

Grignard Metathesis Chain–Growth Polymerization for Poly(bithienylmethylene)s: Ni Catalyst Can Transfer across the Non-Conjugated Monomer

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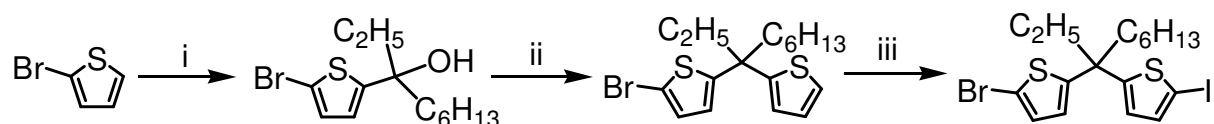
General methods and materials.....	S2
Synthesis and characterizations of monomer.....	S2-8
Synthesis and characterization of homopolymer PBTM	S9-11
Polymerization with 50% Ni(dppe)Cl ₂ and characterizations of dimer.....	S12-13
Synthesis of triblock copolymer P3HT-<i>b</i>-PBTM-<i>b</i>-P3HT	S14-15
References.....	S15

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AV 300 spectrometer at 300 MHz and Bruker AV 400 spectrometer at 400 MHz in CDCl_3 with tetramethylsilane (TMS) as an internal reference, respectively. Gas chromatography (GC) measurements were carried out on a SHIMADZU GC-14C instrument equipped with an OV-1701 column with 1,4-dipentyloxybenzene or 1,4-dioctyloxybenzene as the 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: tetrahydrofuran (THF), flow rate: 1.00 ml/min, temperature: 40°C , standard: polystyrene). High Performance Liquid Chromatography (HPLC) measurement was carried out on a Waters 600 controller equipped with two Agilent RX-SIL columns and a Waters 2487 dual λ absorbance detector (λ : 329 nm, eluent: hexane, flow rate: 0.8 mL/min, temperature: 20°C). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Kratos AXIMA-CFR Kompact MALDI Mass Spectrometer with terthiophene as the matrix in linear mode.

Materials. Tetrahydrofuran (THF) was distilled over sodium-benzophenone. *n*-Butyllithium ($^n\text{BuLi}$, 2.5 M solution in hexane, Acros), diisopropylamine (Acros, 99%), 3-nonanone (Alfa Aesar, 98%), Boron trifluoride ethyl etherate ($\text{BF}_3\cdot\text{Et}_2\text{O}$, Aldrich), Isopropylmagnesium chloride ($^i\text{PrMgCl}$, 2.0 M solution in THF, Aldrich), *t*-butylmagnesium chloride ($^t\text{BuMgCl}$, 1.7 M solution in THF, Acros), $\text{Ni}(\text{dppp})\text{Cl}_2$ (1,3-bis(diphenylphosphino)propane nickel dichloride, Pacific ChemSource, Inc., Zhengzhou, China, 98%), $\text{Ni}(\text{dppe})\text{Cl}_2$ (1,2-bis (diphenylphosphino)ethane nickel dichloride, Pacific ChemSource Inc., Zhengzhou, China, 98%), $\text{Ni}(\text{dppf})\text{Cl}_2$ (1,1'- bis(dipenylphosphino)ferrocene nickel dichloride, Pacific ChemSource, Inc., Zhengzhou, China, 98%) and $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ (bis(triphenylphosphine) nickel dichloride, Pacific ChemSource, Inc., Zhengzhou, China, 98%) were used as received without further purification. 1,4-dipentyloxybenzene,¹ 1,4-dioctyloxybenzene² and 2,5-dibromo-3-hexylthiophene (**3**)³ were synthesized according to the references. Their purities are all above 99.5% according to GC measurements.

Synthesis and characterizations of monomer

Scheme S1. The synthesis of monomer.



i) 1) LDA, THF, -78 °C to 0 °C; 2) 3-nonanone, 0 °C; ii) thiophene, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, room temperature; iii) $\text{HOAc}/\text{CHCl}_3$, N-iodosuccinimide, 0 °C to room temperature.

3-(5-Bromo-2-thienyl)-3-nanol. Under an argon atmosphere, $n\text{BuLi}$ (2.5 M in hexane, 43.2 mL, 108 mmol) was added to a stirred solution of diisopropylamine (17.4 mL, 124 mmol) in dry THF (250 mL) at -78 °C. The mixture was warmed to 0 °C, stirred for 5 min, and then cooled to -78 °C. After 2-bromothiophene (10 mL, 103 mmol) was added, the mixture was warmed to 0 °C again and stirred for 30 min. Then 3-nonanone (17.5 mL, 101 mmol) was added via syringe. The mixture was stirred at 0 °C for a further 60 min, and then large amount of water was poured in for extraction with Et_2O . The organic extracts were washed with brine and dried over anhydrous MgSO_4 . After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether (PE)/ CH_2Cl_2 = 6/1) to give pure product (25.9 g, 84%) as a pale yellow liquid. ^1H NMR (300 MHz, CDCl_3) δ = 6.89 (d, J = 3.9 Hz, 1H), 6.59 (d, J = 3.9 Hz, 1H), 1.90 (s, 1H), 1.85-1.74 (m, 4H), 1.36-1.13 (m, 8H), 0.86 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 153.7, 129.5, 122.8, 110.1, 42.5, 35.5, 31.7, 29.5, 23.4, 22.6, 14.0, 7.8 ppm.

