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LiCl-Promoted Chain Growth Kumada Catalyst-Transfer Polycondensation of the "Reversed" Thiophene Monomer

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Supporting Information

ABSTRACT: The effect of LiCl on the chain growth Kumada catalyst-transfer polycondensation (KCTP) of the "reversed" thiophene monomer, 5-bromo-2-chloromagnesio-3-hexylthiophene (**3a**) (that has bulky substituent adjacent to the chloromagnesium group), was investigated. LiCl promotes the polymerization of **3a**, and the polymerization also exhibits living characteristics similar to those of the "normal" monomer, 2-bromo-5-chloromagnesio-3-hexylthiophene (**3b**). However, initiation is much slower than chain propagation due to the steric hindrance between hexyl groups in the transmetalation (TM) step that leads to the formation of the initiator



via head-to-head (HH) coupling. Consequently, regioregular poly(3-hexylthiophene) (P3HT) with large polydispersity (PDI) and higher number-average molecular weight (M_n) than the theoretical value was obtained. Because of the slow initiation with 3a, the polymerization of 3a occurs primarily after the consumption of 3b in the copolymerization of 3a and 3b, and P3HT with high regioregularity was still obtained.

■ INTRODUCTION

Chain growth Kumada catalyst-transfer polycondensation (KCTP) has become an attractive method for the controlled synthesis of conjugated polymers.¹⁻⁴ Particularly, KCTP with living characteristics has been demonstrated for several polymers, such as polythiophenes (PThs),^{5–17} polyphenylenes (PPs),^{17,18} polypyrroles (PPys),^{17,19,20} and poly(bithienylmethylene)s (PBTMs).²¹ This has enabled the synthesis of fully conjugated block copolymers,^{8,19,22–26} rod–coil block copolymers,^{27–31} and polymer brushes 3^{2-36} in a well-defined way. It has been demonstrated that KCTP is strongly affected by both catalyst and the monomer structures.^{8,13-15,23,24,37-39} One of those factors, the effect of alkyl substituents on monomer reactivity, plays an important role in KCTP of certain monomers.^{8,13,15,39} For example, KCTP of a 85:15 mixture of the "normal" monomer, 2-bromo-5-chloromagnesio-3-hexylthiophene (3b), and the "reversed" monomer, 5-bromo-2-chloromagnesio-3-hexylthiophene (3a), prepared by the metalation of 2,5-dibromo-3-hexylthiophene (4) affords P3HT with regioregularity values of 95%-97%.⁸ Previous studies attribute this regioselectivity to the steric hindrance caused by the hexyl group that is adjacent to the chloromagnesio group in the "reversed" monomer 3a. Therefore, the polymerization takes place predominantly with the "normal" monomer 3b.8 Recently, Kiriy and Luscombe independently studied the polymerization of the "reversed" monomer 3a. They found that no polymer was produced with either 1,3-bis-(diphenylphosphino)propane nickel dichloride (Ni(dppp) Cl_2)

Scheme 1. Homopolymerizations of (A) 3a and (B) 3b in the Presence of 1 equiv of LiCl

(A)
$$Br \leftarrow C_{6}H_{13} iPrMgCl, LiCl \\ THF, -20 °C Br \leftarrow S MgCl \\ 3a \\ (B) I \leftarrow C_{6}H_{13} iPrMgCl, LiCl \\ S H \\ C_{6}H_{13} iPrMgCl, LiCl \\ THF, -20 °C CIMg \\ S H \\ C_{6}H_{13} Ni(dppp)Cl_{2} \\ C_{6}H_{13} Ni(dppp)Cl_{2} \\ C_{6}H_{13} Ni(dppp)Cl_{2} \\ C_{6}H_{13} Ni(dppp)Cl_{2} \\ THF, -20 °C CIMg \\ S H \\ THF \\ P3HT \\ P3HT$$

or 1,3-bis(diphenylphosphino)ethane nickel dichloride (Ni(dppe)- Cl_2) as catalyst,^{13,15} since the HH coupling of two 3a molecules, which is required for the formation of initiator, was prohibited.¹⁵ In the surface-initiated KCTP to prepare poly(*p*-phenylene) (PPP) brushes, it was found that monomers with shorter side chains could be more easily polymerized and result in smoother and thicker films.³⁵ In the synthesis of all conjugated diblock copoly(3-alkylthiophene)s, Yang et al. found that the monomer with the shorter side chain had to be polymerized first in order to obtain the copolymer with the targeted molar ratio of the two segments, implying the influence of the different bulkiness of alkyl substituents in the monomer on block copolymerization

