickel catalysts often required multiple synthetic steps or glove box techniques even though there have recently been significant advances for the catalyst preparation.[6] Therefore, to overcome these issues, the Suzuki-Miyaura reaction, using air and moisture stable boronates, has emerged as a promising alternative for KCTP.[7]

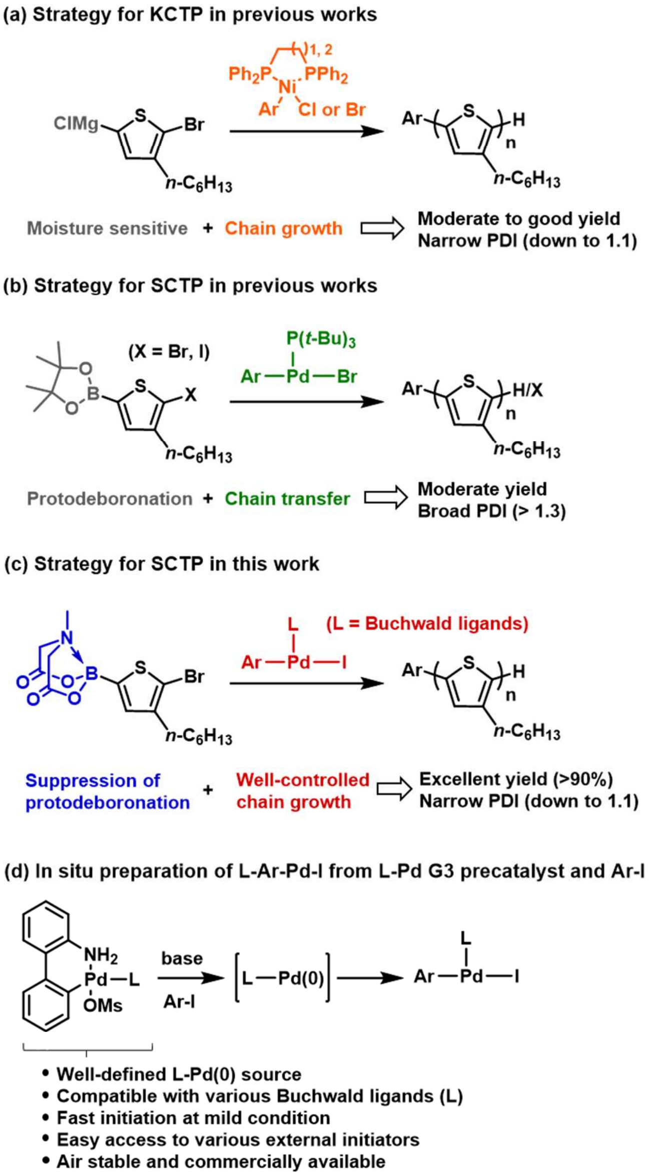


Figure 1. Strategies for the controlled chain-growth polymerization of P3HT using (a) KCTP and (b) SCTP methods in previous works; (c) our strategy using L-Pd G3 precatalysts and MIDA-boronates for SCTP of 3HT; and (d) preparation of externally initiated catalysts.

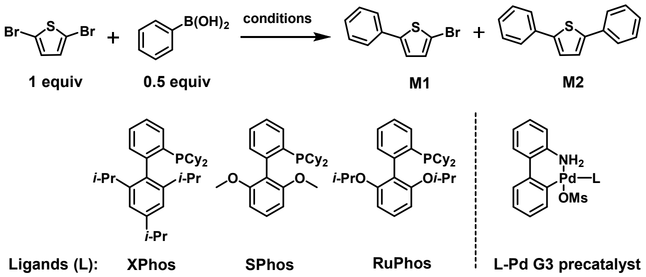
Suzuki-Miyaura reaction has attracted growing academic and industrial interest because its synthetic advantages based on mild reaction conditions, broad substrate scope, high functional group tolerance, and non-toxic monomers, particularly which are a sharp contrast to analogous Stille reaction requiring toxic tin compounds, have been overwhelming for synthesizing both small molecules and macromolecules.[8-10] Indeed, huge efforts have been devoted to fine-tuning the structures of palladium (Pd)-ligands and boronates to develop milder, more efficient, and versatile Suzuki-Miyaura reactions.[8,9] While there has been remarkable progress in Suzuki-Miyaura coupling reactions as popular organic reactions and step-growth polymerization methods,[8-10] to date, the controlled chain-growth polymerization of 3-alkylthiophenes (P3AT) using Suzuki-Miyaura catalyst-transfer polycondensation (SCTP) is challenging. This is mainly because of the use of a less efficient catalyst system and the competing protodeboronation of heterocyclic boronate monomers (Figure 1b). For example, SCTP of 3-hexylthiophene containing a pinacol boronic ester, using well-defined $P(t\text{-Bu})_3$-Pd-Ph-Br or Pd-containing *N*-heterocyclic carbenes, produced P3HT with a broad PDI (>1.3), mixed chain-ends, and moderate yields due to competing protodeboronation.[11] As a result, well-defined block copolymers containing two polythiophene moieties have not been demonstrated by SCTP. Therefore, even though the SCTP method exhibited many advantages over KCTP, its overall efficiency as a controlled polymerization of P3AT was less than satisfactory, thereby prohibiting the wide use of SCTP for P3AT synthesis. Very recently, the interest in SCTP of 3HT was further illustrated by Yokozawa group who reported improved SCTP resulting in narrow PDI for P3HT having relatively low molecular weights (DP 20).[12] Thus, given the importance of P3AT with its wide range of applications, developing a more efficient SCTP method that achieves both excellent controllability and productivity would be highly desirable.

Herein, we report a breakthrough on the controlled chain-growth polymerization of 3-alkylthiophenes via a catalyst-transfer process using highly active, fast initiating, and bench-stable Buchwald palladacycle precatalysts and *N*-methylimidodiacetic (MIDA) boronate protection to suppress protodeboronation (Figure 1c). As a result of these two modifications, SCTP of P3AT proceeded with excellent control on molecular weight and chain-ends, narrow PDI, excellent regioregularity, and quantitative conversion. Moreover, for the first time, the utility of this highly controlled polymerization protocol was expanded to successful block copolymerization of fully conjugated diblock copolymers comprising both polythiophene moieties. Lastly, the power of the new SCTP protocol over the widely used KCTP method was further demonstrated by one-shot block copolymerization.