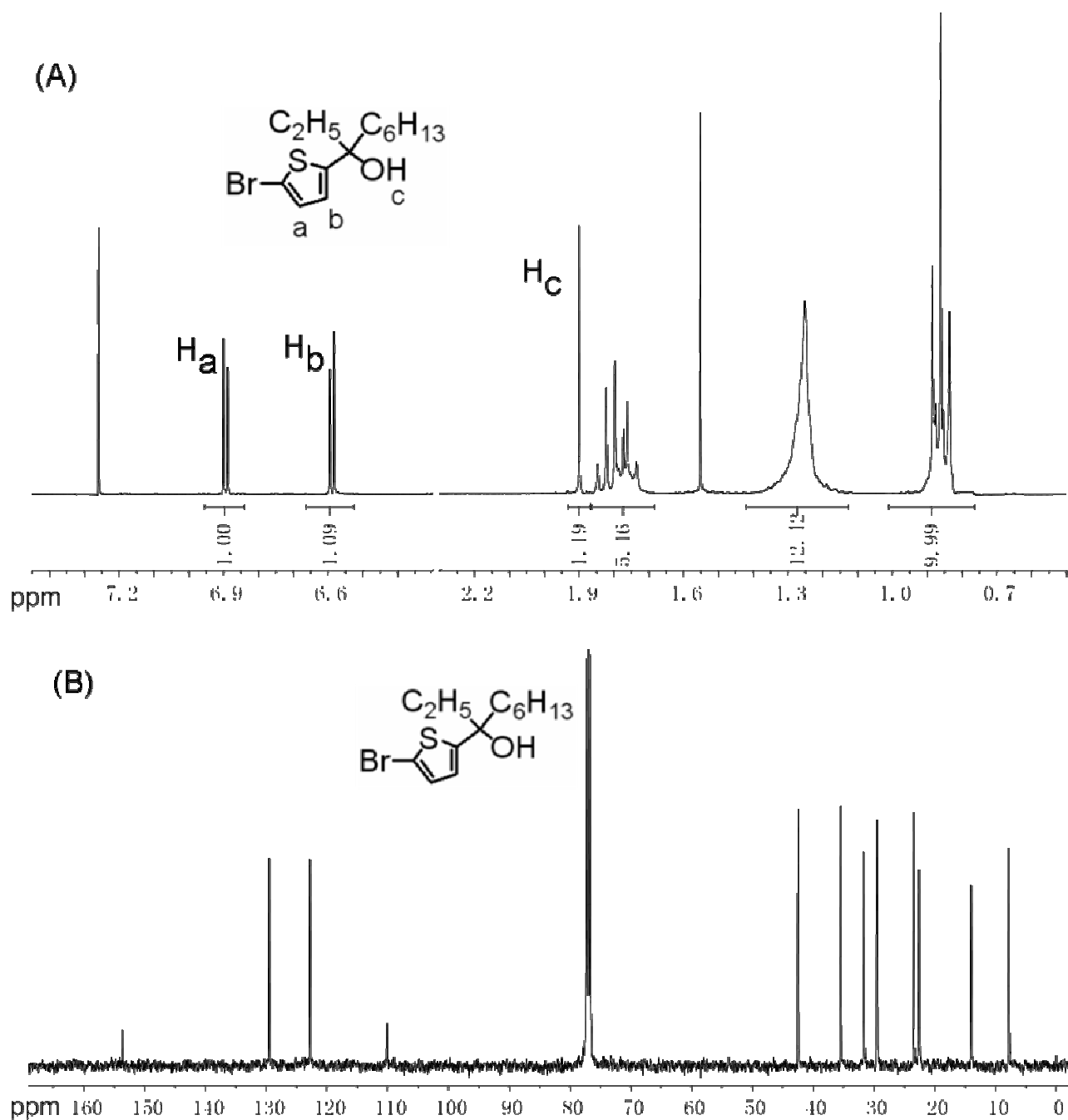


Figure S1. (A) ^1H NMR and (B) ^{13}C NMR spectra of 3-(5-bromo-2-thienyl)-3-nonanol.

3-(5-Bromo-2-thienyl)-3-(2-thienyl)nonane. Under an argon atmosphere, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.77 mL, 21.9 mmol) was added to a stirred solution of 3-(5-bromo-2-thienyl)-3-nonanol (6.7 g, 21.9 mmol) in thiophene (34.6 mL) via syringe in one portion at room temperature. After stirred for 10 min, a large amount of aqueous Na_2CO_3 solution was poured in. The mixture was extracted with PE, and the organic extracts were washed with brine, dried over anhydrous MgSO_4 . After concentrated under reduced pressure, the residue was purified with column chromatography on silica gel with PE as the eluent to afford pure product (6.5 g, 80%) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz) δ = 7.18 (dd, J = 5.2, 1.2 Hz, 1H), 6.92 (dd, J = 5.2, 3.6 Hz, 1H), 6.88 (dd, J = 3.6, 1.2 Hz, 1H), 6.84 (d, J = 3.6 Hz, 1H), 6.63 (d, J = 3.6 Hz, 1H), 2.17-2.00 (m, 4H), 1.29-1.11 (m, 8H), 0.88-0.77 (m, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 155.8, 153.1, 128.8, 126.1, 124.1, 124.1, 123.8, 110.3, 47.7, 39.6, 32.9, 31.7, 29.7, 23.8, 22.6, 14.0, 8.5 ppm.

