

**LiCl-Promoted Chain Growth Kumada Catalyst-Transfer Polycondensation of  
the “Reversed” Thiophene Monomer**

Shupeng Wu,<sup>a,b</sup> Li Huang,<sup>a,b</sup> Hongkun Tian,<sup>a</sup> Yanhou Geng,<sup>\*a</sup> and Fosong Wang<sup>a</sup>

*<sup>a</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied  
Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. <sup>b</sup>Graduate  
School of Chinese Academy of Sciences, Beijing 100049, P. R. China*

E-mail: yhgeng@ciac.jl.cn

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## 1. Materials.

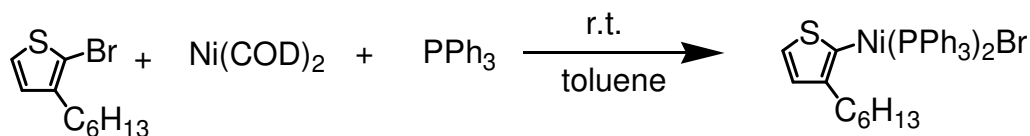
Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Isopropylmagnesium chloride (*i*PrMgCl, 2.0 M solution in THF, Acros), *t*-butylmagnesium chloride (*t*BuMgCl, 1.7 M solution in THF, Acros), Ni(dppp)Cl<sub>2</sub>, (Pacific ChemSource, Inc., Zhengzhou, China, 98%) were used as received. 1,4-Dipentyloxybenzene,<sup>1</sup> 5-bromo-3-hexyl-2-iodothiophene (**1**),<sup>2</sup> 2-bromo-3-hexyl-5-iodothiophene (**2**),<sup>3</sup> 2,5-dibromo-3-hexylthiophene (**4**)<sup>4</sup> and 2-bromo-3-(2-ethylhexyl)-5-iodothiophene (**13**)<sup>5</sup> were synthesized according to the references. Their purities are all above 99.5% according to gas chromatography (GC) measurements.

## 2. Instrumentation.

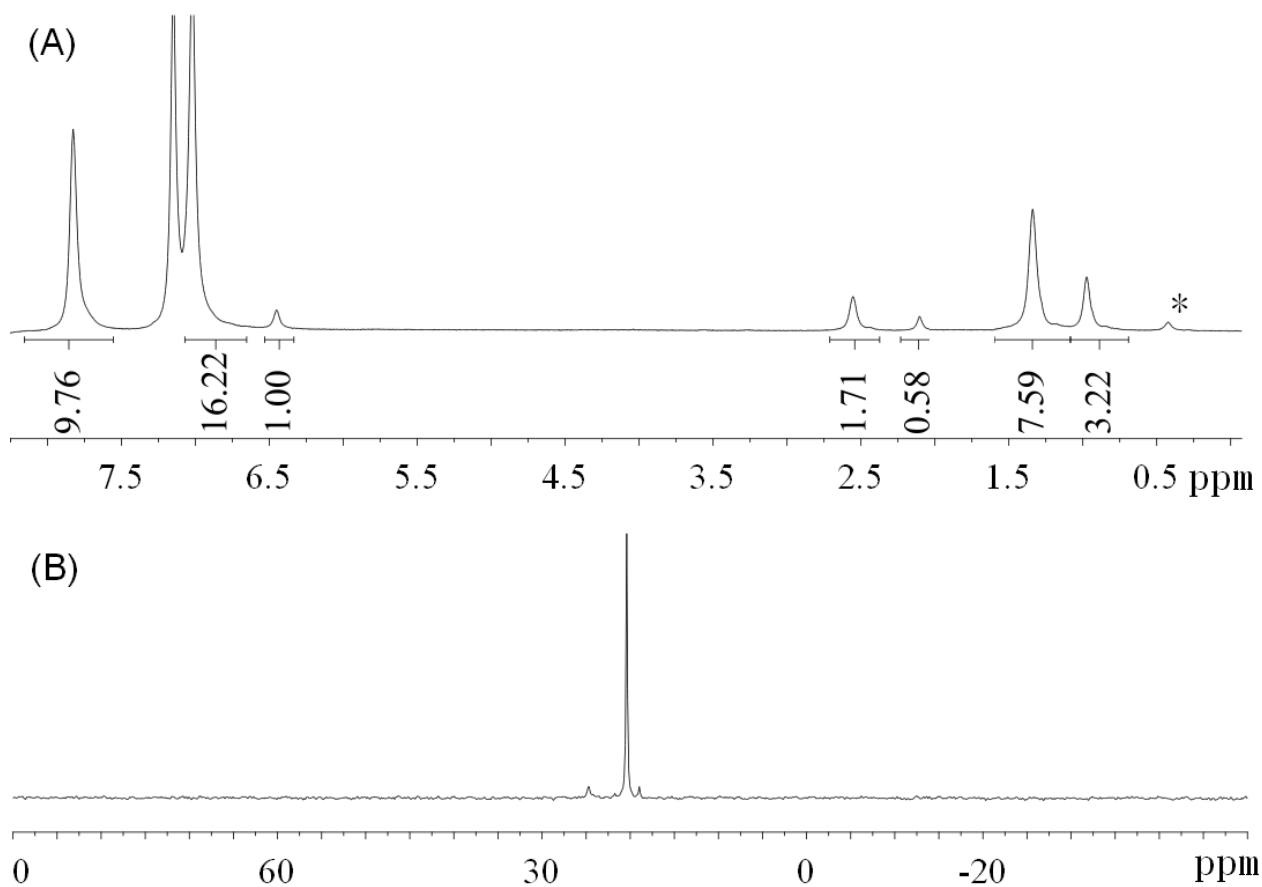
Unless otherwise noted, <sup>1</sup>H NMR spectra were recorded on Bruker AV 300, AV 400 or AV 600 spectrometer (CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal reference was used as the solvent except specified otherwise), and <sup>31</sup>P NMR spectra were recorded on Bruker AV 400 spectrometer at 162 MHz with H<sub>3</sub>PO<sub>4</sub> (85% aq) as an external reference. GC and GC-mass spectroscopy (GC-MS) measurements were carried out on a SHIMADZU GC-14C instrument equipped with an OV-1701 column and an Agilent 5975/6890N GC-MS instrument equipped with an Agilent HP-5 column (30 m), respectively, with 1,4-dipentyloxybenzene as an internal reference. Gel-permeation chromatography (GPC) analysis was conducted on a Waters 2414 system equipped with Waters HT4 and HT3 column-assembly and a Waters 2414 refractive index detector (eluent: THF; flow rate: 1.00 ml/min; temperature: 40 °C; standard: polystyrene). Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) was performed using a Bruker Autoflex III Smartbeam MALDI Mass Spectrometer using linear mode in the absence of cationizing salt. Polymer/matrix solution was prepared by mixing 5 μL of polymer solution (2 mg/mL in CHCl<sub>3</sub>) and 5 μL of terthiophene solution (20 mg/mL in CHCl<sub>3</sub>). The solution 1 μL was dropped on a 384 ground steel target, vaporized and ionized using a nitrogen laser operating at 337 nm for MALDI-TOF analysis. The accelerating voltage, low mass gate and sampling rate were 20 kV, 600.0 Da and 1.0 GHz, respectively. All spectra were collected from 1000 laser pulses fired at 5 different positions.

3. Synthesis and characterizations of external initiator *cis*-bromo-(3-hexyl-2-thienyl)-1,3-bis(diphenylphosphino)propane nickel (II) (**10**):

***trans*-Bromo-(3-hexyl-2-thienyl)bis(triphenylphosphine)nickel (II).**

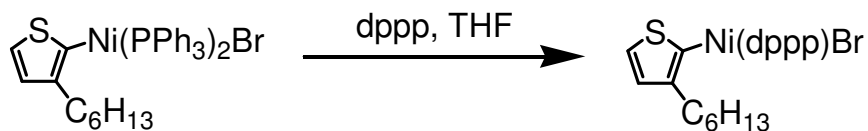


In the glovebox,  $\text{Ni(COD)}_2$  (0.375 g, 1.36 mmol) and triphenylphosphine ( $\text{PPh}_3$ ) (0.717 g, 2.73 mmol) were dissolved in toluene (10 mL) in a thoroughly dried flask equipped with a stir bar. 2-bromo-3-hexylthiophene (551 mg, 2.25 mmol) in toluene was added and the reaction was stirred for 60 min at room temperature. Then most toluene was removed under reduced pressure and stored overnight, the resultant red precipitate was collected via filtration and washed with hexanes. After removing most toluene of filtrate, hexanes (2 equiv – 3 equiv of the volume of filtrate) was added and the resultant precipitate was collected via filtration and washed with hexane to yield product as a red powder (637 mg, 56% yield).