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Figure 1. (A) M_n and PDI versus conversion of **3a**. (B) M_n and PDI versus [converted **3a**]/[Ni(dppp)Cl₂] in monomer addition experiments. (C) GPC elution curves of P3HT in monomer addition experiments. (D) MALDI-TOF mass spectrum of polymer from **3a**. All polymerizations were carried out at room temperature in the presence of LiCl with $[1]_0 = 0.1 \text{ mol/L}$. For (A), the polymerization was conducted with 4 mol % Ni(dppp)Cl₂. For (B) and (C), the polymerization was conducted with 1.8 mol % Ni(dppp)Cl₂ to total **1**. For (D), the polymerization was carried out with 10 mol % Ni(dppp)Cl₂ (P3HT: $M_n = 5.1 \times 10^3$, PDI = 1.48 measured by GPC with polystyrene as the standard).

results.²⁵ Accordingly, it is clear that understanding the steric effects on KCTP and developing approaches to promote the polymerization are important for the development of this new polymerization method.

Grignard reagents form complicate aggregates in solution, and dispersing the aggregates can significantly improve reactivity toward electrophiles; 40 thus, the steric hindrance issues in the TM step might be alleviated. The literature has indications that lithium salts such as LiCl exhibit this function. 41–43 It was found that the addition of 1 equiv of LiCl in the reaction medium could promote magnesium-halogen exchange.^{41,42} This phenomenon was also observed in KCTP for conjugated polymers. For example, Yokozawa et al. found that the polymerization of 1-bromo-4-chloromagnesio-2,5-dihexyloxybenzene exhibited living characteristics in the presence of 1 equiv of LiCl.¹⁸ Recent studies by McNeil indicated that LiCl can form aggregates with the monomer and that the effect of LiCl on the polymerization depends on the catalyst used.^{37,38} When Ni-(dppp)Cl₂ was used as the catalyst, a faster polymerization was observed in the presence of LiCl at monomer concentrations lower than 0.4 M.³⁸ For polymerization with Ni(dppe)Cl₂, LiCl may affect only the initiation, but not chain propagation.³⁷ In the synthesis of polyfluorenes, Geng et al. found that the addition of LiCl could enhance the conversion of the magnesium-halogen exchange and $M_{\rm p}$ of the resulting polymers.⁴⁴ However, the effect of LiCl on the polymerization of thiophene monomers has not been studied in detail yet, although we and others have independently reported the synthesis of P3HT in the presence of LiCl.^{16,24} In the current contribution, we systematically studied the KCTP homopolymerization and copolymerization of thiophene monomers in the presence of 1 equiv of LiCl and found that LiCl can promote the polymerization of the "reversed" monomer 3a. However, the polymerization is characterized by slow initiation and fast chain propagation.

RESULTS

Homopolymerizations of 3a and 3b. A factor in the polymerization of **3a** that cannot be ignored is the purity of **1**.¹⁵ Kiriy et al. found that a small amount of 2 can significantly affect the polymerization. Therefore, in our experiments, 1 was exhaustively purified and the measured purity of 1 was 99.5% (see Figure S4 in the Supporting Information). As shown in Scheme 1A, 3a was synthesized by Grignard metathesis of 1 with ⁱPrMgCl in the presence of 1 equiv of LiCl. The magnesiumhalogen exchange took place selectively with iodine to afford Grignard reagent 3a in a yield of \sim 95% in 1 h. The resulting solution was characterized by ¹H NMR. Compared with the ¹H NMR spectrum of 3a without the addition of LiCl, an obvious peak shift was observed in the ¹H NMR spectra of 3a with the addition of LiCl (Figure S5, ¹H NMR spectra of the other monomers mentioned in this paper with and without LiCl are also shown in Figure S5), suggesting that the addition of LiCl may inhibit the aggregation of 3a and that a new aggregate between LiCl and 3a was formed.^{37,38} Polymerization of 3a with 4 mol % Ni(dppp)Cl₂ as the catalyst was almost complete after 10 min to render P3HT in a yield of 85% with $M_{\rm p}$, PDI, and regioregularity of 1.3×10^4 , 1.50, and 93%, respectively. As shown in Figure 1A, M_ns of the polymers increased with conversions, but not linearly. In contrast, no polymer was afforded even after 5 h in the absence of LiCl, consistent with the results of Luscombe and Kiriy.^{13,15} This indicates that the addition of LiCl can overcome the steric hindrance issue in the polymerization of 3a. Polymerizations of 3b were also conducted under the same conditions for comparison (Figure S6). In the presence of LiCl, the polymerization was also complete in ~ 10 min (Figure S6A), $M_{\rm p}$ increased linearly versus conversion with PDI <1.23 (Figure S6B), and P3HT with $M_{\rm p}$, PDI, and regioregularity of 6.5 \times 10³, 1.23, and 92%, respectively, was afforded in a yield of 86%. Clearly, the polymerization of 3a is