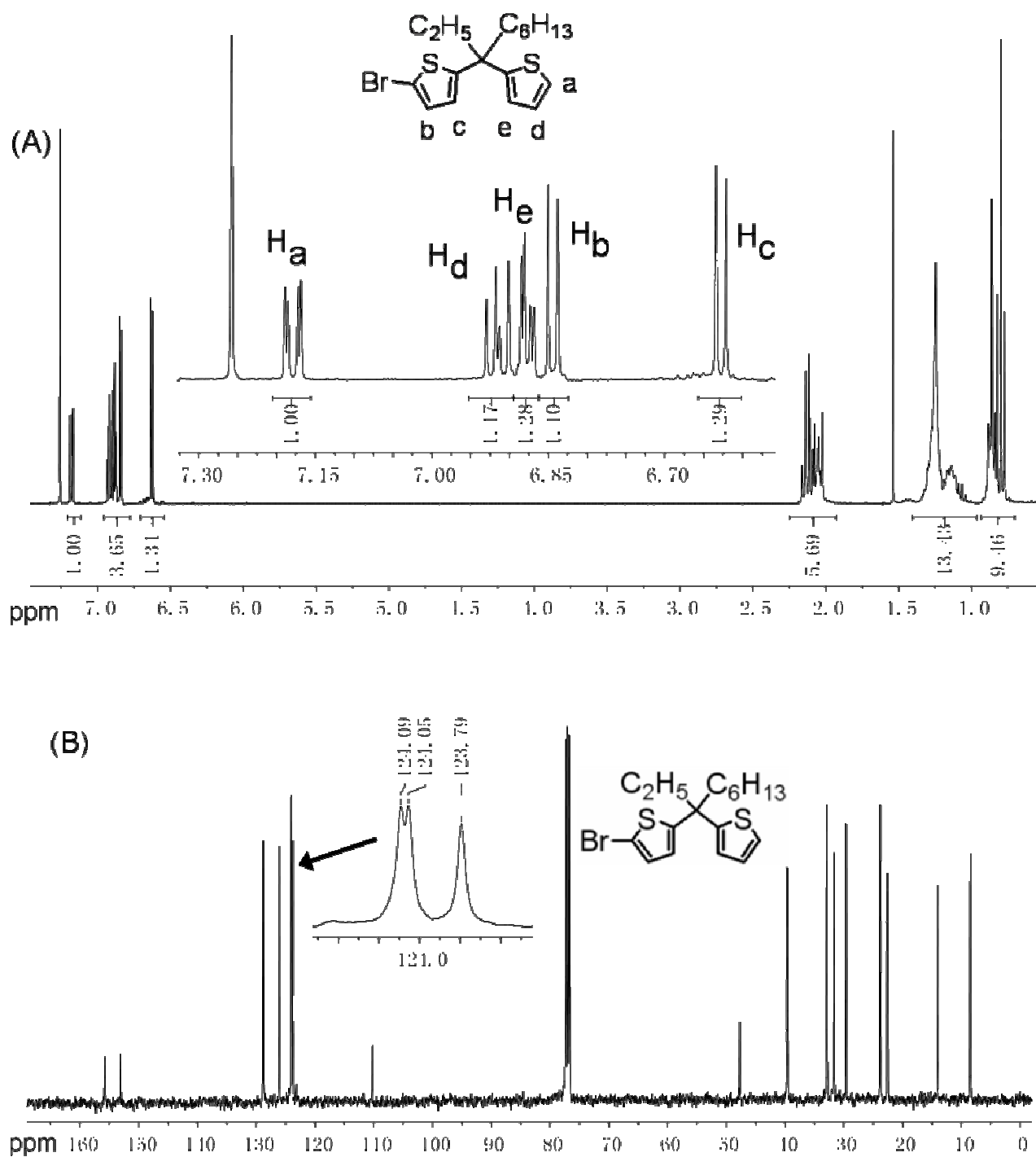


Figure S2. (A) ^1H NMR and (B) ^{13}C NMR spectra of 3-(5-bromo-2-thienyl)-3-(2-thienyl)nonane.

3-(5-Bromo-2-thienyl)-3-(5-iodo-2-thienyl)nonane (1). 3-(5-bromo-2-thienyl)-3- (2-thienyl)nonane (10.28 g, 27.7 mol) was dissolved in acetic acid and CHCl_3 (125 mL:125mL). N-iodosuccinimide (6.85 g, 30.4 mmol) was added to the solution in several portions at 0°C. The solution was allowed to warm to room temperature and stirred overnight in absence of light. Then a large amount of Na_2CO_3 solution was poured in, the mixture was extracted with CHCl_2 . The organic extracts were washed with $\text{Na}_2\text{S}_2\text{O}_3$ and brine, dried over anhydrous MgSO_4 . After concentrated under reduced pressure, the residue was purified with column chromatography on silica gel with PE as the eluent to afford the product (11.2 g, 81%) as a colorless solid. The purity is 99.6% according to GC measurement. mp 49-50 °C; ^1H NMR (CDCl_3 , 300 MHz) δ = 7.05 (d, J = 3.6 Hz, 1H), 6.85 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.6 Hz, 1H), 2.11-1.54 (m, 4H), 1.32-1.08 (m, 8H), 0.88-0.83 (m, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 159.2, 154.8, 136.1, 129.0, 125.8, 124.4, 110.6, 71.7, 48.2, 39.5, 32.7, 31.6, 29.6, 23.7, 22.6, 14.0, 8.4 ppm.