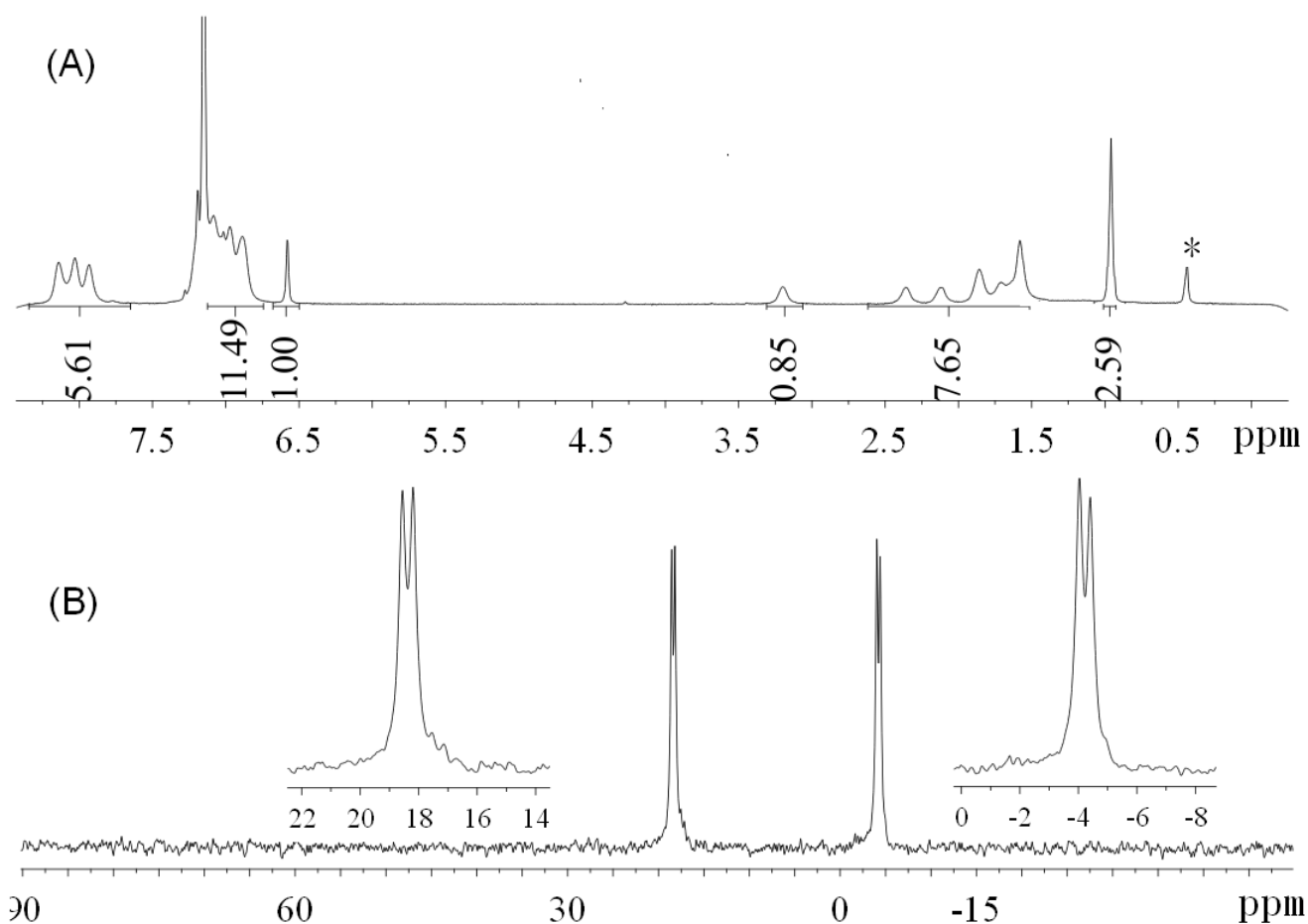


**Figure S1.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ) and  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ) spectra of *trans*-bromo-(3-hexyl-2-thienyl) bis(triphenylphosphine)nickel (II). (\* indicates the signal of water)

***cis*-bromo-(3-hexyl-2-thienyl)-1,3-bis(diphenylphosphino)propane nickel (II) (10):**



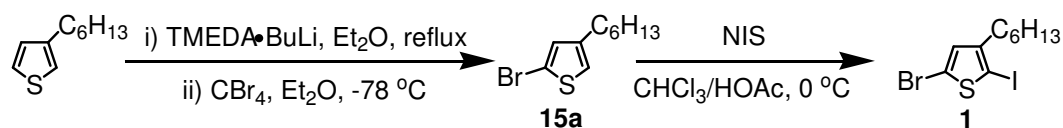
In the glovebox, *trans*-bromo-(3-hexyl-2-thienyl)bis(triphenylphosphine)nickel (II) (327 mg, 0.39 mmol, 1.00 equiv) was dissolved in THF (10 mL) in a thoroughly dried flask equipped with a stir bar. Then 1,3-bis(diphenylphosphino)propane (dppp) (181 mg, 0.43 mmol, 1.10 equiv) was added and the reaction was stirred for 1.5 h at room temperature, then hexane was added and the resultant precipitate was isolated via filtration. The powder was then washed with hexane, dried in vacuum to yield product as orange power (170 mg, 60%).



**Figure S2.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) and <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>) spectra of *cis*-bromo-(3-hexyl-2-thienyl)-1,3-bis(diphenylphosphino)propane nickel (II). (\* indicates the signal of water)

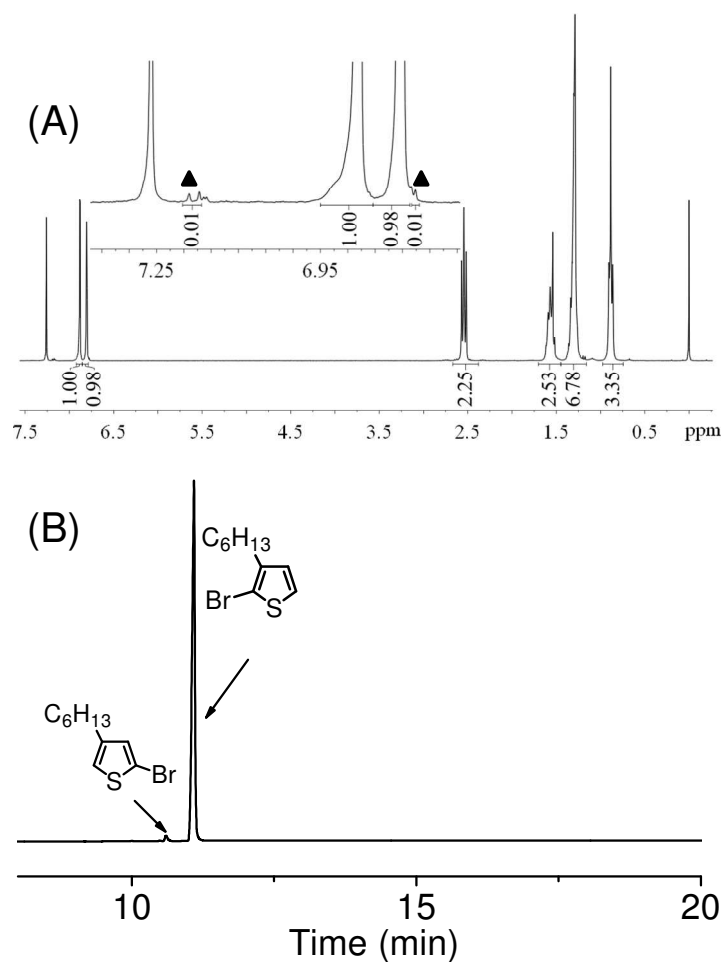
#### 4. Synthesis and purity of 5-bromo-3-hexyl-2-iodothiophene (**1**):

The compound **1** was prepared according to the reference 2 as follows:



#### Synthesis and purity of 2-bromo-4-hexylthiophene (**15a**):

Under Ar atmosphere, 2.5 M *n*-BuLi (35.7 mL, 89.2 mmol) was added to tetramethylethylenediamine (TMEDA) (13.2 g, 93.3 mmol) in anhydrous Et<sub>2</sub>O (150 mL) at -78 °C. After stirred at 0 °C for 1 h, the mixture was added dropwise to 3-hexylthiophene (13.7 g, 81.1 mmol) in anhydrous Et<sub>2</sub>O (80 mL) at such a rate that slow reflux is maintained. Then the mixture was refluxed for 30 min and then cooled to -78 °C. A solution of carbon tetrabromide (18.2 g, 55.2 mmol) in anhydrous Et<sub>2</sub>O (30 mL) was added dropwise and the mixture stirred for 2.5 h at -78 °C. The mixture was then poured into a large amount of NH<sub>4</sub>Cl aqueous solution for extraction with petroleum ether (PE). The organic extracts were washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution and brine, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the resulting liquid was passed through a plug of silica with PE as eluent. The resulting light yellow liquid was purified via vacuum distillation for twice to afford colorless liquid (8.1 g, 40%). According to <sup>1</sup>H NMR (Figure S3A) and GC (Figure S3B) measurements, the content of 2-bromo-3-hexylthiophene (**15b**) in **15a** was estimated to be 1.0% and the purity of **15a** was 99.0%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.88 (d, *J* = 1.7 Hz, 1H), 6.80 (d, *J* = 1.7 Hz, 1H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.61-1.51 (m, 2H), 1.39-1.30 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H).