Figure 2. (A) Conversions of 3a and 3b and regioregularity of P3HT versus time. (B) M_n versus conversion of 3b. (C) M_n and PDI versus the sum of the conversions of 3a and 3b. (D) GPC elution curves of P3HT at different polymerization times. The polymerization was carried out at room temperature in the presence of 1 equiv of LiCl with 2 mol % Ni(dppp)Cl₂ and [4]₀ = 0.10 mol/L.

remarkably different from that of **3b**. To determine whether the polymer chain is still living after the polymerization of **3a**, monomer addition experiments were carried out. Gel permeation chromatography (GPC) profiles as shown in Figure 1C shifted to higher molecular weight regions and remained unimodal after the addition of each portion of **3a**, indicating that the polymer chain remains active during the whole process. Figure 1D shows the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of P3HT from **3a**; the main signals correspond to polymers with H/Br ends. These data clearly confirm the living character of the polymerization of **3a**. We attribute the nonlinear increase of M_n versus conversion of **3a** and [converted **3a**]/[Ni(dppp)Cl₂] to reasons other than the presence of chain termination or transfer (see Discussion section).

Copolymerization of 3a and 3b. Copolymerization of 3a and 3b was initially carried out using a 3a/3b ratio of 16/84 (Scheme 2A). The 3a/3b mixture was prepared from magnesium-halogen exchange of 2,5-dibromo-3-hexylthiophene (4) following McCullough's method,⁸ with the exception that 1 equiv of LiCl was added. Figure 2A depicts the conversions of 3a and 3b versus time. In contrast to the polymerization without LiCl (only 3b polymerized), both 3a and 3b were consumed when LiCl was present. The polymerization can be divided into

three stages. In the first 5 min (the first stage), 3a essentially did not polymerize while over 80% 3b was consumed. The second stage involved a very short period of time during which both 3a and 3b were involved in the polymerization accompanied by a slight decrease of regioregularity. In the third stage, the conversion of 3b terminated at \sim 96% while the polymerization of the remaining 3a continued until reaching a conversion of 91%. $M_{\rm n}$ increased during the whole process. As shown in Figure 2B, after the consumption of **3b** stopped, $M_{\rm n}$ still increased with the polymerization of **3a**. Meanwhile, $M_{\rm p}$ versus conversion of [3a + 3b]was almost linear. The GPC profiles as shown in Figure 2D are also consistent with the above observation and show that the peak gradually moves to the higher molecular weight region over the course of polymerization. This indicates that 3a propagates the living polymer chains instead of new chains. Considering that polymerization of **3b** is living and the resting state of the Ni catalyst after the polymerization is P3HT-Ni(dppp)Br as reported in the literature,³² the block copolymerization of **3a** and **3b** is reasonable.

All the above results confirm that LiCl can promote the polymerization of the "reversed" monomer 3a. Polymerizations with different amounts of catalyst were also conducted for the 3a/3b (16:84) mixture. As shown in Table 1, all three of the polymerizations in the presence of LiCl afforded P3HT with

	regioregularity (%)		yield (%)		$M_{\rm n}/{ m PDI}$				
amount of catalyst (mol %)	without LiCl	with LiCl	without LiCl	with LiCl	without LiCl	with LiCl			
4	81	85	62	85	3500/1.13	6400/1.27			
2	92	91	59	89	9200/1.13	12600/1.34			
1	94	92	62	80	16000/1.20	20000/1.26			
^a All polymerizations were carried out at room temperature with $[4]_0 = 0.1 \text{ mol/L}$.									

Table 1. Polymerization Results from 4 Catalyzed by Different Amounts of $Ni(dppp)Cl_2$ without and with 1 equiv LiCl^a



Figure 3. (A) Conversions of **3a** and **3b** and regioregularity of P3HT versus time. (B) M_n versus the conversion of **3b**. (C) M_n and PDI versus the sum of the conversions of **3a** and **3b**. (D) GPC elution curves of P3HT at different polymerization times. The polymerization was carried out at room temperature with 1 equiv of LiCl and 2 mol % Ni(dppp)Cl₂ to the sum of 1 and 2. $[1]_0 = [2]_0 = 0.05$ mol/L.

yields \geq 80%, which are significantly higher than those without LiCl. This is consistent with the fact that **3a** does not polymerize in the absence of LiCl.^{13,15} We emphasize that the regioregularity of the resulting P3HT decreased only slightly. The above results indicate that the addition of LiCl can significantly enhance the yield of regioregular P3HT. This would be of obvious importance for the mass production of regioregular P3HT for commercial purposes.