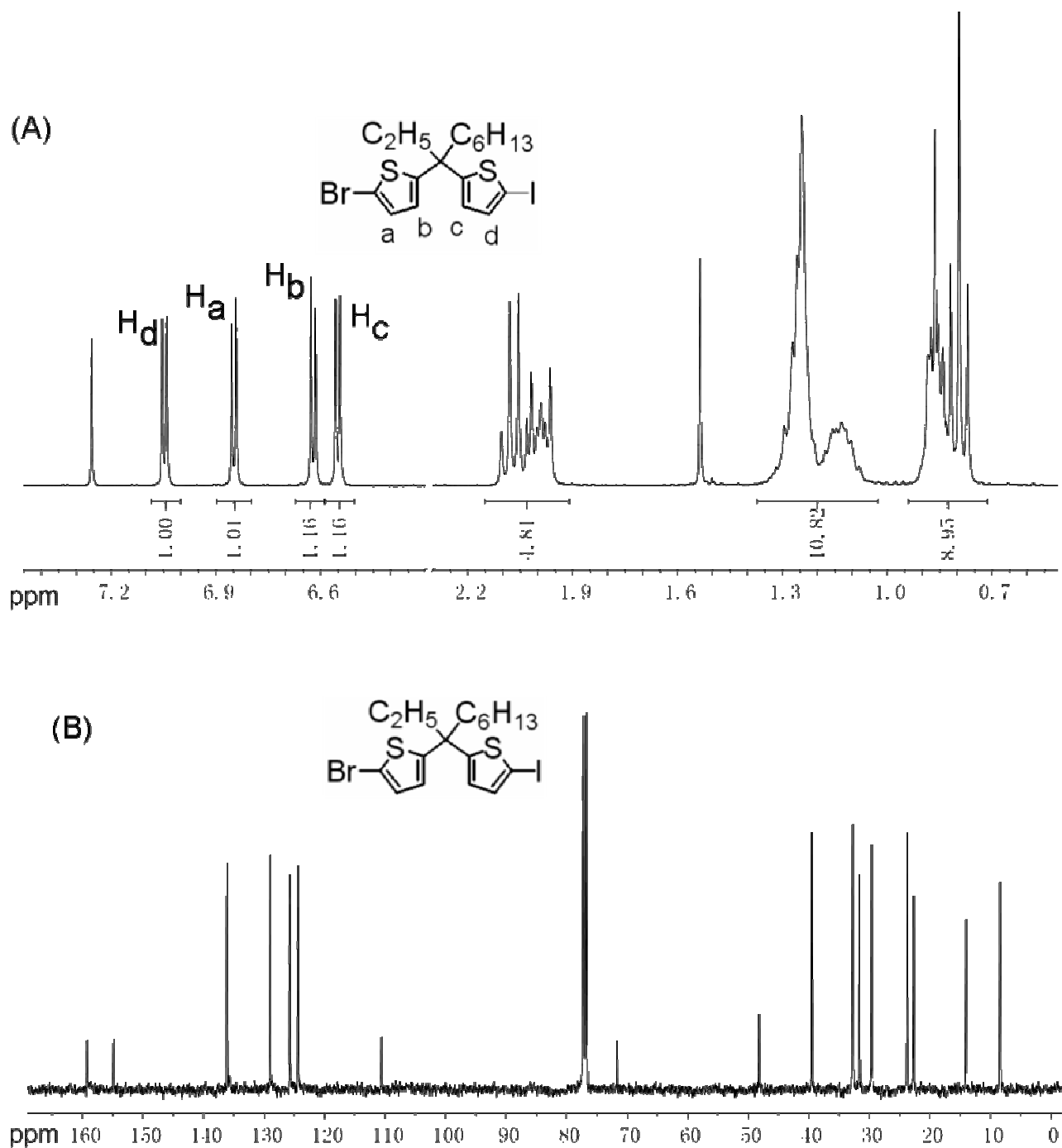


Figure S3. (A) ^1H NMR and (B) ^{13}C NMR spectra of 3-(5-bromo-2-thienyl)-3-(5-iodo-2-thienyl)nonane.

Synthesis and characterization of homopolymer PBTM

General procedure for the Synthesis of poly(2,5-thienylene-1-ethyl-1-hexylmethylen-2,5-thienylene) (PBTM). In an thoroughly dried Schlenk tube, $i\text{PrMgCl}$ (0.49 mL, 0.98 mmol) was added into a mixture of **1** (497 mg, 1.00 mmol), 1,4-dioctyloxybenzene (internal standard for GC analysis, 72 mg, 0.25 mmol) and dry THF (5 mL), after stirring at $-20\text{ }^{\circ}\text{C}$ for 1 h, 0.2 mL solution was withdrawn for GC analysis (conversion of **1** was 98%). At $0\text{ }^{\circ}\text{C}$, a suspension of Ni(dppe)Cl_2 (10.6 mg, 0.02 mmol) in dry THF (3 mL) was added. After 70 min (91% of Grignard reagent **2** was consumed), the polymerization was quenched by addition of 5 M HCl aqueous solution. The mixture was extracted with CHCl_3 , and the organic extracts were washed with brine, dried over anhydrous MgSO_4 . After concentrated under reduced pressure, the solution was dropped into methanol for precipitation. The solid was filtered and dried to give **PBTM** ($M_n = 1.4 \times 10^4$, PDI = 1.3) as a white solid (226 mg, 80%). ^1H NMR (300 MHz, CDCl_3) δ = 6.88 (d, $J = 3.9$ Hz, Th-*H*), 6.73 (d, $J = 3.9$ Hz, Th-*H*), 2.13-2.02 (m, Th-C(CH_2CH_3)($\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$)), 1.38-1.05 (m, Th-C(CH_2CH_3)($\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$)), 0.88-0.78 (m, Th-C(CH_2CH_3)($\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$)).