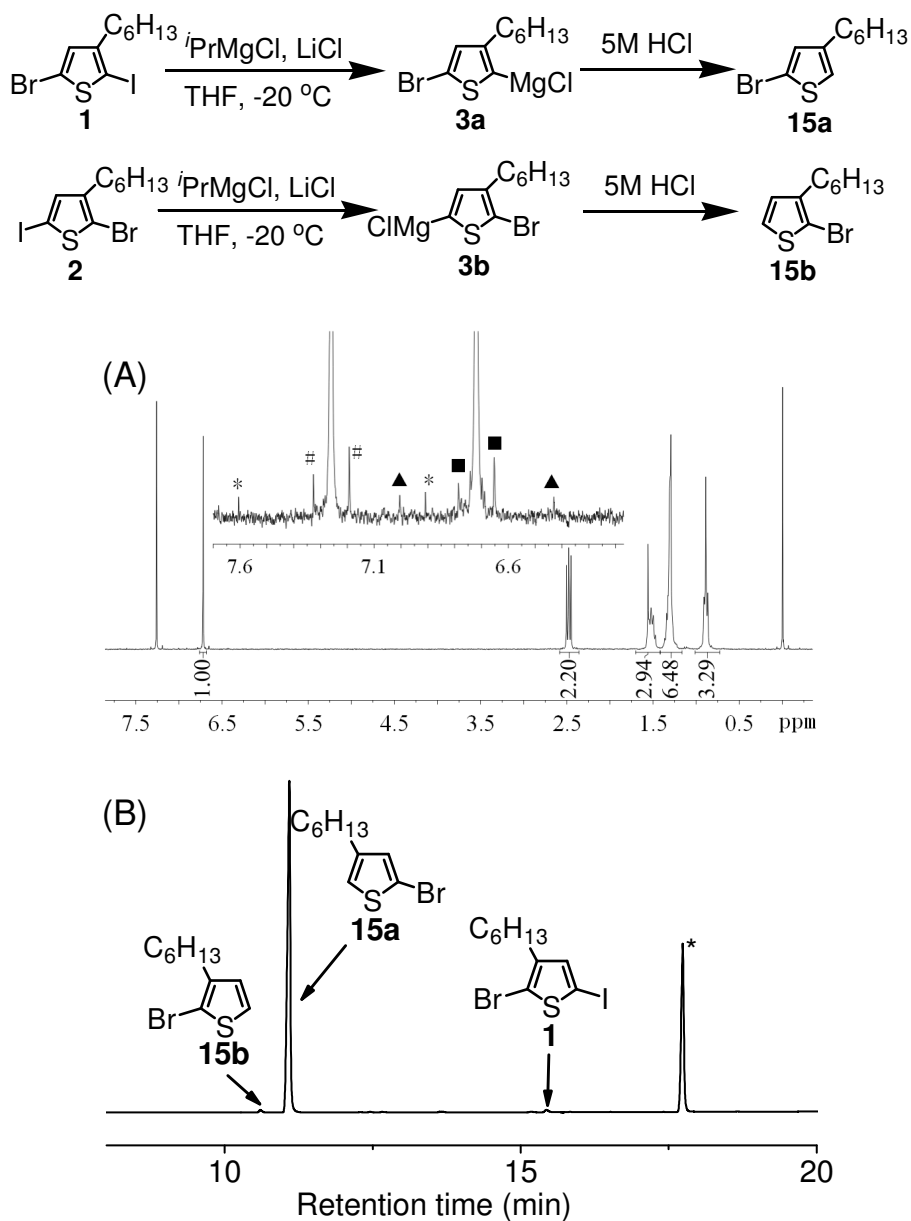
**Figure S3.** (A)  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of 2-bromo-4-hexylthiophene ( $\blacktriangle$  is the signal corresponding to 2-bromo-3-hexylthiophene). (B) GC curve of **15a**, the ratio of **15b** : **15a** is 1.0:100.

#### Synthesis and purity of 5-bromo-3-hexyl-2-iodothiophene (**1**):

2-bromo-4-hexylthiophene (7.6 g, 32.4 mmol) was dissolved in a mixture of  $\text{CHCl}_3$  (100 mL) and HOAc (100 mL). N-iodosuccinimide (7.2 g, 34.0 mmol) was added to the solution at  $0^\circ\text{C}$  over a period of 2.5 h. The solution was stirred at room temperature overnight in absence of light. The reaction mixture was poured into large amount of  $\text{Na}_2\text{S}_2\text{O}_3$  aqueous solution for extraction with  $\text{CH}_2\text{Cl}_2$ . The organic extracts were washed with brine and dried over anhydrous  $\text{MgSO}_4$ . After concentrated, the residue was purified by distillation twice to obtain the product as colorless liquid (9.2 g, 81%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.72 (s, 1H), 2.48 (t,  $J$  = 7.2 Hz, 2H), 1.55-1.48 (m, 2H), 1.39-1.30 (m, 6H), 0.89 (t,  $J$  = 6.9 Hz, 3H).

We found that the trace amount of **2** in **1** could not be determined by  $^1\text{H}$  NMR spectrometer (Figure S4A). Meanwhile, **1** and **2** exhibited the same retention time in our GC measurements. However, after Grignard

metathesis, quenched products **15a** and **15b** could be distinguished, as shown in Figure S4B. Then the content of **2** in **1** was estimated to be 0.5% and the purity of **1** was 99.5%.



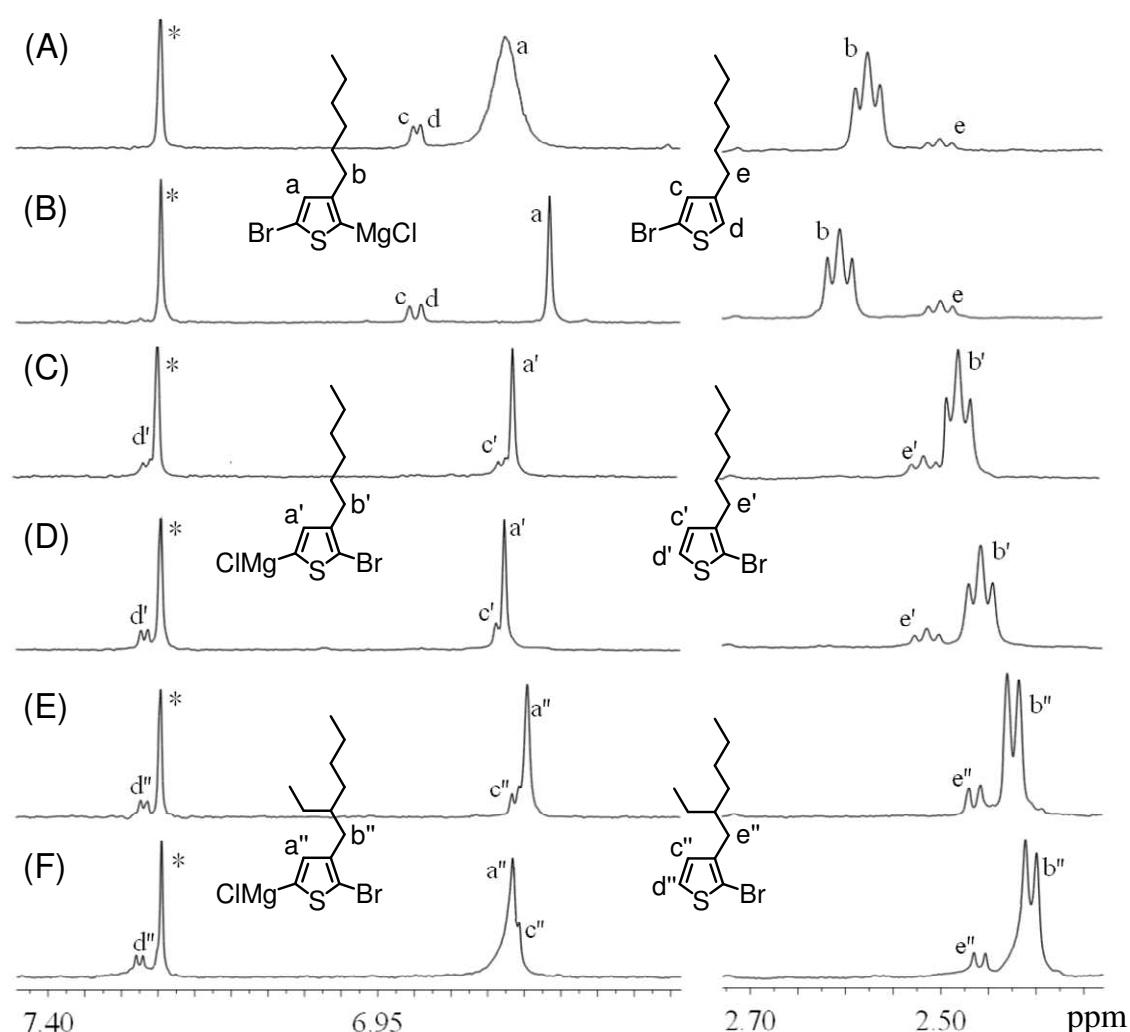
**Figure S4.** (A)  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of **1** ( $\blacktriangle$ ,  $\blacksquare$ ,  $*$  and  $\#$  indicate  $^{13}\text{C}$  satellites). (B) GC curve of the product from Grignard metathesis of **1** after quenching by aqueous HCl, the ratio of **15b** (from **3b**):**15a** (from **3a**) is 0.5:100. ( $*$  is ascribed to the internal standard 1,4-dipentyloxybenzene)



5. In-situ  $^1\text{H}$  NMR spectra of 5-bromo-2-chloromagnesio-3-hexylthiophene (**3a**), 2-bromo-5-chloromagnesio-3-hexylthiophene(**3b**), and 2-bromo-5-chloromagnesio-3-(2-ethylhexyl)thiophene (**14**)

Since in-situ  $^1\text{H}$  NMR characterizations of **3a**, **3b** and **14** were conducted in the same manner, only the characterization of **3a** is depicted as follows.

In a thoroughly dried Schlenk tube,  $i\text{PrMgCl}$  (0.05 mL, 0.10 mmol) was added into a mixture of **1** (37.3 mg, 0.10 mmol), LiCl (4.2 mg, 0.10 mmol) (or without LiCl) and dry THF (1 mL). After stirred at  $-20\text{ }^\circ\text{C}$  for 1 h, 0.6 mL solution was withdrawn and injected into a NMR tube with a capillary column containing  $\text{C}_6\text{D}_6$  for shimming and a capillary column with benzene dissolved in THF (10 mg/mL) as an external reference.