To further verify the polymerization of 3a in the presence of 3b, a 50/50 mixture of 3a and 3b was prepared for copolymerization (Scheme 2B). As shown in Figure 3A, similar to the situation of the 16/84 mixture of 3a and 3b, polymerization of 3a also began after 80% 3b had been consumed (Figure 3A). However, GPC profiles become bimodal along with an increase of PDI from \sim 1.3 to \sim 2.0. The peak in the low molecular weight region only moved slightly to lower elution time, and a new peak appeared in the higher molecular weight region. This interesting phenomenon indicates that chain propagation for polymerization of 3a occurs in only some P3HT chains, although all P3HT chains should be living. The conversion of 3a was complete in \sim 30 min, noticeably faster than that of 3a prepared from 4 (about 100 min as shown in Figure 2A). We also conducted the polymerization of the 16/84 mixture of 3a and 3b which was prepared from 1 and 2; the conversion of 3a was also very fast.

Therefore, this difference in the polymerization rate must originate from the difference of the starting materials (4 versus 1 and 2), although the actual reason is not currently clear.

DISCUSSION

According to the polymerization mechanism of 3b proposed by Yokozawa (Scheme 3B),⁷ the initiator 7b is formed by the coupling of Ni(dppp)Cl₂ with 2 equiv of 3b followed by an immediate insertion of Ni into one C-Br bond of the bithiophene with two bromine atoms. Polymerization then proceeds following an intramolecular catalyst transfer polycondensation mechanism. As reported by Luscombe and Kiriy,^{13,15} in the absence of LiCl, the coupling of Ni(dppp)Cl₂ with 3a stopped at the stage of 5a due to the large steric hindrance caused by the hexyl group. As a result, the polymerization of 3a could not proceed. The successful polymerization of 3a with 1 equiv of LiCl in our case implies that the coupling of 5a with 3a and intramolecular catalyst transfer to afford the initiator 7a can proceed smoothly. To validate that the polymerization of 3a follows a mechanism similar to that of 3b (Scheme 3A), the structures of the chain ends of the polymers were characterized by an ¹H NMR spectrometer. An additional P3HT sample was also prepared by polymerizing 3b with an external initiator, i.e.,





Figure 4. Chemical structures of P3HT (A) and ¹H NMR spectra (600 MHz, CDCl₃) of P3HT from polymerization of **3b** with 4% external initiator **10** in the absence of LiCl [(B) structure 1 in (A): $M_n = 3.7 \times 10^3$, PDI = 1.14 by GPC), P3HT from polymerization of **3a** with 10% Ni(dppp)Cl₂ in the presence of LiCl [(C) structure 2 in (A): $M_n = 5.1 \times 10^3$, PDI = 1.48 by GPC), and P3HT after Grignard metathesis of the sample in (C) with ¹BuMgCl [(D) structure 3 in (A). The polymerizations were carried out with [**1**]₀ or [**2**]₀ = 0.1 mol/L. * and # in the spectra indicate ¹³C satellites.

cis-bromo(3-hexyl-2-thienyl)-1,3-bis(diphenylphosphino)propane nickel(II) (**10**), to help in the assignment of the chain ends. According to the polymerization mechanism, the structure of the afforded P3HT should be structure **1** in Figure 4A, and two types of H-terminated chain ends (TH-1 and TH-2) should be observed in the ¹H NMR spectrum of this polymer. As shown in Figure 4B, the two doublets at 7.16 and 6.93 ppm are attributed to H_a and H_b in the TH-1 chain end, according to the assignment of the ¹H NMR signals of the model compounds and P3HT chain ends reported in the literature.^{32,45} The singlet peak at 6.90 ppm is ascribed to H_c in the TH-2 chain end, which is apparent in P3HT prepared by the polymerization of **3b** with



Figure 5. ³¹P NMR spectra (162 MHz, THF) of the polymerization mixture after consumption of 3a (A) and then further stored for 1 h in a N₂ atmosphere (B). The polymerization was carried out at room temperature with 1 equiv of LiCl, 10 mol % Ni(dppp)Cl₂, and $[1]_0 = 0.10$ mol/L.