RESULTS AND DISCUSSION

Pd-catalyzed Suzuki-Miyaura coupling of aryl halides and aryl boronic acids is one of the most versatile, efficient, and widely used reactions employed to construct biaryl moieties; thus, numerous efforts have been made to develop more powerful catalyst systems.[8] Among them, dialkylbiarylphospine ligand-Pd(0) (L-Pd(0)) species, commonly known as Buchwald catalysts, are one of the most popular catalysts in the Suzuki-Miyaura reaction not only because they are highly active, stable, and user-friendly, but also because many variants are commercially available for easy optimization screening.[8e-i] Interestingly, despite the versatility of the Buchwald L-Pd(0) system in cross-coupling reactions, its catalyst-transfer process,

Table 1. Screening of the catalyst-transfer process in small molecule reaction using Pd(0)/ligands and Pd G3 precatalysts



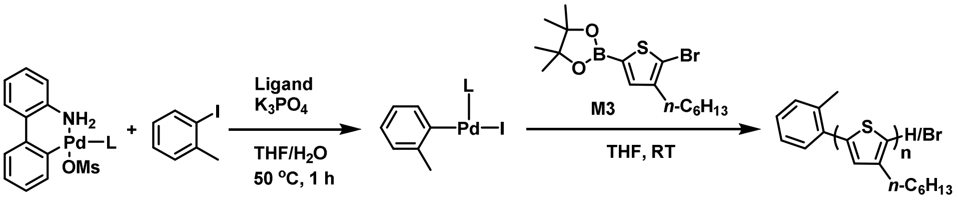
Entry	Pd catalyst (equiv.)	Ligand (equiv.)	THF/H$_2$O (conc., v/v)	Molar ratio (M1:M2)
1	Pd$_2$dba$_3$ (0.02)	none	0.4 M, 2/1	70:30
2	Pd$_2$dba$_3$ (0.02)	XPhos (0.04)	0.4 M, 2/1	39:61
3	Pd$_2$dba$_3$ (0.02)	XPhos (0.08)	0.4 M, 2/1	15:85
4	Pd$_2$dba$_3$ (0.02)	XPhos (0.08)	0.03 M, 30/1	6:94
5	Pd$_2$dba$_3$ (0.02)	SPhos (0.08)	0.03 M, 30/1	4:96
6	Pd$_2$dba$_3$ (0.02)	RuPhos (0.08)	0.03 M, 30/1	4:96
7	SPhos Pd G3 (0.04)	SPhos (0.04)	0.03 M, 30/1	2:98
8	RuPhos Pd G3 (0.04)	RuPhos (0.04)	0.03 M, 30/1	2:98

Reaction conditions: 2,5-dibromothiophene (0.2 mmol), phenylboronic acid (0.1 mmol), K$_3$PO$_4$ (1.2 mmol), THF/H$_2$O (12 mL/0.4 mL for 0.03 M), room temperature, overnight. Molar ratio and yield were determined by gas chromatography-mass spectrometry (GC-MS) calibrated using undecane as a standard.

which could potentially lead to SCTP, has not been demonstrated to date. Therefore, to investigate the possibility of a catalyst-transfer process by L-Pd(0), we carried out some model studies by conducting small molecule Suzuki-Miyaura reactions of 2,5-dibromothiophene (1 equiv.) and phenylboronic acid (0.5 equiv., Table 1). A substoichiometric amount of phenylboronic acid was intentionally employed in the model reaction. In this way, analysis of product distribution of mono-functionalized 2-bromo-5-phenylthiophene (**M1**) and di-functionalized 2,5-diphenylthiophene (**M2**) would demonstrate the degree of the catalyst-transfer process by various L-Pd(0) systems (Table 1).[11c] In more detail, conventional statistics would favor the formation of **M1** over **M2** in the absence of a catalyst-transfer process. However, if the Pd catalyst undergoes intramolecular oxidative addition via the catalyst-transfer process, **M2** should be dominantly produced over **M1**. To investigate the possibility of the catalyst-transfer process, the small molecule model reaction was initially performed using tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$dba$_3$; 0.02 equiv.) in THF/H$_2$O (0.4 M, v/v = 2/1) at room temperature as a control experiment. As expected, **M1** was preferentially produced over **M2** (**M1**:**M2** = 70:30) (Table 1, entry 1). In contrast, adding one equiv. of 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) ([Pd]:[XPhos] = 1:1) to the reaction switched the preference from **M1** to **M2** (**M1**:**M2** = 39:61), implying a partial catalyst-transfer process (Table 1, entry 2). To enhance this effect, the amount of XPhos ligand was doubled ([Pd]:[XPhos] = 1:2) and the preference of **M2** further increased (**M1**:**M2** = 15:85) (Table 1, entry 3). To push the selectivity for **M2** over to **M1**, the reaction was performed in dilute conditions to further promote the intramolecular catalyst-transfer process (0.03 M, THF/H$_2$O (v/v) = 30/1), and indeed, the preference improved significantly (**M1**:**M2** = 6:94; Table 1, entry 4). With these results in hand, we subsequently tested other Buchwald ligands such as 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) and 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (RuPhos) and found that in both cases, the selectivity for **M2** increased further (**M1**:**M2** = 4:96; Table 1, entries 5 and 6). Finally, we observed that commercially available SPhos Pd G3 and RuPhos Pd G3 precatalysts were the best choices, affording the highest selectivity (**M1**:**M2** = 2:98). This high selectivity for **M2** was probably attributed to more efficient formation of the active Pd(0) catalysts (Table 1, entries 7 and 8).[8i] Additionally, we observed consistently high selectivity for **M2** throughout the reaction progress (Table S2). This result suggested in favor of the catalyst-transfer mechanism of L-Pd(0) over the effect of reactivity difference between 2,5-dibromothiophene and **M1** on the distribution of the final products.[13b] In short, excellent catalyst-transfer of XPhos-Pd(0), SPhos-Pd(0), and RuPhos-Pd(0) in the Suzuki-Miyaura reaction was realized.