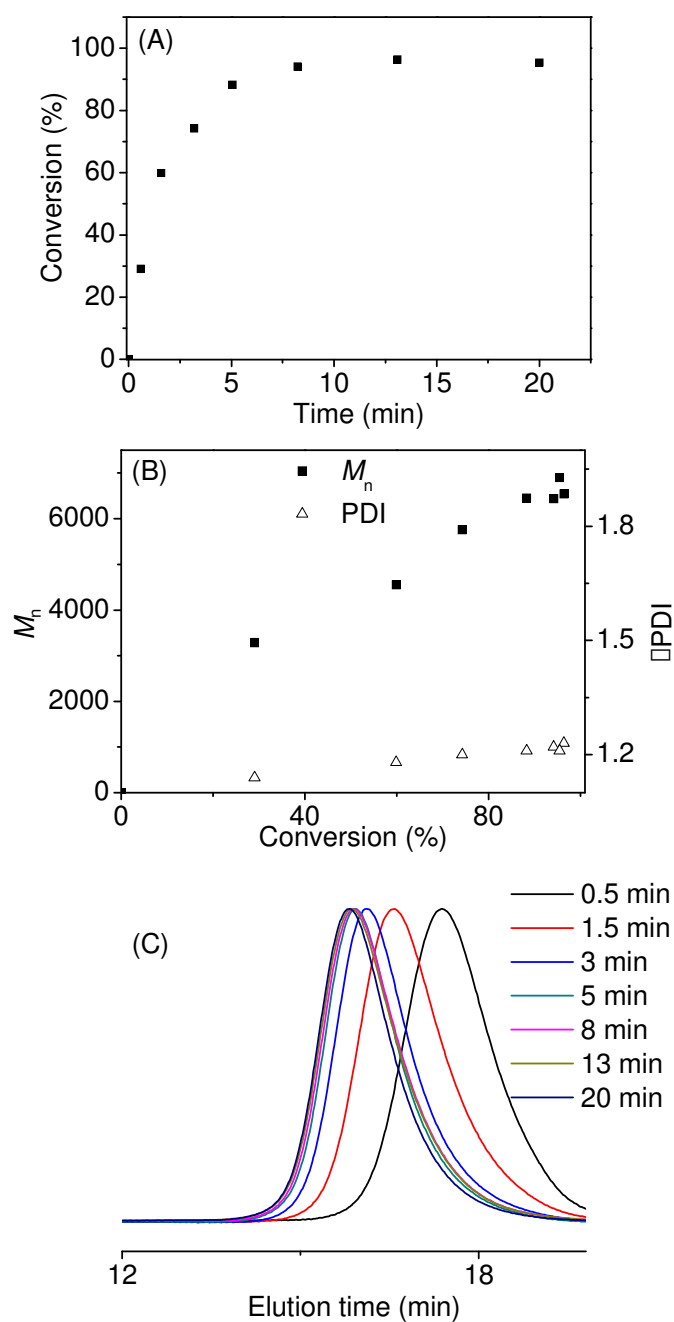
**Figure S5.**  $^1\text{H}$  NMR spectra (600 MHz, THF) of **3a** (A and B), **3b** (C and D) and **14** (E and F) in the absence (A, C and E) and presence (B, D and F) of LiCl. (\*) is the signal of benzene as external reference)

## 6. Polymerization of **3a** in the presence of LiCl.

Since polymerizations of **3a** and **3b** were conducted in the same manner, only the polymerization of **3a** is depicted as follows.

In a thoroughly dried Schlenk tube,  $i\text{PrMgCl}$  (0.50 mL, 1.00 mmol) was added into a mixture of **1** (373 mg, 1.00 mmol), LiCl (42 mg, 1.00 mmol), 1,4-dipentyloxybenzene (internal standard for GC analysis, 40 mg, 0.16 mmol) and dry THF (7 mL). After stirred at  $-20\text{ }^{\circ}\text{C}$  for 1 h, 0.4 mL solution was withdrawn for GC analysis (conversion of **1** was 94%). Then a suspension of  $\text{Ni(dppp)Cl}_2$  (21.7 mg, 0.04 mmol) in dry THF (3 mL) was added for polymerization at room temperature. After 50 min (95% of Grignard reagent **3a** was consumed), the polymerization was quenched by adding 5 M HCl aqueous solution. The mixture was extracted with  $\text{CHCl}_3$ , and the organic extracts were washed with brine, dried over anhydrous  $\text{MgSO}_4$ . After concentrated under reduced pressure, the solution was dropped into methanol for precipitation. The solid was filtered and dried to give **P3HT** ( $M_n = 1.3 \times 10^4$ , PDI = 1.50) as a dark purple solid (135 mg, 81%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.98 (s, T), 2.83-2.50 (m, Th-  $\text{CH}_2\text{C}_5\text{H}_{11}$ ), 1.76-1.66 (m, Th- $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$ ), 1.46-1.28 (m, Th- $\text{C}_2\text{H}_4\text{C}_3\text{H}_6\text{CH}_3$ ), 0.94-0.89 (t,  $J = 6.6\text{ Hz}$ , Th- $\text{C}_5\text{H}_{10}\text{CH}_3$ ).

7. Polymerizations of **3b** in the presence of LiCl.

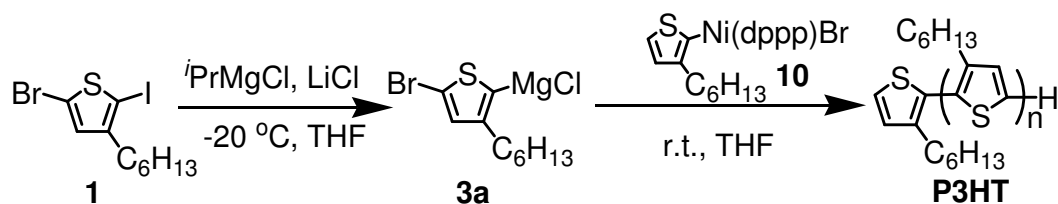


**Figure S6.** (A) Conversion-time curves of polymerization of **3b** in the presence of LiCl. (B)  $M_n$  and polydispersity (PDI) as a function of the conversion of **3b** in the presence of LiCl. (C) Gel-permeation chromatography (GPC) elution curves of **P3HT** at different polymerization time in the presence of LiCl. The polymerization was carried out at room temperature with 4 mol% Ni(dppp)Cl<sub>2</sub>. [**2**]<sub>0</sub> = 0.10 mol/L.

#### 8. Copolymerization of **3a** and **3b** in the presence of LiCl.

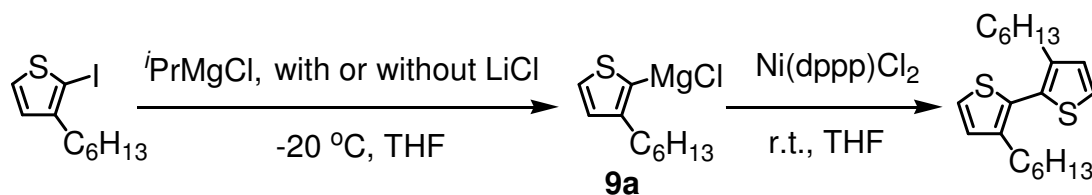
In a thoroughly dried Schlenk tube,  $t$ BuMgCl (2.9 mL, 5.00 mmol) was added into a mixture of **4** (1.63 g, 5.00 mmol), LiCl (212 mg, 5.00 mmol), 1,4-dipentyloxybenzene (internal standard for GC analysis, 200 mg, 0.80 mmol) and dry THF (40 mL). After stirred at room temperature for 24 h, 0.4 mL solution was withdrawn for GC analysis (conversion of **4** was quantitative, **3a/3b** = 16/84). Then a suspension of Ni(dppp)Cl<sub>2</sub> (108 mg, 0.20 mmol) in dry THF (10 mL) was added. After 45 min (conversions of **3a** and **3b** were 83% and 93%, respectively), the polymerization was quenched by adding 5 M HCl aqueous solution. The mixture was extracted with CHCl<sub>3</sub>, and the organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>. After concentrated under reduced pressure, the solution was dropped into methanol for precipitation. The solid was filtered and dried to give **P3HT** ( $M_n = 6.4 \times 10^3$ , PDI = 1.27) as a dark purple solid (638 mg, 85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.98 (s, Th-**H**), 2.83-2.50 (m, Th- **CH**<sub>2</sub>C<sub>5</sub>H<sub>11</sub>), 1.76-1.66 (m, Th-CH<sub>2</sub>**CH**<sub>2</sub>C<sub>4</sub>H<sub>9</sub>), 1.46-1.28 (m, Th-C<sub>2</sub>H<sub>4</sub>C<sub>3</sub>**H**<sub>6</sub>CH<sub>3</sub>), 0.94-0.89 (t,  $J = 6.6$  Hz, Th-C<sub>5</sub>H<sub>10</sub>**CH**<sub>3</sub>). 50/50 mixture of **3a** and **3b** was prepared by magnesium-halogen exchange reaction of 50/50 mixture of **1** and **2** with  $i$ PrMgCl.

9. Polymerization of **3a** with external initiator **10**:



In a thoroughly dried Schlenk tube,  $i\text{PrMgCl}$  (0.50 mL, 1.00 mmol) was added into a mixture of **1** (373 mg, 1.00 mmol),  $\text{LiCl}$  (42 mg, 1.00 mmol), 1,4-dipentyloxybenzene (internal standard for GC analysis, 40 mg, 0.16 mmol) and dry THF (7 mL). After stirred at  $-20\text{ }^{\circ}\text{C}$  for 1 h, the solution was allowed to warm to room temperature and 0.4 mL solution was withdrawn for GC analysis (the conversion of **1** was 94%). Then a solution of external initiator **10** (28.2 mg, 0.04 mmol) in dry THF (3 mL) was added. After reacted at room temperature for 80 min (91% of **3a** was consumed), the polymerization was quenched by adding 5 M  $\text{HCl}$  aqueous solution. The mixture was extracted with  $\text{CHCl}_3$ , and the organic extracts were washed with brine, dried over anhydrous  $\text{MgSO}_4$ . After concentrated under reduced pressure, the solution was dropped into methanol for precipitation. The solid was filtered and dried to give **P3HT** ( $M_n = 9.7 \times 10^3$ , PDI = 1.74) as a dark purple solid (103 mg, 71%).