Ni(dppp)Cl₂ as the catalyst.⁴⁵ Figure 4C is the ¹H NMR spectrum of P3HT prepared by the polymerization of 3a with $Ni(dppp)Cl_2$ in the presence of LiCl. The two doublets at 7.16 and 6.93 ppm, identical to those in Figure 4B, clearly confirm the presence of the TH-1 chain end, which was produced by quenching the active chain ends. It was, however, difficult to identify the characteristic signals corresponding to Br-terminated chain ends formed by HH coupling of 3a (Figure 4A, TB-1 in structure 2). The P3HT sample was treated with excessive ^tBuMgCl and then quenched with dilute HCl to convert the Br-terminated chain ends to H-terminated chain ends following the method proposed by Mccullough.⁸ Figure 4D displays the ¹H NMR spectrum of the resulting polymer. A new doublet appeared at 7.31 ppm which can be ascribed to H_d of the HH coupling chain end TH-3 according to the ¹H NMR spectrum of 3,3'-dihexyl-2,2'-bithiophene (Figure S7). Although another doublet due to the same thiophene unit, which may overlap with other strong signals, could not be distinguished, the presence of this new doublet clearly confirms the occurrence of HH coupling in the initiation stage. Moreover, the integration value of the H_d doublet is close to that of H_a doublet, implying that initiation is dominated by HH coupling of 3a. The catalyst resting state after the polymerization was also monitored by a ³¹P NMR spectrometer. Figure 5A shows the ³¹P NMR spectrum of the reaction mixture with 10 mol % Ni(dppp)Cl₂. Two peaks at 18.84 and -3.25 ppm were observed, indicating that the resting state of the catalyst after polymerization is P3HT-Ni(dppp)Br.³⁸ It is noticeable that no obvious changes were found after 1 h storage in a N₂ atmosphere, as shown in Figure 5B, implying that this

catalyst resting state is relatively stable. This confirms the living characteristic of the polymerization of 3a and indicates that polymer chains are still active after the polymerization. All the above discussion indicates that polymerization of 3a also follows a mechanism similar to that of 3b, as shown in Scheme 3A.

According to Kiriy's recent study, the presence of \sim 3% 3b could cause the polymerization of **3a** in the absence of LiCl.¹⁵ To exclude the effect of the trace amount of 3b on the polymerization, polymerizations of 3a were carried out with the external initiator 10 in the presence and absence of LiCl, respectively, as shown in Scheme 4. In this situation, the effect of a trace amount of 3b can be reduced substantially since the reaction of 3b with 10 still afforded a Ni complex with an alkyl group neighboring -Ni(dppp)Cl. As expected, in the presence of LiCl, the polymerization proceeded smoothly (see Supporting Information). In contrast, no polymer was formed after 6.5 h in the absence of LiCl. Kiriy et al. have also shown that the reverse monomer 3a can not polymerize with Ni(dppp)Cl₂ or Ni(dppe)Cl₂ as the catalyst in the absence of LiCl, since the HH coupling of two 3a molecules leading to the formation of initiator was prohibited. The above results imply that LiCl can promote the HH coupling, leading to the polymerization of 3a.

To further confirm the promotion effect of LiCl on the HH coupling, reactions of 4 equiv of 2-chloromagnesio-3-hexylthiophene (9a) and 1 equiv of Ni(dppp)Cl₂ in the absence and presence of LiCl as shown in Scheme 5A were carried out, and the products were analyzed using gas chromatography (GC). Without LiCl, only 5% 9a was converted to 3,3'-dihexyl-2,2'-bithiophene in 10 min. In contrast, in the presence of LiCl, the conversion of 9a was 33% after the same time. The chemical structure of 3,3'-dihexyl-2,2'-bithiophene was confirmed by the ¹H NMR spectrum. Reactions were also carried out as shown in Scheme 5B for in situ ³¹P NMR characterization. Consistent with Kiriy's observation,^{15,39} without LiCl, only the signals of *cis*chloro-(3-hexyl-2-thienyl)-1,3-bis(diphenylphosphino)propane—nickel(II) (12) (two doublets at 17.68 and -3.97 ppm, J = 63 Hz)

Scheme 4. Polymerizations of 3a with External Initiator 10 in the (A) Absence and (B) Presence of LiCl



along with a small peak corresponding to $Ni(dpp)_2$ were observed (Figure 6A). The complex **12** was stable after 30 min storage (Figure 6B). However, once 1 equiv of LiCl was added, in 10 min, the peaks assigned to **12** almost disappeared, and the signal attributed to $Ni(dppp)_2$ became dominant (Figure 6C). These results clearly confirm the promotion effect of LiCl on the HH coupling.

As shown in Figure 1, the $M_{\rm n}$ of P3HT from the polymerization of 3a is higher than the theoretical value, and the corresponding PDI is relatively large. According to theoretical studies on living polymerization, these phenomena could indicate a slow initiation and fast propagation rate.^{46,47} To explore the characteristics of the polymerization of 3a in the presence of LiCl, the reaction of 2 equiv of Grignard reagent 3a (added 1 equiv by 1 equiv) with 1 equiv of Ni(dppp)Cl₂ was conducted. A similar reaction of 3b was also carried out for comparison. The reaction mixtures were quenched with 5 M HCl for characterization by GC-mass spectroscopy (GC-MS). 1,4-Dipentyloxybenzene was used as a standard, and its concentration was normalized as 100. The relative concentrations of thiophene and bithiophene derivatives are listed in Table 2. Polymers or oligomers with numbers of repeat units ≥ 3 could not be detected by GC/MS in the current experimental condition due to their high boiling points. A small amount of bithiophene byproducts (HThThH and BrTh-ThBr) was also observed. As shown in Table 2, lines A and B show the concentrations of thiophene and bithiophene derivatives in the quenched solutions of the fresh Grignard reagents