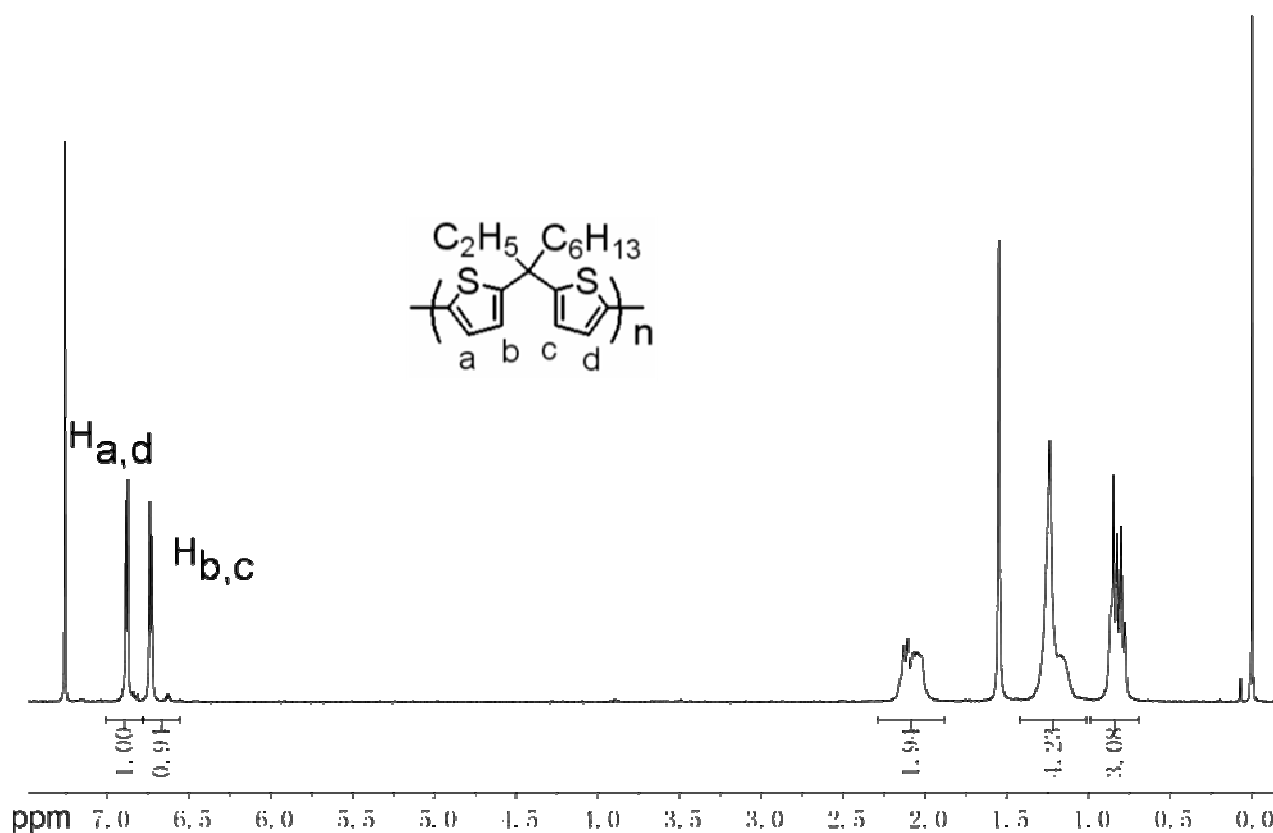


Figure S4. ^1H NMR spectrum of **PBTM** ($M_n = 1.4 \times 10^4$, PDI = 1.28).

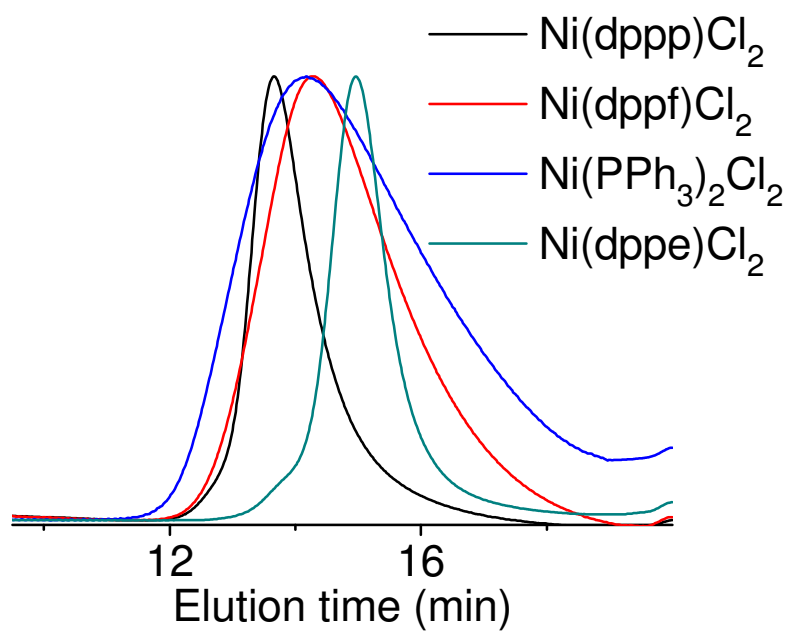


Figure S5. GPC profiles of **PBTM** synthesized with various catalysts. All polymerizations were carried out at 0 °C with 2% Ni catalysts.