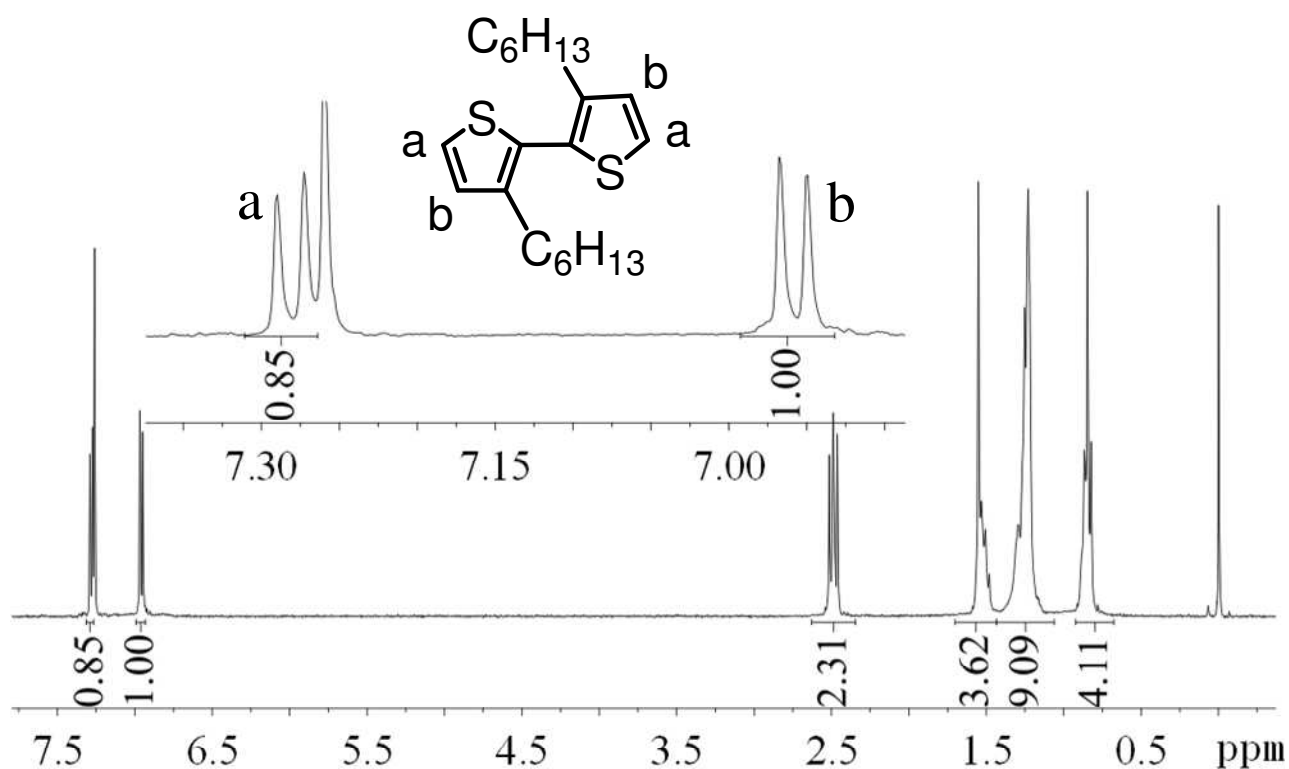
10. The model reaction of HH coupling with and without LiCl:



**Without LiCl:** In a thoroughly dried Schlenk tube, *i*PrMgCl (0.50 mL, 1.00 mmol) was added into a mixture of 3-hexyl-2-iodothiophene (294 mg, 1.00 mmol), 1,4-dihexyloxybenzene (internal standard for GC analysis, 80 mg, 0.29 mmol) and dry THF (7 mL), after stirring at -20 °C for 1 h, 0.3 mL solution was withdrawn for GC analysis (conversion = 100%). At room temperature, Ni(dppp)Cl<sub>2</sub> (136 mg, 0.25 mmol) in dry THF (5 mL) was added. During reaction, 1.0 mL solution was withdrawn in 2 times at 10.0 min (5%) and 30.0 min (5%). After 90 min, the reaction was quenched by addition of 5 M HCl aqueous solution. The mixture was extracted with petroleum ether (PE), and the organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>, the conversion was 6% according to GC measurement.

**With LiCl:** In a thoroughly dried Schlenk tube, *i*PrMgCl (0.50 mL, 1.00 mmol) was added into a mixture of 3-hexyl-2-iodothiophene (294 mg, 1.00 mmol), LiCl (42.4 mg, 1.00 mmol), 1,4-dihexyloxybenzene (internal standard for GC analysis, 80 mg, 0.29 mmol) and dry THF (7 mL), after stirring at -20 °C for 1 h, 0.3 mL solution was withdrawn for GC analysis (conversion = 100%). At room temperature, Ni(dppp)Cl<sub>2</sub> (136 mg, 0.25 mmol) in dry THF (5 mL) was added. During reaction, 2.0 mL solution was withdrawn in 4 times at 0.5 min (5%), 2.0 min (20%), 5.0 min (32%) and 10.0 min (33%). After 30 min, the reaction was quenched by addition of 5 M HCl aqueous solution. The mixture was extracted with PE, and the organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>, the conversion was 34% according to GC measurement. After concentrated under reduced pressure, purification by chromatography over SiO<sub>2</sub> with PE as an eluent afforded product as colorless liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J* = 5.3 Hz, 2H), 6.96 (d, *J* = 5.2 Hz, 2H), 2.49 (t, *J* = 7.5 Hz, 4H), 1.55–1.48 (m, 4H), 1.30–1.23 (m, 12H), 0.85 (t, *J* = 6.3, 6H).

$^1\text{H}$  NMR spectrum of 3,3'-dihexyl-2,2'-bithiophene:



**Figure S7.**  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of 3,3'-dihexyl-2,2'-bithiophene, which is yielded by coupling of  $\text{Ni}(\text{dppp})\text{Cl}_2$  and 2-chloromagnesio-3-hexylthiophene in the presence of  $\text{LiCl}$ . The signals were assigned according to the literature.<sup>6</sup>

#### 11. In-situ $^{31}\text{P}$ NMR characterization of model reaction of HH coupling

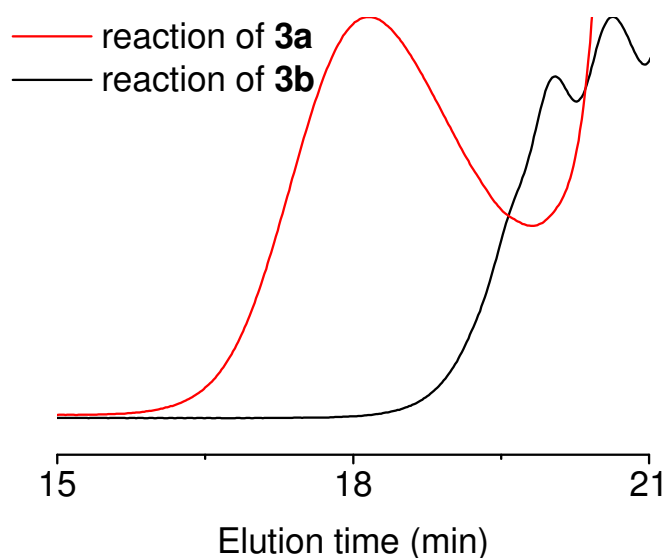
In a thoroughly dried Schlenk tube,  $i\text{PrMgCl}$  (0.25 mL, 0.50 mmol) was added into a mixture of 3-hexyl-2-iodothiophene (147 mg, 0.50 mmol), 1,4-dihexyloxybenzene (internal standard for GC analysis, 40 mg, 0.15 mmol) and dry THF (5 mL), after stirring at  $-20\text{ }^{\circ}\text{C}$  for 1 h, 0.3 mL solution was withdrawn for GC analysis (conversion = 100%). At  $0\text{ }^{\circ}\text{C}$ , 4 mL solution was injected into a suspension of  $\text{Ni(dppp)Cl}_2$  (54.2 mg, 0.10 mmol) in dry THF (0.5 mL) dropwise, after 10 min, 0.3 mL and 0.6 mL solution was withdrawn for GC (conversion of **9a** was 4%) and  $^{31}\text{P}$  NMR measurement, respectively. After a further 20 min, another 0.3 mL and 0.6 mL solution was withdrawn for GC (conversion of **9a** was 4%) and  $^{31}\text{P}$  NMR measurement, then  $\text{LiCl}$  (10.2 mg, 0.27 mmol) solution in THF (2.5 mL) was added into reaction mixture, after stirred for another 10 min, 0.3 mL and 0.6 mL solution was withdrawn for GC (conversion of **9a** was 39%) and  $^{31}\text{P}$  NMR measurement, respectively.