Figure 6. ³¹P NMR spectra (162 MHz, THF) of reaction mixture of 4 equiv of **9a** and 1 equiv of Ni(dppp)Cl₂ without the addition of LiCl after reaction for 10 min (A) and 30 min (B) and after the addition of LiCl for 10 min (C). The reactions were carried out at 0 °C with $[9a]_0 = 0.09 \text{ mol/L}$. The signals were assigned according to the literature³⁹ and the ³¹P NMR spectrum of the external initiator **10** (in the same measurement condition, **10** showed two doublets at 19.00 and -3.22 ppm with J = 57 Hz).





and reaction mixtures after the addition of 1 equiv of Grignard reagent, respectively. Over 80% 3b was converted to the initiator 7b (the quenching product is 8b), indicating that the formation of the initiator is a very fast process. However, the reaction behavior of **3a** and Ni(dppp)Cl₂ was remarkably different. Only a small amount of 8a, which is the quenched product of 7a as shown in Scheme 3C, was observed. According to the kinetics study as shown in Figure 1A, the polymerization of 3a is very fast (over in \sim 10 min with 4 mol % catalyst). Kiriy et al. also showed that 3a reacts smoothly with Ni(dppp)Cl₂ to yield 5a.³⁹ Therefore, we postulate that the conversion of 5a to 6a and then to the initiator 7a is much slower than the formation of 5a and the chain propagation process. The reaction results with 2 equiv of Grignard reagent also support above conclusion. Before characterizations, the reaction mixture was stirred for 10 min to ensure 3a was completely consumed. All Ni(dppp)Cl₂ was converted as indicated by its complete dissolution. Meanwhile, in situ ³¹P NMR spectra (Figure S9D) only exhibit signals corresponding to aryl-Ni(dppp)-X (X = Br or Cl). Therefore, 5d was the quenched product of **5a** (Scheme 3C). From the concentration of **5d**, we can estimate that about 60% 3a was consumed by \sim 20% catalyst. These observations indicate that the bithiophene initiator

Table 2. Relative Concentrations of Thiophene and Bithiophene Derivatives in Quenched Solutions of 3a and 3b before (Line A) and after (Lines B and C) Polymerization^{*a*}

	3a				3b			
	5d	HThThH	8a	BrThThBr	5e	HThThH	8b	BrThThBr
А	570	0	0	0	592	0	0	0
B^b	440	0	11	2	102	2	240	2
C^{c}	230	0	4	3	48	3	94	2

^{*a*} Concentration of standard 1,4-dipentyloxybenzene was normalized as 100, and the reaction was carried out at room temperature. ^{*b*} After addition of 1 equiv of Grignard reagent in 1 min. ^{*c*} 10 min after addition of 2 equiv of Grignard reagent.

Scheme 6. Reaction of the External Initiator 10 with Grignard Reagents 9a and 9b



7a rapidly grows to an oligomer or polymer once it is formed, as supported by the presence of high molecular weight products as indicated by GPC measurements (Figure S8). Moreover, no signals corresponding to **6a** were observed in ³¹P NMR spectra (Figure S9). This phenomenon together with the fact that most **5a** remained and only a small amount of **8a** was observed indicates that the TM step leading to **6a** is the rate-limiting step in the formation of the initiator **7a**.

To further confirm the slow initiation and fast propagation characteristics of the polymerization of 3a, the reaction of the external initiator 10 with a mixture of 9a (5 equiv) and 2chloromagnesio-4-hexylthiophene (9b, 5 equiv) was carried out in the presence of 1 equiv of LiCl, and the resulting product was analyzed (Scheme 6, for experimental details please see Supporting Information). Two bithiophene derivatives, i.e., 3,4'-dihexyl-2,2'-bithiophene (11b) and 3,3'-dihexyl-2,2'-bithiophene (11a), with a ratio of 15:1 (11b:11a) were found. This implies that the propagation rate is an order of magnitude faster than the initiation rate in the polymerization of 3a. According to the theoretical studies on living polymerizations,^{46,47} initiator not involved in the polymerization and PDI can be estimated from the ratio of initiation and propagation rates, the ratio of monomer and initiator, and the conversion of the monomer. In the polymerization as shown in Scheme 1A, it was estimated that about 20% initiator remained after the polymerization. However, the theory assumes that initiator is soluble in the solvent, and in the current system the formation of the initiator involves a dissolution process of the catalyst since the solubility of $Ni(dppp)Cl_2$ in THF is poor. Therefore, the catalyst which was not involved in the polymerization should be more than 20%, leading to a $M_{\rm p}$ that is \sim 2 times of the theoretical value. According to the theory, 46,47 the PDI of P3HT should be in the range of 1.3-1.4, slightly lower than the observed value.