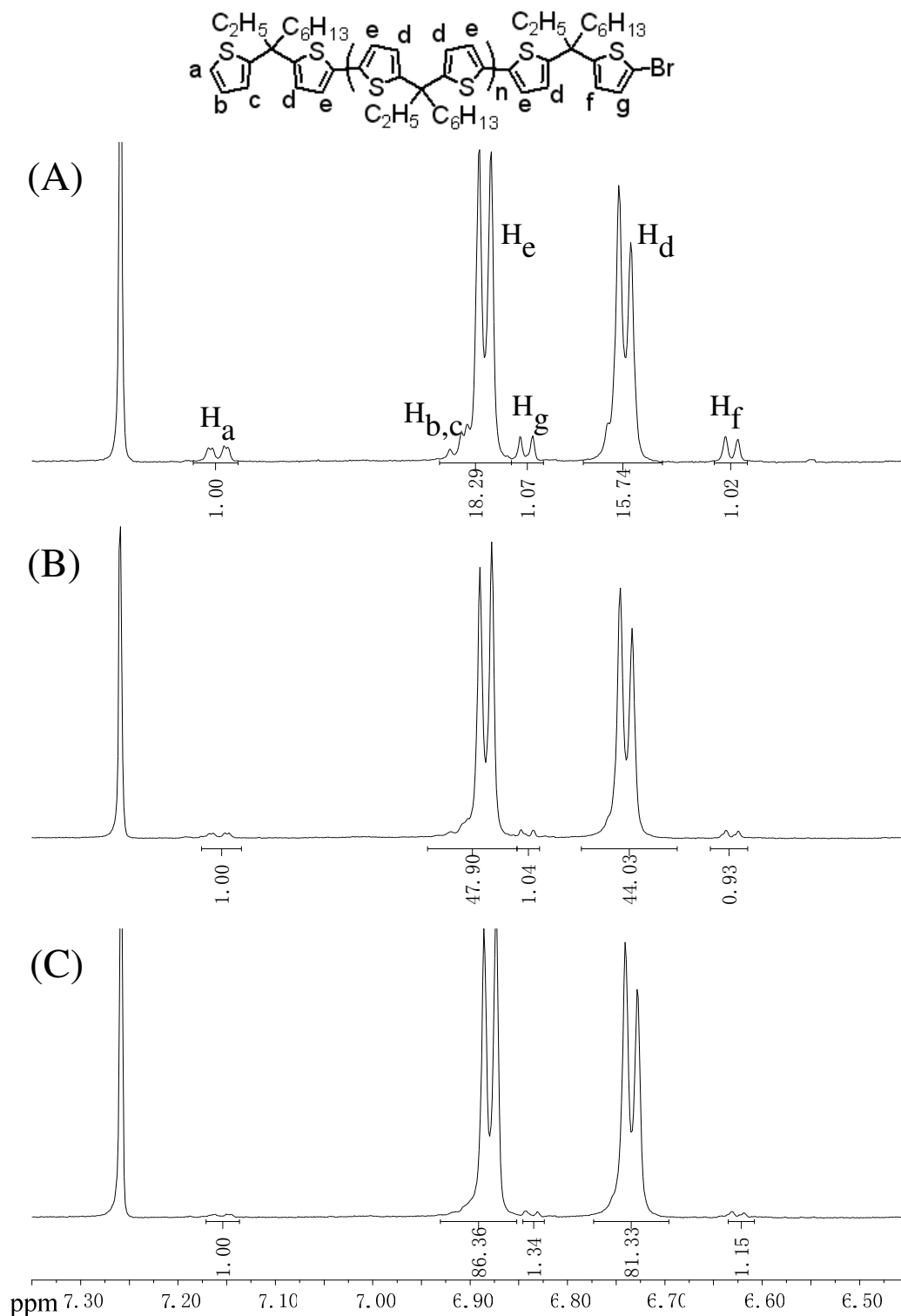


Figure S6. ^1H NMR spectrum of (A) **PBTM** ($M_n = 3.0 \times 10^3$, PDI = 1.12) catalyzed by 10% Ni(dppe)Cl₂, (B) **PBTM** ($M_n = 8.7 \times 10^3$, PDI = 1.09) catalyzed by 4% Ni(dppe)Cl₂, (C) **PBTM** ($M_n = 1.3 \times 10^4$, PDI = 1.28) catalyzed by 2% Ni(dppe)Cl₂. The assignment is determined according to the ^1H NMR spectrum of dimer. The integral ratio of H end (H_a) to Br end (H_g or H_f) is about 1:1 for the polymers with all the three different M_n s, consistent with the dominant H/Br end groups.

Polymerization with 50% Ni(dppe)Cl₂ and characterizations of dimer. In an thoroughly dried Schlenk tube, ⁱPrMgCl (0.15 mL, 0.29 mmol) was added into a mixture of **1** (149 mg, 0.30 mmol), 1,4-dioctyloxybenzene (internal standard for GC analysis, 20 mg, 0.60 mmol) and dry THF (2.4 mL), after stirring at -20 °C for 1 h, 0.1 mL solution was withdrawn for GC analysis (conversion of **1** was 96%). At 0 °C, a suspension of Ni(dppe)Cl₂ (79 mg, 0.15 mmol) in dry THF (3.0 mL) was added. After 10 min (96% of **2** was consumed), the polymerization was quenched by addition of 5 M HCl aqueous solution. The mixture was extracted with CHCl₃, and the organic extracts were washed with brine, dried over anhydrous MgSO₄. After concentrated under reduced pressure, separation by column chromatography on silica gel (PE/CH₂Cl₂ = 30/1) afforded dimer of 46 mg and higher oligomers of 49 mg both as colorless liquids. The purity of dimer is 99.9% according to HPLC measurement. ¹H NMR (CDCl₃, 300 MHz) δ = 7.17 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.93-6.88 (m, 4H), 6.85 (d, *J* = 3.9 Hz, 1H), 6.74 (t, *J* = 3.9 Hz, 2H), 6.63 (d, *J* = 3.9 Hz, 1H), 2.17-1.99 (m, 8H), 1.29-1.11 (m, 16H), 0.88-0.78 (m, 12H) ppm.

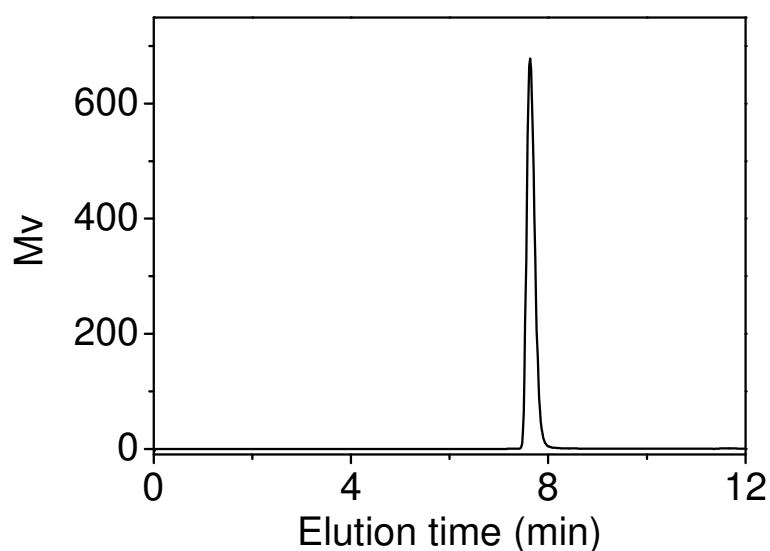


Figure S7. HPLC profile of dimer, the one-peak shape curve verifies a unique structure.