12. Polymerization of **3a** or **3b** with 50 mol% catalyst in the presence of LiCl.

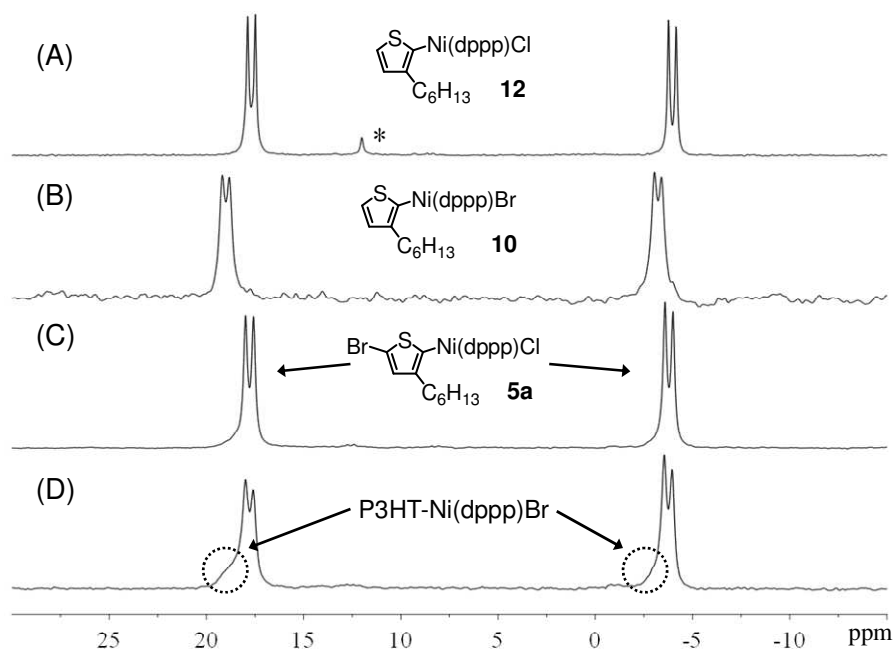
Since the experiments of **3a** and **3b** were conducted in the same manner, only the polymerization of **3a** is depicted as follows.

In a thoroughly dried Schlenk tube,  $i\text{PrMgCl}$  (1.00 mL, 2.00 mmol) was added into a mixture of **1** (746 mg, 2.00 mmol), LiCl (84 mg, 2.00 mmol), 1,4-dipentyloxybenzene (internal standard for GC analysis, 80 mg, 0.32 mmol) and dry THF (14 mL). After stirred at  $-20\text{ }^{\circ}\text{C}$  for 1 h, the solution was allowed to be warmed to room temperature, and 0.4 mL solution was withdrawn for GC analysis (conversion of **1** was quantitative). Then the **3a** solution was added to the suspension of  $\text{Ni(dppp)Cl}_2$  (542 mg, 1.00 mmol) in dry THF (6 mL) dropwise. After 1 equiv **3a** was added in about 1 min, a small amount of reaction solution was withdrawn for GC/MS characterization. After the addition of the second 1 equiv **3a**, the mixture was continued to react at room temperature for 10 min before quenched with 5M HCl. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic extracts were washed with brine, dried over anhydrous  $\text{MgSO}_4$  for GC/MS characterization, and concentrated under reduced pressure for GPC measurement.



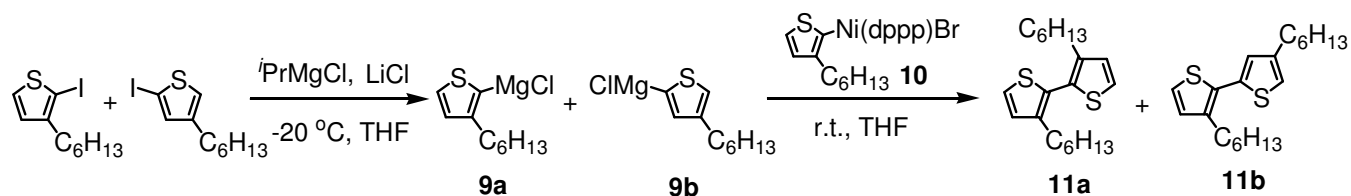
**Figure S8.** GPC profiles of the polymerization mixtures of **3a** and **3b** with 50 mol%  $\text{Ni(dppp)Cl}_2$  catalyst. For **3b**, only oligomers with low molecular weight were yielded, and for **3a**, the  $M_p$  of the product was 1800. The polymerizations were carried out at room temperature with 1 equiv LiCl and  $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.10\text{ mol/L}$ . Both samples were not purified via precipitation or Soxhlet extraction.

*Note:* By comparing the spectra with those of *cis*-chloro-(3-hexyl-2-thienyl)-1,3-bis(diphenylphosphino)propane nickel (II) (**12**) (Figure S9A) and *cis*-bromo-(3-hexyl-2-thienyl)-1,3-bis(diphenylphosphino)propane nickel (II) (**10**) (Figure S9B), we can assigned the two doublets (17.78 and -3.79 ppm,  $J = 66$  Hz) in (C) to the intermediate **5a**. After 2 equiv **3a** was added, the shoulder peaks appeared in (D) can be assigned to the Ni-terminated polymer chains (**P3HT-Ni(dppp)-Br**). Cl in some of **5a** may also changed to Br, and the signals overlapped with those of **P3HT-Ni(dppp)-Br**.



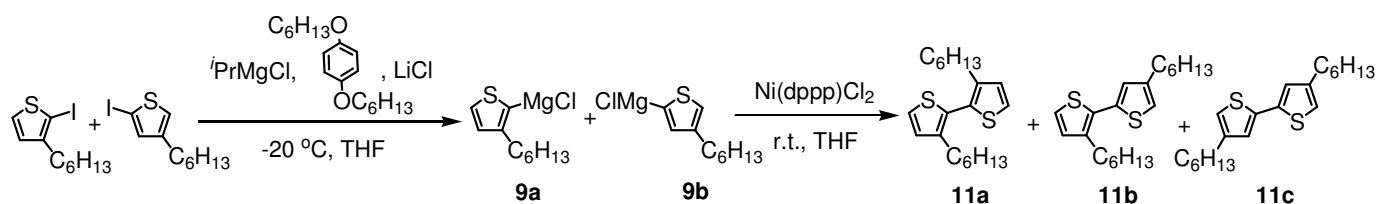
**Figure S9.** In-situ  $^{31}\text{P}$  NMR spectra (162 MHz, THF) of the reacting mixture of 4 equiv **9a** and 1 equiv  $\text{Ni(dppp)Cl}_2$  without LiCl after reaction for 10 min (A), **10** in THF (B), the reacting mixtures of 1 equiv (C) and 2 equiv (D) **3a** with 1 equiv  $\text{Ni(dppp)Cl}_2$  in the presence of 1 equiv LiCl. For A, the reaction was carried out at 0 °C with  $[\mathbf{9a}]_0 = 0.09$  mol/L (\* indicates the signal of  $\text{Ni(dppp)}_2$ ). For C and D, the reactions were carried out at room temperature with  $[\mathbf{1}]_0 = 0.10$  mol/L.

13. The model reaction for demonstrating the ratio between propagation and initiation rates:

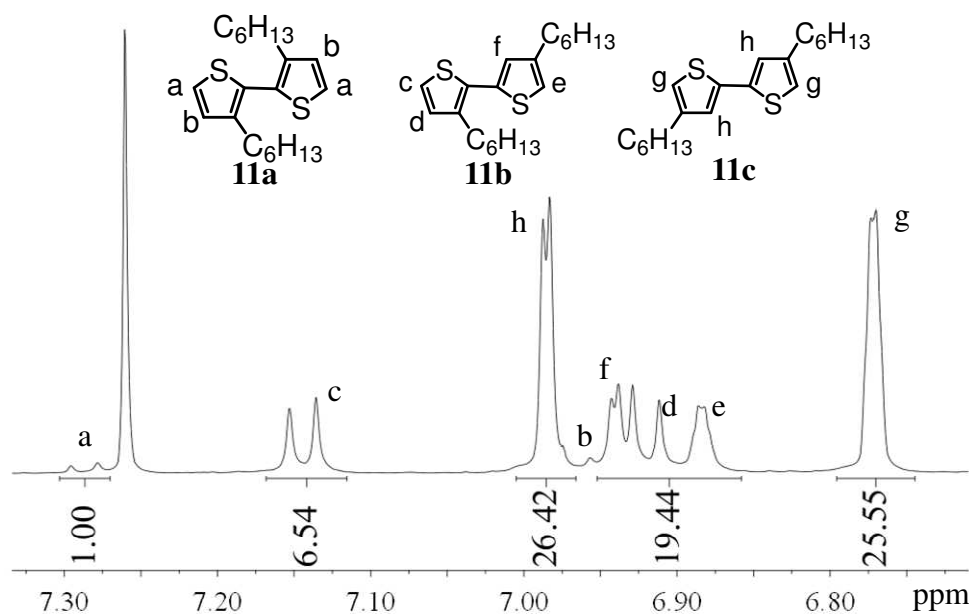


In a thoroughly dried Schlenk tube, *i*PrMgCl (0.25 mL, 0.49 mmol) was added into a mixture of 3-hexyl-2-iodothiophene (73.5 mg, 0.25 mmol), 4-hexyl-2-iodothiophene (73.5 mg, 0.25 mmol), LiCl (21.2 mg, 0.5 mmol), 1,4-dihexyloxybenzene (internal standard for GC analysis, 20 mg, 0.07 mmol) and dry THF (5 mL), after stirring at -20 °C for 1 h, 0.3 mL solution was withdrawn for GC analysis (conversion = 100%). At room temperature, a solution of **10** (35.9 mg, 0.05 mmol) in dry THF (3 mL) was added. After string for 30 min, the reaction was quenched by addition of 5 M HCl aqueous solution. The mixture was extracted with PE, and the organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub> for GC measurement. (**11b** : **11a** = 15 : 1).