After successful demonstration of the catalyst-transfer of L-Pd(0) in small molecule model studies, we moved on to develop a new controlled chain-growth polymerization method. Synthesis of P3HT was selected as the model polymerization because not only it was widely used in polymer electronics but also its previous examples of controlled polymerization, using the SCTP method, exhibited some limitations such as low DP, broad PDI, and moderate polymerization yields (Figure 1b).[11] Based on our observation from the small molecule model studies, we slightly modified the reaction condition for the polymerization, i.e. higher [ligand]/[Pd] ratio to further stabilize the Pd-bound polymer chain-end and lower concentration with less amount of water to suppress the protodeboronation, and to increase the solubility of P3HT. As an initial trial, we carried out the polymerization of 5-bromo-4-*n*-hexylthien-2-yl-pinacol-boronate (**M3**) using a catalyst system of Pd$_2$dba$_3$, SPhos, and 2-iodotoluene (**M3**:[Pd] = 25:1) in THF/H$_2$O mixed solvents (0.02 M, v/v = 40/1) at room temperature (Table 2, entry 1). As a result, polymerization of **M3** afforded P3HT with a large number average molecular weight (M_n) value of 7.1 kg/mol, broad PDI of 1.45, and 64% isolated yield in 14 h (Table 2, entry 1). This result implied that despite the catalyst-transfer process of SPhos-Pd(0), the initiation must have been very slow, presumably due to the inefficient formation of

Table 2. Screening of SCTP using M3 and various Pd catalysts



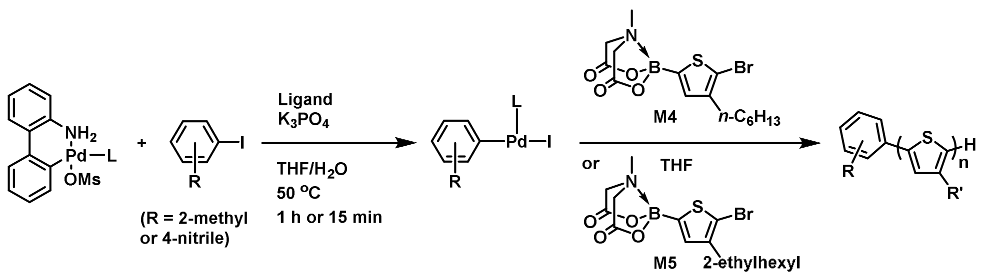
Entry	M/I	Pd catalyst (equiv.)	Ligand (equiv.)	THF/H_2O (conc., v/v)	Time	M_n (PDI)[a]	Yield[b]
1	25	Pd_2dba_3 (0.02)	SPhos (0.10)	0.02 M, 40/1	14 h	7.1k (1.45)	64%
2	25	SPhos Pd G3 (0.04)	none	0.02 M, 40/1	24 h	4.2k (1.51)	85%
3	25	SPhos Pd G3 (0.04)	SPhos (0.06)	0.02 M, 40/1	21 h	4.8k (1.16)	82%
4	25	RuPhos Pd G3 (0.04)	RuPhos (0.06)	0.02 M, 40/1	21 h	3.9k (1.14)	78%
5	25	XPhos Pd G3 (0.04)	XPhos (0.06)	0.02 M, 40/1	14 h	5.1k (1.37)	62%
6	25	P(*t*-Bu)$_3$ Pd G3 (0.04)	P(*t*-Bu)$_3$ (0.06)	0.02 M, 40/1	18 h	7.0k (1.58)	83%
7	50	SPhos Pd G3 (0.02)	SPhos (0.03)	0.02 M, 40/1	16 h	10.4k (1.34)	64%
8	50	RuPhos Pd G3 (0.02)	RuPhos (0.03)	0.02 M, 40/1	16 h	8.1k (1.60)	60%

Reaction conditions: **M3** (0.2 mmol, 1 equiv.), Pd G3 precatalyst, ligand, K_3PO_4 (1.2 mmol), THF (12 mL), H_2O (0.3 mL), room temperature. [a]Absolute molecular weight was determined by THF SEC using multi-angle laser light scattering (MALLS) detector. [b]Isolated yield.

the externally initiated SPhos-Pd(II)-(o-tolyl)-I catalyst. Thus, to attain fast initiation, 2-iodotoluene and a well-defined SPhos Pd G3 precatalyst, known to rapidly form active Pd(0), were used instead to efficiently generate the actual initiator (Table 2, entry 2).[8i] Indeed, switching to the SPhos precatalyst afforded P3HT with a molecular weight equal to 4.2 kg/mol that was closer to the theoretical value (M_{theo} = 4.3 kg/mol), even though dispersity of P3HT was still broad (1.51). Encouraged by this improvement, we further optimized the polymerization conditions by adding another 0.06 equiv. of SPhos ligands during the catalyst preparation step to increase the stability of the catalysts attached at the polymer chain-end and to facilitate the catalyst-transfer process (Table 2, entry 3). Notably, the addition of an extra amount of SPhos ligand further improved the polymerization control by reducing the PDI to 1.16 (Table 2, entry 3). Next, using these conditions, we screened other G3 precatalyst derivatives containing RuPhos, XPhos, and P(*t*-Bu)$_3$. We discovered that the RuPhos G3 precatalyst led to excellent controlled polymerization, affording P3HT with M_n of 3.9 kg/mol and narrow PDI of 1.14 in 78% yield (Table 2, entry 4). Disappointingly, moderate control (PDI = 1.37) was observed with the XPhos Pd G3 precatalyst (Table 2, entry 5), although this system exhibited reasonable catalyst-transfer process during small molecule model reactions (Table 1, entry 4). Moreover, the P(*t*-Bu)$_3$ Pd G3 precatalyst yielded unsatisfactory control (broad PDI of 1.58), even though well-defined P(*t*-Bu)$_3$-Pd(II)-(*o*-tolyl)-I was presumably employed in the SCTP (Table 2, entry 6). To test the versatility of this new SCTP method using an SPhos or RuPhos Pd G3 precatalyst, we increased the M/I ratio to 50 to acquire a higher molar mass. Unfortunately, both cases afforded P3HT with broad PDI values (1.34–1.60) in significantly lower yields (60–64%), probably due to the side reactions such as protodeboronation of **M3** (Table 2, entries 7 and 8).