On the basis of above discussion, we can conclude that LiCl can promote the coupling of **3a** to form HH bithiophene initiator **7a** for polymerization (Scheme 3A). However, this process is much slower than chain propagation due to the large steric hindrance between the two hexyl groups in HH coupling. Therefore, the number of active chains in the polymerization process was not constant, resulting in the large PDI and non-linear increase of M_n versus conversion of **3a** and [converted **3a**]/[Ni(dppp)Cl₂] (Figure 1A,B). The low molecular weight tail was also observed as shown in Figure 1C due to a slow initiation relative to propagation. Moreover, molecular weight was higher than the theoretical value since not all catalyst was involved in the polymerization. The KCTP with slow initiation

Scheme 7. Proposed Mechanism of the Copolymerization of 3a and 3b in the Presence of 1 equiv of LiCl



was also observed recently by MeNeil et al. in the polymerization of 1-bromo-4-chloromagnesio-2,5-dihexyloxybenzene with Ni- $(depe)Cl_2$ (depe =1,3-bis(diethylphosphino)ethane) as the catalyst.¹⁷ On the basis of ³¹P NMR studies, they proposed that the slow initiation was caused by the slow reductive elimination of a symmetric biaryl Ni complex, which is the precursor to form the initiator via intramolecular catalyst transfer. However, in the current paper, the slow initiation in the polymerization of 3a is attributed to the slow TM step for the formation of intermediate 6a due to the large steric hindrance (reductive elimination of 6a and subsequent intramolecular catalyst transfer lead to bithiophene initiator 7a). Kiriy et al. also observed the slow initiation phenomenon in the polymerization of 3a (containing $\sim 3\%$ 3b) with Ni(dppp)Cl₂ or Ni(dppe)Cl₂ as the catalyst in the absence of LiCl.¹⁵ However, the mechanism is different. In their system, the slow formation of the initiator 7d (as shown in Scheme 7) is due to the low concentration of 3b.

The copolymerizations of 3a and 3b are more complicate since four possible initiators (7a-d) may be involved, as shown in Scheme 7. In order to qualitatively elucidate the probability of the formation of these initiators, a model reaction as shown in Scheme 8 was carried out. Ni(dppp)Cl₂ (1 equiv) was reacted with a mixture of 9a (5 equiv) and 9b (5 equiv), and the resulting products were analyzed by GC-MS and ¹H NMR. Three bithiophene derivatives (11a-c) were found in a ratio of 1:14:29 (11a:11b:11c) by GC-MS and 1:13:26 (11a:11b:11c) by ¹H





NMR (Figure S10). This indicates HH coupling is unfavorable in the coupling process. Therefore, in the copolymerization, initiator 7a is formed in very limited amount while initiator 7b is the most abundant. Head-to-tail (HT) and tail-to-head (TH) coupling can afford both 7c and 7d due to the random ringwalking process.¹⁴ 7c should exhibit similar polymerization activity to 7b. Both 7b and 7c prefer chain propagation with 3b due to the large steric hindrance between two hexyl groups in the HH coupling. 7a and 7d should be able to initiate the polymerization of both 3a and 3b. However, the overall amount of 7a and 7d should be much less than that of 7b and 7c. In addition, once 3b is coupled with 7a and 7d, the resulting active centers are the same as those of 7c and 7b. Therefore, growing chain ends become identical in a short time, and the polymerization proceeds predominantly with monomer 3b in the early stage of the copolymerization. With the decrease of the concentration of 3b, 3a begins to take part in chain growth, leading to the formation of HH coupling. This HH coupling is similar to the formation of the initiator 7a and is a slow process. However, once the polymer chain terminated with 3a unit is formed, this new active chain can initiate the polymerization of 3a to afford block copolymer. Since HH coupling is slow and chain propagation is fast, only part of the P3HT chains from 3b can grow to block copolymers. Therefore, as shown in Figures 2D and 3D, the shoulder peak for the 16/84 mixture of 3a and 3b and the new peak for the 50/50mixture of 3a and 3b in the high molecular weight region of the GPC profiles are attributed to the diblock copolymers comprising poly(3a) and poly(3b) blocks, and the peaks in the low molecular weight region should be ascribed to the 3b-dominated polymers.