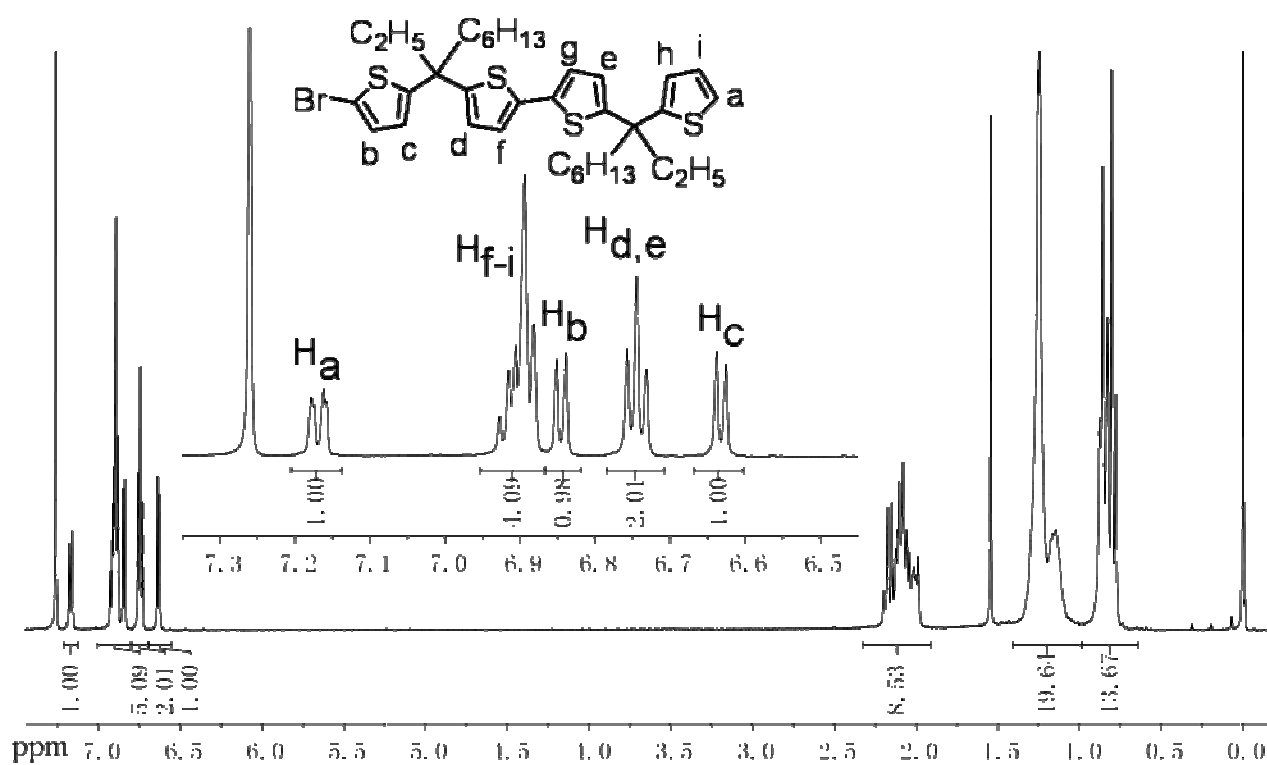


Figure S8. ^1H NMR spectrum of dimer.

Synthesis of P3HT-*b*-PBTM-*b*-P3HT. Since triblock copolymerizations in both routes were conducted in a similar manner, here only one example was depicted as follows. Three Schlenk tubes were thoroughly dried prior to use. In one tube, a mixture of **1** (249 mg, 0.50 mmol), ⁱPrMgCl (0.25 mL, 0.49 mmol) and 1,4-dioctyloxybenzene (internal standard for GC analysis, 40 mg, 0.12 mmol) in dry THF (4.0 mL) was stirred at -20 °C for 1 h (solution A, 99% of **1** was converted). In the other tube, a mixture of **3** (659 mg, 1.80 mmol), ^tBuMgCl (1.06 mL, 1.80 mmol) and 1,4-dipentyloxybenzene (internal standard for GC analysis, 120 mg, 0.48 mmol) in THF (15 mL) was stirred at 25 °C for 24 h (solution B, 80% of **3** was converted). According to GC analysis, conversions of **1** and **3** were 99% and 80%, respectively. For triblock copolymerization, 7.5 mL of solution B was added into the third Schlenk tube at room temperature, then a suspension of Ni(dppe)Cl₂ (10.6 mg, 0.02 mmol) in dry THF (3 mL) was added. After stirred for 60 min, 0.5 mL of the solution was withdrawn for GC and GPC analysis (78% of **4** was consumed, *M_n* and PDI of homopolymer **P3HT** are 5.0 × 10³ and 1.3, respectively). The homopolymer solution was cooled to 0 °C and the solution A was added via syringe. After 100 min, 1 mL of the solution was withdrawn for GC and GPC analysis (96% of **2** was consumed, *M_n* and PDI of the diblock copolymer are 1.1 × 10⁴ and 1.4, respectively). Finally, the left solution B was added via syringe and the reaction mixture was allowed to warm to room temperature again. After reacting for 120 min (90% of **4** was consumed), the polymerization was quenched by addition of adequate 5 M HCl solution. The mixture was extracted with CH₂Cl₂, and the organic layer was washed with brine, dried over anhydrous MgSO₄. After concentrated under reduced pressure, the solution was dropped into methanol for precipitation. The solid was filtered and the residual methanol was removed under reduced pressure to give the product (*M_n* = 1.6 × 10⁴, PDI = 1.4) as a dark purple solid (222 mg, 54%). ¹H NMR (300 MHz, CDCl₃) δ = 6.98 (s, Th-*H* of **P3HT**), 6.88 (d, *J* = 3.9 Hz, Th-*H* of **PBTM**), 6.73 (d, *J* = 3.9 Hz, Th-*H* of **PBTM**), 2.83-2.59 (m, Th-CH₂C₅H₁₁ of **P3HT**), 2.13-2.02 (m, Th-C(CH₂CH₃)CH₂C₄H₈CH₃ of **PBTM**), 1.73-1.66 (m, Th-CH₂CH₂C₄H₉ of **P3HT**), 1.38-1.05 (m, Th-C(CH₂CH₃)CH₂C₄H₈CH₃ of **PBTM**), 0.88-0.78 (m, Th-C₅H₁₀CH₃ of **P3HT** + Th-C(CH₂CH₃)CH₂C₄H₈CH₃ of **PBTM**).