Generally, Pd-catalyzed Suzuki-Miyaura reactions of heterocyclic boronic acid and boronates are challenging because of the unavoidable and undesired protodeboronation, which lowers the yield of the products.[8h,9,10c,14] Nevertheless, we initially chose heterocyclic **M3**-containing pinacol boronate as a monomer, hoping for successful SCTP, because it was reported that highly active SPhos-Pd(0) and RuPhos-Pd(0) catalysts could significantly facilitate the Suzuki-Miyaura reaction over the undesired competing protodeboronation in small molecule studies.[8e,8h] However, unsatisfactory yields of P3HT from **M3** clearly indicated that protodeboronation due to the fast release of boronic acid from pinacol-protected **M3**, inevitably occurred. Then, it became obvious that suppressing protodeboronation should improve the molecular weight control and yield of polymerization. To realize this idea, we switched the pinacol boronate monomer (**M3**) to MIDA-protected 5-bromo-4-*n*-hexylthien-2-yl-MIDA-boronate (**M4**) because slow hydrolysis of MIDA boronates under mild basic conditions would definitely maximize the effective [catalyst]/[boronic acid] ratio, thereby favoring the C–C bond coupling reaction over the undesired protodeboronation throughout the polymerization.[9,10b] Initially, the same polymerization, under the previously optimized conditions for **M3** (Table 2, entries 3 and 4), was carried out using **M4** instead (Table 3). Our initial trial using **M4** (M/I=25) and SPhos-Pd(II)-(o-tolyl)-I, which was *in situ*-generated from SPhos Pd G3

Table 3. SCTP of M4 or M5 using L-Pd G3 precatalysts

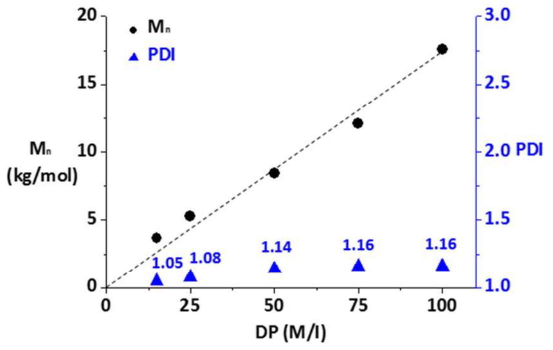


Entry	M/I	R	Pd catalyst (equiv.)	Ligand (equiv.)	THF/H_2O (conc., v/v)	Tempe rature	Time	M_n (PDI)[a]	Yield[b]
1	25	2-Me	SPhos Pd G3 (0.04)	SPhos (0.04)	0.02 M (12/1)	RT	72 h	6.0k (1.10)	82 %
2	25	2-Me	SPhos Pd G3 (0.04)	SPhos (0.04)	0.02 M (12/1)	35 °C	48 h	5.4k (1.21)	85 %
3	25	2-Me	SPhos Pd G3 (0.04)	SPhos (0.04)	0.02 M (12/1)	45 °C	24 h	6.5k (1.20)	82 %
4	25	2-Me	RuPhos Pd G3 (0.04)	RuPhos (0.06)	0.01 M (30/1)	45 °C	22 h	5.0k (1.06)	94 %
5[c]	25	-	RuPhos Pd G3 (0.04)	RuPhos (0.06)	0.01 M (30/1)	45 °C	21 h	3.1k (1.36)	18 %
6	15	2-Me	RuPhos Pd G3 (0.067)	RuPhos (0.10)	0.01 M (30/1)	45 °C	16 h	3.2k (1.08)	90 %
7	50	2-Me	RuPhos Pd G3 (0.02)	RuPhos (0.03)	0.01 M (30/1)	45 °C	25 h	8.2k (1.15)	96 %
8	75	2-Me	RuPhos Pd G3 (0.013)	RuPhos (0.02)	0.01 M (30/1)	45 °C	22 h	9.6k (1.45)	97 %
9	75	4-CN	RuPhos Pd G3 (0.013)	RuPhos (0.02)	0.01 M (30/1)	45 °C	23 h	9.8k (1.32)	93 %
10[d]	75	4-CN	RuPhos Pd G3 (0.013)	RuPhos (0.02)	0.01 M (30/1)	45 °C	15 h	12.1k (1.16)	95 %
11[d]	100	4-CN	RuPhos Pd G3 (0.01)	RuPhos (0.015)	0.01 M (30/1)	45 °C	15 h	17.6k (1.16)	90 %
12[d]	15	4-CN	RuPhos Pd G3 (0.067)	RuPhos (0.10)	0.01 M (30/1)	45 °C	23 h	3.7k (1.05)	99%
13[d]	25	4-CN	RuPhos Pd G3 (0.04)	RuPhos (0.06)	0.01 M (30/1)	45 °C	15 h	5.3k (1.08)	95%
14[d]	50	4-CN	RuPhos Pd G3 (0.02)	RuPhos (0.03)	0.01 M (30/1)	45 °C	15 h	8.4k (1.14)	96%
15[d, e]	25	4-CN	RuPhos Pd G3 (0.04)	RuPhos (0.06)	0.01 M (30/1)	45 °C	15 h	5.9k (1.12)	96 %
16[d, e]	50	4-CN	RuPhos Pd G3 (0.02)	RuPhos (0.03)	0.01 M (30/1)	45 °C	15 h	9.2k (1.20)	97 %
17[d, e]	75	4-CN	RuPhos Pd G3 (0.013)	RuPhos (0.02)	0.01 M (30/1)	45 °C	15 h	13.1k (1.19)	96 %
18[d, e]	100	4-CN	RuPhos Pd G3 (0.01)	RuPhos (0.015)	0.01 M (30/1)	45 °C	24 h	15.8k (1.32)	99 %