14. The model reaction for the initiation step of copolymerization of **3a** and **3b** with LiCl:

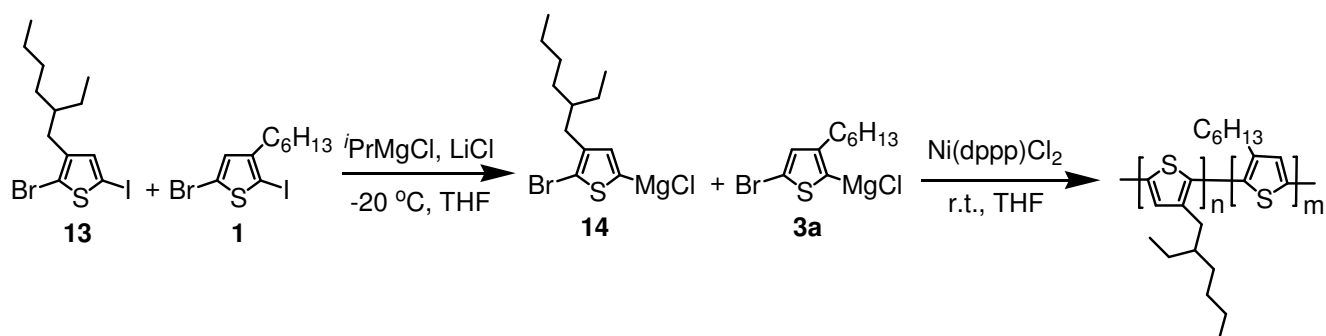


In a thoroughly dried Schlenk tube,  $i\text{PrMgCl}$  (0.50 mL, 1.0 mmol) was added into a mixture of 3-hexyl-2-iodothiophene (147 mg, 0.50 mmol), 4-hexyl-2-iodothiophene (147 mg, 0.50 mmol),  $\text{LiCl}$  (43 mg, 1 mmol), 1,4-dihexyloxybenzene (internal standard for GC analysis, 80 mg, 0.29 mmol) and dry THF (7 mL), after stirring at  $-20\text{ }^{\circ}\text{C}$  for 1 h, 0.3 mL solution was withdrawn for GC analysis (conversion = 100%). At room temperature,  $\text{Ni(dppp)Cl}_2$  (68 mg, 0.125 mmol) in dry THF (3 mL) was added. After string for 20 min, the reaction was quenched by addition of 5 M  $\text{HCl}$  aqueous solution. The mixture was extracted with PE, and the organic extracts were washed with brine, dried over anhydrous  $\text{MgSO}_4$ , filtered for GC measurement (**11a:11b:11c** = 1:14:29). After concentrated under reduced pressure, purification by chromatography over  $\text{SiO}_2$  with PE as an eluent afforded a mixture of **11a**, **11b** and **11c** (72 mg, 87%), corresponding  $^1\text{H}$  NMR (Figure S10) revealed the ratio of **11a:11b:11c** as 1:13:26, close to the result from GC analysis.

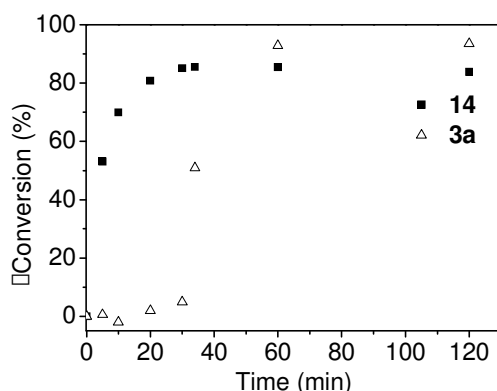


**Figure S10.**  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of the product from the model reaction for the initiation step of copolymerization of **3a** and **3b** in the presence of  $\text{LiCl}$ . The signals were assigned according to the literature.<sup>6</sup>

### 15. Copolymerization of **13** and **3a**:

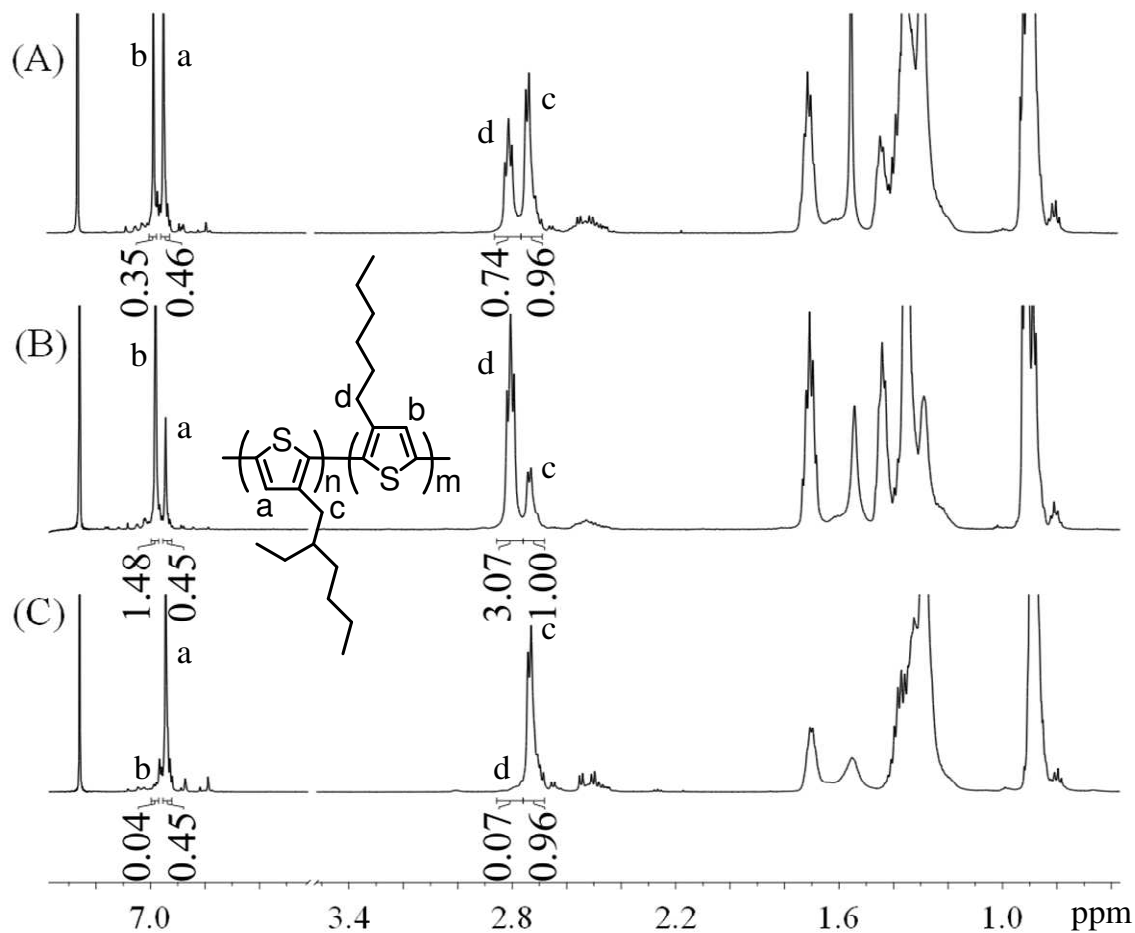


In a thoroughly dried Schlenk tube, *i*PrMgCl (1.0 mL, 2.00 mmol) was added into a mixture of **13** (400 mg, 1.00 mmol), **1** (373 mg, 1.00 mmol), LiCl (85 mg, 2.00 mmol), 1,4-dipentyloxybenzene (internal standard for GC analysis, 40 mg) and dry THF (16 mL). After stirred at -20 °C for 1 h, 0.5 mL solution was withdrawn for GC analysis (conversion of **1** and **14** were both quantitative, **14/3a** = 52/48). Then a suspension of Ni(dppp)Cl<sub>2</sub> (21.6 mg, 0.40 mmol) in dry THF (4 mL) was added. During polymerization, 12 mL solution was withdrawn in 6 times at 5.0 min, 10 min, 20min, 30min, 45 min and 60 min. After 2 h (conversions of **14** and **3a** were 84% and 94%, respectively), the polymerization was quenched by adding 5 M HCl aqueous solution. The mixture was extracted with CHCl<sub>3</sub>, and the organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>. After concentrated under reduced pressure, the solution was dropped into methanol for precipitation. The solid was filtered and dried to give copolymerization mixture as a dark purple solid (104 mg, 88%). 76 mg copolymerization mixture was added into 4.0 mL PE and stirred overnight, the suspension was filtrated to obtain the precipitation as poly(**14**)-*b*-poly(**3a**) (40 mg, 57%) as dark purple solid, while the filtrate was concentrated under reduced pressure to afford poly(**14**) (30 mg, 43%) as red solid.