To provide more evidence for the aforementioned block copolymerization mechanism, the copolymerization of 14 and 3a was conducted (Scheme 9). As expected, the copolymerization of monomer 14 (synthesized by Grignard metathesis of

Scheme 9. Copolymerization of 3a and 14 in the Presence of 1 equiv of LiCl



Figure 7. (A) GPC profiles of copolymerization mixture of 14 and 3a ($M_n = 1.1 \times 10^4$, PDI = 2.38) and its two fractions (poly(14)-*b*-poly(3a): $M_n = 2.1 \times 10^4$, PDI = 1.55; poly(14): $M_n = 4.8 \times 10^3$, PDI = 1.21). (B) MALDI-TOF mass spectrum of poly(14); the inset is the expanded spectrum. The polymerization was carried out at room temperature with 1 equiv of LiCl and 2 mol % Ni(dppp)Cl₂ to the sum of 13 and 1. [1]₀ = [13]₀ = 0.05 mol/L.

'PrMgCl and 13) and 3a gave a polymer with a bimodal GPC profile (Figure 7A), identical to that of the copolymerization of 3a and 3b as shown in Figure 3D. Moreover, the polymerization of 3a began at \sim 30 min, after 14 was almost consumed (Figure S11). The slow polymerization of 14 can be ascribed to the larger steric hindrance of ethylhexyl than hexyl. According to the mechanism shown in Scheme 7, the peaks at the shorter and longer elution time in Figure 7A should correspond to the block copolymer and monomer 14-dominated polymer, respectively, which are named as poly(14)-*b*-poly(3a) and poly(14). The branched alkyl group (ethylhexyl) endows poly(14) good solubility in petroleum ether (PE). In contrast, poly(14)-b-poly(3a) exhibits poor solubility in this solvent due to the strong intermolecular interaction of poly(3a) or P3HT block. Therefore, poly(14)-b-poly(3a) and poly(14) can be easily separated by washing the copolymerization mixture with PE, as shown in Figure 7A.

The separated poly(14)-*b*-poly(3a) and poly(14) were characterized by an ¹H NMR spectrometer. As shown in Figure S12, the ratio of poly(14) and poly(3a) blocks in poly(14)-b-poly-(3a) is 23:77, and poly(14) is indeed dominated by monomer 14. Poly(14) was further characterized by MALDI-TOF mass spectrometer (Figure 7B). There are five series of peaks. For easy analysis, the spectrum was expanded with a group of peaks including one from each series. The peak with molecular weight of 3967.6 is corresponding to H/Br end-capped poly(14) $(194.35 \times 20 + 1 + 79.9 = 3967.9)$, and the other four peaks with molecular weight of 3939.1, 3911.3, 3883.4, and 3855.6 can be attributed to H/Br end-capped polymers consisting of poly-(14) and one to four 3a units $(194.35 \times 19 + 166.3 + 1 + 79.9 =$ 3939.9, 194.35 × 18 + 166.3 × 2 + 1 + 79.9 = 3911.8, 194.35 × $17 + 166.3 \times 3 + 1 + 79.9 = 3883.8$ and $194.35 \times 16 + 166.3 \times 10^{-1}$ 4 + 1 + 79.9 = 3855.7), respectively. The ¹H NMR spectrum of poly(14)-b-poly(3a) indicates the presence of an H-end from 3a (Figure S13A). However, this type of chain-end was not observed in the ¹H NMR spectrum of poly(14) (Figure S13B), implying that a small amount of 3a (~5%) in poly(14) is incorporated in the initiation step or the polymerization process via HT or TH coupling process. This is consistent with the proposed mechanism shown in Scheme 7, and thus the bimodal GPC profile resulted from the slow initiation-fast chain propagation KCTP of the reversed monomer 3a instead of the termination of poly(14) chain. In fact, when another portion of 14 was added after the copolymerization of 14 and 3a (see Supporting Information), the GPC peak with longer elution time (corresponding to poly(14)) shifted to the high molecular weight region (Figure S14), indicating the living nature of the polymer chain.

CONCLUSION

Literature studies of the KCTP of 5-bromo-2-chloromagnesio-3-hexylthiophene (**3a**) showed that this "reversed" monomer does not polymerize due to the difficulty of the formation of the bithiophene initiator. Our current study indicates that LiCl can promote the formation of the initiator permitting the polymerization of **3a** and that the polymerization exhibits living characteristics. However, the formation of the initiator is much slower due to the large steric hindrance between hexyl groups at the TM step, leading to a slow initiation—fast chain propagation polymerization process. As a result, the PDI of the obtained polymer is rather large, and the molecular weight is higher than the theoretical value. In the copolymerization of **3a** and **3b**, the polymerization of **3a** occurs primarily after the consumption of **3b**, yielding fully conjugated block copolymers. This finding further deepens the understanding of KCTP.

ASSOCIATED CONTENT

Supporting Information. All experimental details, GPC profiles of the polymerization mixture of **3a** and **3b** with 50 mol % catalyst, ¹H NMR spectra of Grignard reagents and 3,3'-dihexyl-2,2'-bithiophene, conversion versus time for the copolymerization of **14** and **3a**, and ¹H NMR spectra of the resulting polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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