Reaction condition: **M4** (0.2 mmol, 1 equiv.), RuPhos Pd G3, Ar-I (0.95 equiv. relative to the catalyst), ligand, K_3PO_4 (1.2 mmol), [a]Absolute molecular weight was determined by THF SEC using MALLS detector. [b]Isolated yield. [c]Catalyst was prepared in the absence of 2-iodotoluene. [d]Catalyst was prepared for 15 min. [e]**M5** was used.

precatalysts and 2-iodotoluene at 50 °C for 1 h in THF/H_2O (0.02 M, v/v = 12/1), produced P3HT with low PDI (1.10) and an isolated yield of 82%, after 72 h at room temperature (Table 3, entry 1). The slow hydrolysis inevitably prolonged the polymerization time, a sharp contrast to the polymerization reaction with **M3**. To speed up the hydrolysis of the MIDA boronate, the reaction temperature was increased to 35 °C and subsequently, to 45 °C. Indeed, the polymerizations were completed within 48 h and 24 h, respectively (Table 3, entries 2 and 3). However, the yield of P3HT was still between 82 and 85%, and PDI from the polymerization was relatively broader (1.20) than that at RT (1.10) (Table 3, entries 2 and 3). To further optimize the polymerization process, we switched the catalyst from SPhos Pd G3 to RuPhos Pd G3, and conducted the polymerization with dilution (THF/H_2O (v/v) = 30/1) at 45 °C. This modification resulted in faster polymerization with shorter reaction times (22 h) and yielded P3HT with excellent PDI control (1.06), high yield (94%), and perfect regioregularity (>99%; Table 3, entry 4 and Figure S1a). Interestingly, polymerization in the absence of 2-iodotoluene under otherwise identical conditions afforded a very low isolated yield of 18%, implying significant protodeboronation of **M4** that was clearly observed by GC-MS spectrum (Table 3, entry 5). Probably, the absence of 2-iodotoluene significantly slowed down the initiation of the RuPhos Pd G3 precatalyst forming the actual propagating catalyst, RuPhos-Pd(II)-3HT-Br. This slow initiation also retarded the propagation or catalyst-transfer process, thus, the competitive protodeboronation became dominant. Hence, we concluded that fast and efficient formation of the active initiator, L-Pd(II)-(*o*-tolyl)-I, prior to polymerization, must be essential for successful controlled SCTP. Furthermore, to get more mechanistic insight into the polymerization, we added 0.04-0.12 equiv. of 2-bromothiophene as a chain-transfer agent to the optimized reaction condition (Table S3). Interestingly, M_n and PDI of the final P3HT stayed the same regardless of the addition of 2-bromothiophene (Table S3). Thus, this preliminary mechanistic investigation also matched with our result on the small molecule mechanistic study (Table S2) suggesting for the catalyst-transfer mechanism of SCTP. Interestingly, this result is a sharp contrast to the previously reported Negishi polymerization of P3HT via chain-growth polymerization through reactivity difference mechanism even though in both cases, the same ligand was employed.[13a]

(a) P3HT



(b) P3EHT

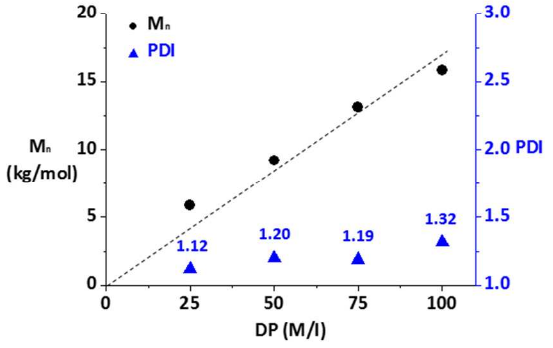


Figure 2. Plot of M_n versus M/I for (a) P3HT and (b) P3EHT prepared by SCTP using **M4**, **M5**, and RuPhos Pd G3 precatalysts in their optimal conditions.

With optimized conditions in hand, we next investigated the possibility of controlled polymerization of P3HT by varying the M/I ratio and examining their molecular weights. For M/I values ranging from 15 to 50, the new SCTP polymerization successfully produced P3HT with a narrow PDI (1.06–1.16), high yield (>90%), and excellent regioregularity (>99%) (Table 3, entries 4, 6, and 7). Moreover, an excellent linear relationship between [**M4**]/[catalyst] and M_n values (3.2–8.2 kg/mol) was observed (Table 3, entries 4, 6, and 7). However, the same polymerization at an M/I value of 75 afforded P3HT with relatively broad PDI (1.45) and a lower M_n (9.6 kg/mol) than the expected M_n value (M_{theo} = 12.6 kg/mol) presumably due to catalyst decomposition at higher turnover numbers (Table 3, entry 8). To improve the initiation process and to increase the life-time of catalyst by the fast initiation, we screened various initiators (Table 3, entry 9 and Table S4, entries 15–17), other than 2-iodotoluene, which required an induction period of 1 h for the formation of the active well-defined initiator due to its bulky *ortho*-methyl group. After this screening, we switched the initiator to 4-iodobenzonitrile containing an electron-withdrawing group and proceeded the polymerization at M/I = 75 with the intention of more efficient formation of the active Pd catalyst. However, we still observed lower M_n values (9.8 kg/mol) than expected M_n (12.6 kg/mol) with moderate PDI (1.32) (Table 3, entry 9). Based on the faster oxidative addition of 4-iodobenzonitrile to L-Pd(0), we reduced the induction period to 15 min and under the otherwise identical conditions, at an M/I value of 75, P3HT with an M_n value of 12.1 kg/mol and a narrow PDI (1.16) was isolated in 95% yield (Table 3, entry 10). To prepare even higher molecular weight polymers, we further increased the M/I ratio to 100 and produced P3HT with an M_n value of 17.6 kg/mol and a narrow PDI (1.16; Table 3, entry 11). As a result, we overall achieved excellent controlled SCTP with linearly increased M_n (3.7–17.6 kg/mol), narrow PDI (1.05–1.16), high yield (>90%), and high regioregularity (>99%) over a wide range of M/I ratios (15–100) (Table 3, entries 10-14 and Figure 2a). In addition to the P3HT results, using the same protocol, polymerization of the more sterically demanding 5-bromo-4-(2'-ethylhexyl)thien-2-yl-MIDA-boronate (**M5**), also proceeded well with excellent control for DP ranging from 25 to 100, producing poly(3-(2'-ethylhexyl)thiophene) (P3EHT) with narrow PDI (1.12–1.32), high yield (>95%), and high