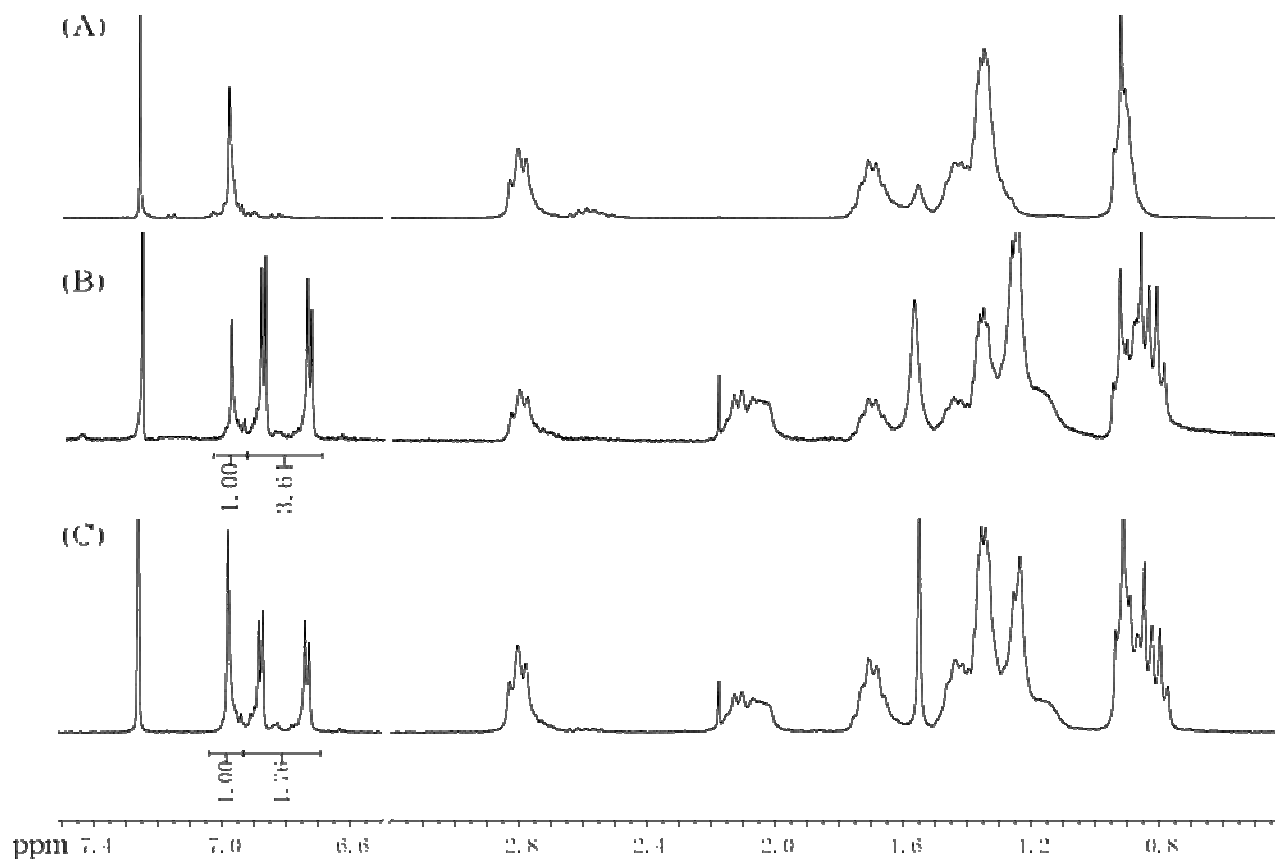


Figure S9. ^1H NMR spectra of (A) **P3HT**, (B) **P3HT-*b*-PBTM** and (C) **P3HT-*b*-PBTM-*b*-P3HT** obtained by triblock copolymerization with monomer addition order of **4**, **2** and then **4**. The signals at 7.01-6.93 ppm and 6.93-6.70 ppm are assigned to the protons in thiophene rings of **P3HT** and **PBTM**, respectively. The actual ratios of the polymerization degrees between **P3HT** and **PBTM** blocks in diblock and triblock copolymers can be calculated based-on the integral ratios of these two signals. The values (52:48 and 69:31) are very close to the ones calculated based-on the ratios of converted monomers/catalyst (51:49 and 72:28).

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