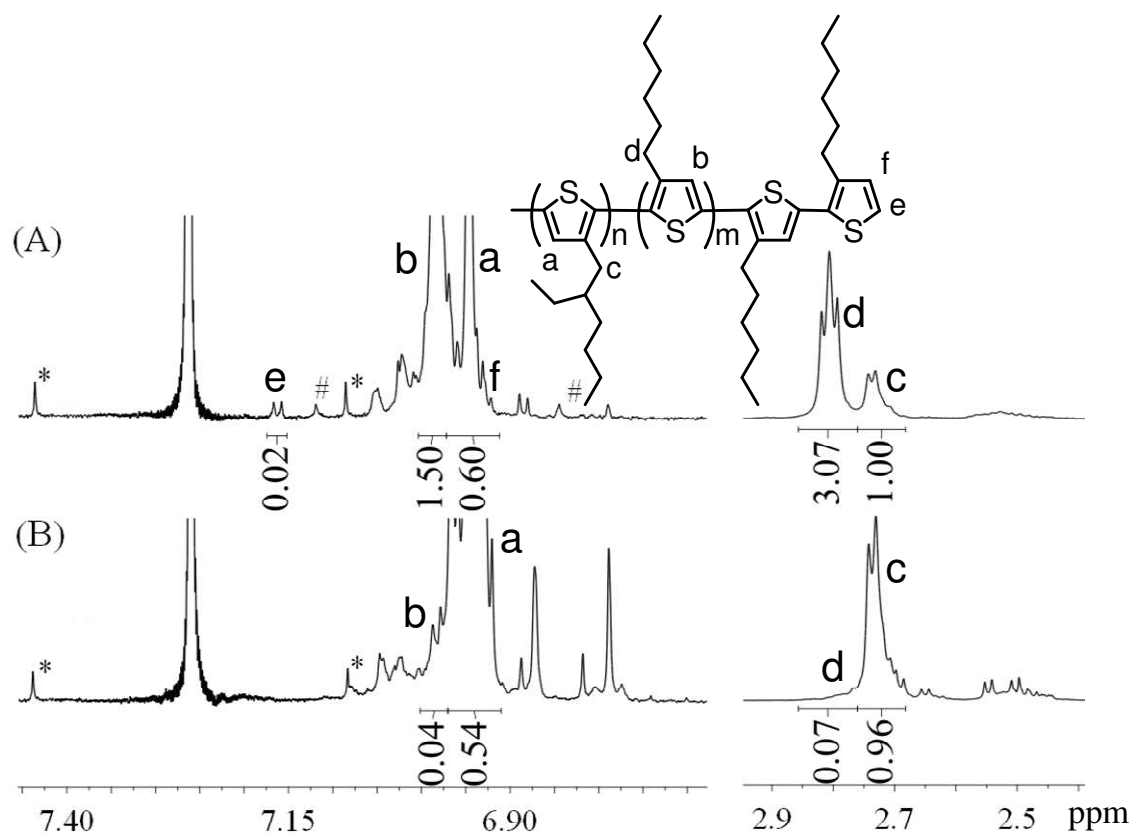
**Figure S11.** Conversions of **14** and **3a** as a function of polymerization time. The polymerization was carried out at room temperature with 1 equiv LiCl and 2 mol% Ni(dppp)Cl<sub>2</sub> to the sum amount of **13** and **1**. [13]<sub>0</sub> = [1]<sub>0</sub> = 0.05 mol/L.

*Note:* As shown in Figure S12, the singlet peak at 6.95 ppm and the doublet peak at 2.73 ppm can be attributed to H<sub>a</sub> and H<sub>c</sub> in ethylhexylthiophene block, while the singlet peak at 6.98 ppm and the triplet peak at 2.81 ppm are the signals of H<sub>b</sub> and H<sub>d</sub> in hexylthiophene block. According to the integration ratio of H<sub>a</sub> and H<sub>b</sub>, the ratio of poly(**14**) and poly(**3a**) blocks in poly(**14**)-*b*-poly(**3a**) is 23:77 (Figure S12B).



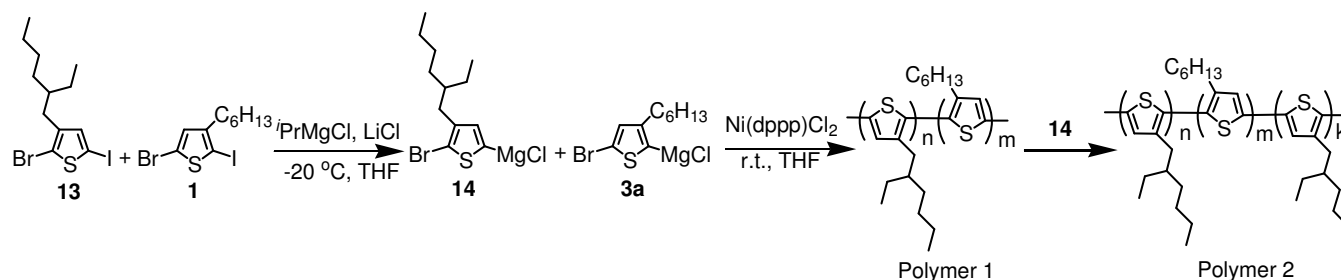
**Figure S12.** <sup>1</sup>H NMR spectra (600 MHz, CDCl<sub>3</sub>) of copolymerization mixture (A) and its two fractions poly(**14**)-*b*-poly(**3a**) (B) and poly(**14**) (C). Figure S12B and 12C were enlarged in Figure S13.

*Note:* No signals corresponding to H<sub>e</sub> and H<sub>f</sub> found in <sup>1</sup>H NMR spectrum of **14**-dominated poly(**14**), implying small amount of **3a** in poly(**14**) should be incorporated in the initiation step or the early stage of the polymerization via HT or TH coupling process.



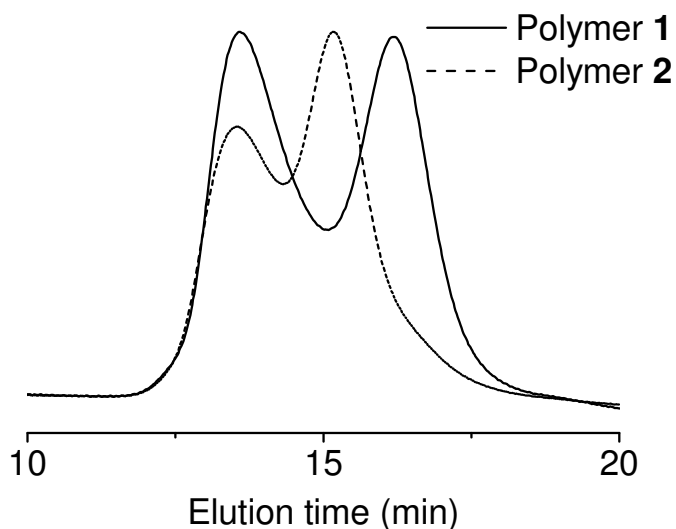
**Figure S13.** Enlarged <sup>1</sup>H NMR spectra (600 MHz, CDCl<sub>3</sub>) of poly(**14**)-*b*-poly(**3a**) (A) and poly(**14**) (B).

16. Copolymerization with monomer addition order as **14** after **14/3a**:



Two Schlenk tubes were thoroughly dried prior to use, in one tube, a mixture of **1** (373 mg, 1.00 mmol), **13** (400 mg, 1.00 mmol),  $i\text{PrMgCl}$  (1.00 mL, 2.00 mmol),  $\text{LiCl}$  (85 mg, 2.00 mmol), 1,4-dihexyloxybenzene (internal standard for GC analysis, 40 mg, 0.14 mmol) and dry THF (16 mL) was stirred at  $-20\text{ }^{\circ}\text{C}$  for 1 h (solution A). In the other tube, solution B was prepared in the same method with **13** (400 mg, 1.0 mmol),  $\text{LiCl}$  (42 mg, 1.0 mmol),  $i\text{PrMgCl}$  (0.5 mL, 1.0 mmol) and 1,4-dihexyloxybenzene (40 mg, 0.14 mmol) in THF (10 mL) (solution B). Then the solutions were allowed to be warmed to room temperature, and 0.5 mL of both solutions were withdrawn for GC analysis (solution A: conversions of **1** and **13** were quantitative, **3a/14** = 46 : 54, solution B: conversion of **13** was quantitative). Into solution A, a suspension of  $\text{Ni(dppp)Cl}_2$  (21.7 mg, 0.04 mmol) in dry THF (4 mL) was added. After 2 h, 1.0 mL solution was withdrawn for GC and GPC analysis (polymer 1: conversions of **3a** and **14** were 93% and 95%, respectively. GPC profile was shown in Figure S14), then the solution B was added via syringe. After another 40 min (90% of the second portion of **14** was consumed), the polymerization was quenched by addition of 5 M  $\text{HCl}$  aqueous solution. The mixture was extracted with  $\text{CHCl}_3$ , and the organic extracts were washed with brine, dried over anhydrous  $\text{MgSO}_4$ . After concentrated under reduced pressure, the solution was dropped into methanol for precipitation. The solid was filtered to give product (polymer 2: GPC profile was shown in Figure S14) as a dark brown solid (392 mg, 71%).





**Figure S14.** GPC profiles of polymer **1** (before addition of the second portion of **14**,  $M_p$ s of the two peaks are  $3.3 \times 10^4$  and  $7.3 \times 10^3$ ) and polymer **2** (after addition of the second portion of **14**,  $M_p$ s of the two peaks are  $3.5 \times 10^4$  and  $1.3 \times 10^4$ ).

## References.

- (1) Lüttringhaus, A. *Liebigs. Ann. Chem.* **1937**, 528, 181–210.
- (2) (a) Consiglio, G.; Spinelli, D.; Gronowitz, S.; Hörnfeldt, A.; Maltesson, B.; Noto, R. *J. Chem. Soc., Perkin Trans. 2.* **1982**, 625-630. (b) Boyd, S. D.; Jen, A. K.-Y.; Luscombe C. K. *Macromolecules* **2009**, 42, 9387-9389.
- (3) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, 127, 17542-17547.
- (4) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, 38, 8649-8656.
- (5) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, 130, 7812–7813.
- (6) Barbarella, G.; Bonghi, A. L.; Zambianchi, M. *Macromolecules* **1994**, 27, 3039-3045.