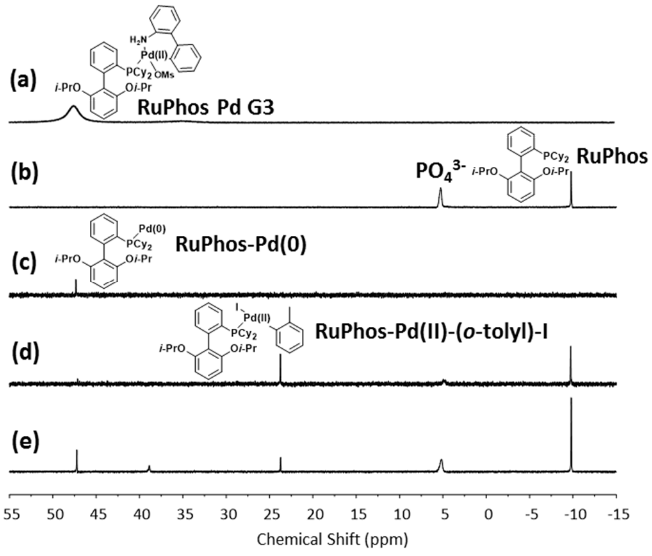


Figure 3. ^{31}P NMR spectra of (a) initial RuPhos Pd G3, (b) RuPhos + K_3PO_4 (c) RuPhos Pd G3 + K_3PO_4, (d) RuPhos Pd G3 + RuPhos + 2-iodotoluene + K_3PO_4, and (e) Pd_2dba_3 + RuPhos + 2-iodotoluene + K_3PO_4 in THF-d_8/D_2O (v/v=4/1) at 50 °C for 1 h.

regioregularity (>99%) (Table 3, entries 15–18 and Figures 2b and S1b).

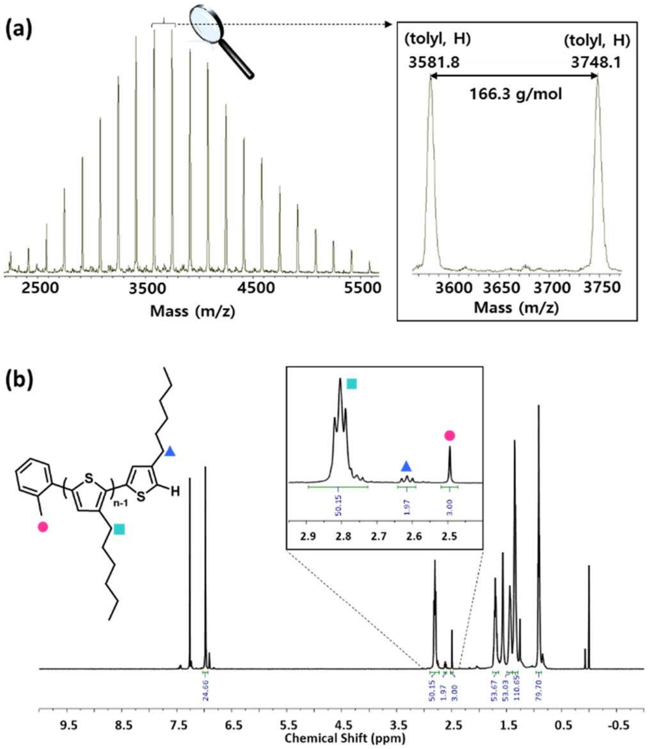


Figure 4. (a) MALDI and (b) 1H NMR spectra of P3HT prepared by SCTP of M4 (Table 3, entry 4).

A key factor to a successful SCTP was the efficient formation of the actual initiator, the well-defined Buchwald L-Pd(II)-aryl-I, from L-Pd G3 precatalysts and aryl iodides. Therefore, we assumed that detailed investigation of this initiation process would provide a better understanding of the controlled SCTP. We monitored catalytic complex formation during initiation with ^{31}P NMR spectroscopy because various catalytic complexes could be easily identified from their distinct chemical shifts. Firstly, the RuPhos Pd G3 precatalyst, displayed as a broad signal at 47.4 ppm (Figure 3a), was treated with 6 equiv. of K$_3$PO$_4$ at 50 °C in THF-d8/D$_2$O for 1 h. The ^{31}P NMR spectrum of the resultant reaction mixture revealed a new sharp peak at 47.2 ppm corresponding to RuPhos-Pd(0), with the complete consumption of the precatalyst (Figure 3c). This result is consistent with previous literature that demonstrated the exclusive formation of RuPhos-Pd(0) from RuPhos Pd G3 precatalysts under mild basic conditions.[8i] Next, to directly identify the externally initiated catalyst or the actual initiator of the polymerization, we carried out the same process in the presence of 1 equiv. of 2-iodotoluene and 1.5 equiv. of additional RuPhos ligands. The ^{31}P NMR spectrum of the crude reaction mixture displayed other new peaks at 23.7 ppm and -9.7 ppm corresponding to RuPhos-Pd(II)-(*o*-tolyl)-I and the additional RuPhos ligand, respectively (Figure 3d).[15] Overall, these results indicated that a fast and high yielding transformation from the RuPhos Pd G3 precatalyst to the actual RuPhos-Pd(II)-(*o*-tolyl)-I initiator via a RuPhos-Pd(0) intermediate occurred efficiently under mild conditions. On the other hand, an attempt to prepare RuPhos-Pd(II)-(*o*-tolyl)-I directly from Pd$_2$dba$_3$, RuPhos, and 2-iodotoluene under the same conditions was less successful. This reaction generated a mixture of three different catalytic complexes comprising RuPhos-Pd(0), RuPhos-Pd(II)-(*o*-tolyl)-I, and another unidentified complex at 38.8 ppm (Figure 3e). Because of this inefficient initiation, P3HT produced from Pd$_2$dba$_3$ resulted in a broad PDI with less control (Table 2, entry 1 and Table S4, entry 1). Thus, we concluded that using L-Pd G3 precatalysts as a well-defined L-Pd(0) source was the key to the exclusive formation of the externally initiated L-Pd(II)-aryl-I, thereby leading to controlled SCTP. Furthermore, the *in situ* preparation protocol was user-friendly because L-Pd G3 precatalysts were bench-stable solids, easy to handle, and commercially available. Moreover, a wide range of aryl iodides could be used to form the externally initiated catalysts, introducing various functional groups to one of the polymer chain-ends (Table S4).

To further confirm chain-growth polymerization, we examined chain-end fidelity of P3HT using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and ^{1}H NMR spectroscopy. The MALDI-TOF spectrum of P3HT, prepared from pinacol-based **M3** or MIDA-based **M4** (M/I=25), revealed a major peak distribution corresponding to m/z values of P3HT comprising the *o*-tolyl/H chain-end (Figures 4a and S2a). However, detailed ^{1}H NMR analysis of P3HT both from **M3** and from **M4** revealed a stark difference in the chain-end fidelity. ^{1}H NMR characterization of P3HT, prepared from **M3**, showed a diagnostic peak of *o*-tolyl

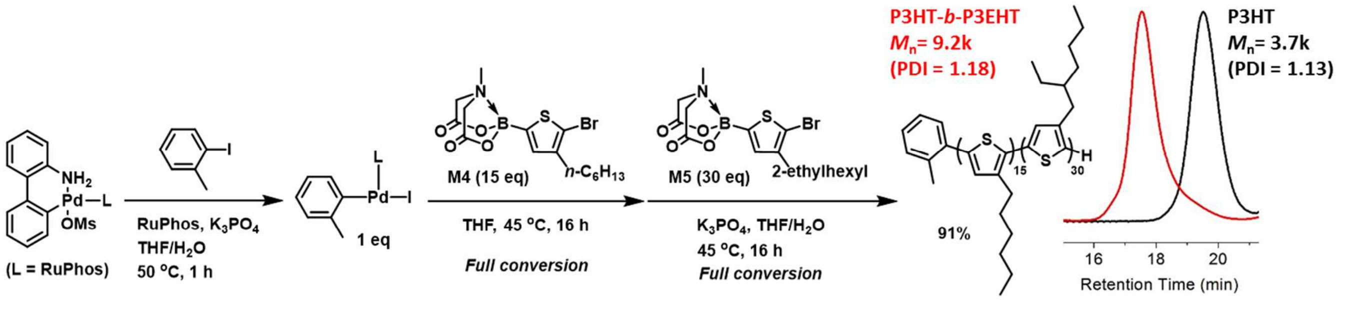


Figure 5. Synthesis of P3HT-*b*-P3EHT by SCTP using **M4** and **M5** with RuPhos Pd G3 precatalyst. Absolute molecular weight was determined by THF SEC using MALLS detector.

chain-end at 2.5 ppm, a methylene peak of H-terminated thiophene chain-end at 2.62 ppm, and an additional peak at 2.56 ppm that is assigned as a methylene peak of Br-terminated thiophene chain-end (Figure S2b).[16] Also, careful integration of each peak revealed the moderate incorporation of *o*-tolyl group into P3HT (~75%) (Figure S2b), and this data suggested the occurrence of undesirable and competing side reactions during SCTP of pinacol-based **M3** monomer. In contrast, ^{1}H NMR analysis of P3HT, prepared from **M4**, exclusively showed two peaks at 2.5 and 2.62 ppm corresponding to *o*-tolyl/H chain-end (Figure 4b). More importantly, the careful integration of the chain-end peaks suggested for high incorporation of *o*-tolyl group into P3HT (>95%) (Figure 4b). In addition, the estimated DP of P3HT was in good agreement with the initial feeding ratio (**M4**/I = 25), again supporting the high incorporation of *o*-tolyl group into P3HT (Figure 4b).

One of the essential criteria for controlled chain-growth polymerization is the retention of living chain-ends, thereby allowing for successful chain extension and block copolymerization from the macroinitiator of the homopolymer. Notably, to date, the well-controlled block copolymerization of two different thiophene monomers using the SCTP method has never been realized. Therefore, we carried out the block copolymerization of P3HT-*b*-P3EHT to highlight the power of this much-improved controlled SCTP protocol for the synthesis of P3AT derivatives. Firstly, a macroinitiator of P3HT, the first block (M_n = 3.7k and PDI = 1.13), was prepared with DP of 15, using our optimized conditions with **M4** and RuPhos Pd G3 precatalysts (Figure 5). Next, to the same reaction pot, **M5** was added to produce P3HT-*b*-P3EHT ([**M5**]/[macro initiator] = 30/1; Figure 5). Indeed, the SEC trace of the P3HT macroinitiator clearly shifted to a higher molecular weight region (M_n = 9.2k and PDI = 1.18; Figure 5). Additionally, the ^{1}H NMR spectrum of the resulting block copolymer displayed two methylene peaks at 2.73 ppm and 2.80 ppm corresponding to P3EHT and P3HT, respectively, and DP of each block (P3HT = 14 and P3EHT = 27) was in good agreement with the initial feeding ratio (Figure S4b). Thus, all these characterization data confirmed successful block copolymerzation of thiophene derivatives using strategies with RuPhos Pd G3 precatalysts and MIDA-boronates.

With this successful block copolymerization by the sequential addition of **M4** and **M5**, we carried out a simpler but more challenging one-shot copolymerization by the simultaneous addition of two monomers to prepare the P3EHT-*b*-P3HT (Figure 6). In general, one-shot block copolymerization is extremely challenging and requires two monomers with very different reactivities.[17] For example, one-shot block copolymerization using KCTP has been virtually impossible due to the similar reactivity of the Grignard monomers.[6d] Previously, such an attempt was made by adding lithium chloride to a mixture of two thiophene Grignard regioisomers.[18] Unfortunately, this resulted in uncontrolled block copolymerization, displaying a bimodal SEC trace and defects in regioregularity.[18] In contrast, we envisioned that one-shot copolymerization using this new SCTP could be possible if one cleverly utilizes the vastly different hydrolysis rates between pinacol boronates and MIDA boronates without compromising

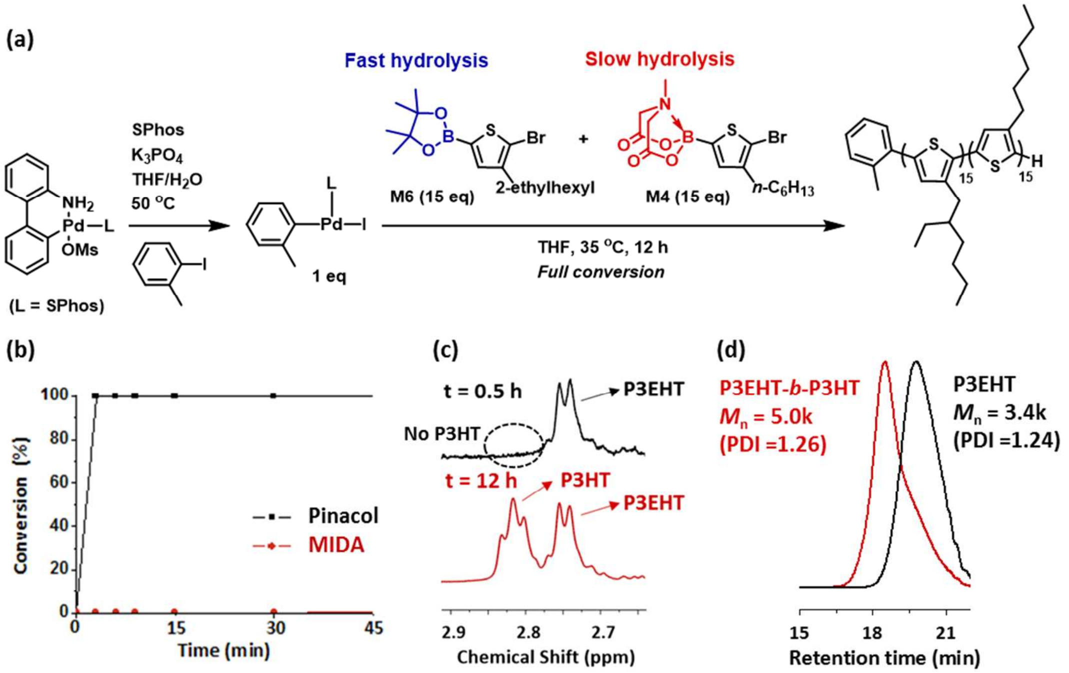


Figure 6. (a) One-shot preparation of P3EHT-*b*-P3HT by SCTP using **M4**, **M6**, and SPhos Pd G3 precatalyst. (b) Conversion vs. time plot of protecting groups of **M4** and **M6** in one-shot SCTP block copolymerization. (c) ^{1}H NMR analysis on the one-shot polymerization of P3EHT-*b*-P3HT. (d) SEC traces of one-shot SCTP block copolymerization. Absolute molecular weight was determined by THF SEC using MALLS detector.

regioregularity as well as the initiation rate of the second block polymerization (Figure 6). To perform one-shot block copolymerization, a monomer mixture of MIDA-based **M4** and 5-bromo-4-(2'-ethylhexyl)thien-2-yl-pinacol-boronate (**M6**) in THF was immediately added to the solution containing *in situ*-generated SPhos-Pd(II)-(o-tolyl)-I from Buchwald SPhos Pd G3 precatalysts; the resulting mixture was stirred at 35 °C for 12 h (Figure 6a). Time-dependent ^{1}H NMR monitoring of the crude copolymerization mixture revealed that the more reactive pinacol boronate **M6** was completely converted to P3EHT within 30 min due to fast release to the corresponding boronic acids (Figures 6b, c and S3). Subsequently, polymerization of the MIDA-protected **M4** began to occur slowly after 1 h (Figure S3). Moreover, the SEC trace measured after 30 min (corresponding to P3EHT, M_n = 3.4k and PDI = 1.24) clearly shifted to a higher molecular weight (M_n = 5.0k and PDI = 1.26) after 12 h, suggesting a successful chain extension, thereby producing P3EHT-*b*-P3HT by one-shot copolymerization (Figure 6d).

CONCLUSIONS

In conclusion, we developed significantly improved strategies for SCTP with a much better controlled polymerization of 3-alkylthiophenes using fast initiating bench-stable Buchwald RuPhos (and SPhos) Pd G3 precatalysts and slow-releasing MIDA-protected boronates. Optimizing model reactions with small molecules revealed that RuPhos (and SPhos) Pd G3 precatalysts were the best catalysts for the catalyst-transfer reactions. For controlled SCTP, the RuPhos Pd G3 precatalyst promoted the rapid formation of well-defined externally initiated catalysts that were the key for a successful controlled polymerization. Moreover, use of MIDA-boronates instead of pinacol boronates, effectively suppressed side reactions such as protodeboronation, resulting in greatly improved controlled polymerization to afford high molecular weight and defect-free P3ATs in excellent yield. Thus, this new SCTP method provided a solution to overcome previous limitations such as air-sensitivity of catalysts, protodeboronation of monomers, and loss of polymerization control. Furthermore, advantages of the new controlled SCTP protocol were highlighted by the first successful demonstration of block copolymerization and even one-shot block copolymerization of two different thiophene monomers. We believe that this new protocol makes SCTP an excellent alternative to the current KCTP method, and this method would certainly expand its utility toward the controlled synthesis of novel conjugated polymers.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and characterization data for new compounds and polymers. The Supporting Information 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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