Using bis(pinacolato)diboron to improve the quality of regioregular conjugated co-polymers†

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We demonstrate the use of bis(pinacolato)diboron to directly polymerize symmetric, bisbromo, thiophene-based monomers *via* a Suzuki homo-polymerization to form co-polymers in less steps than the corresponding co-polymerization. We compare this method to the commonly used Stille co-polymerization by preparing four thiophene-based co-polymers using both methods. We use MALDI-TOF mass spectrometry to show that this new method produces high-quality, uniform polymers with narrow distributions of end-groups. By varying the electronegativity of the monomers, we demonstrate rudimentary control over these end-groups, forming either bis-H-, mono-H-mono-Br-, or bis-Br-terminated polymers in order of increasing electronegativity.

1. Introduction

This paper describes the highly reproducible synthesis of regioregular, thiophene-based, conjugated co-polymers using bis(pinacolato)diboron (BiPi) to generate the active species for Suzuki homo-polymerizations *in situ*, obviating the need for co-polymerization reactions. We used MALDI-TOF mass spectrometry to demonstrate that this approach produces well-defined polymer chains and generally increases the quality of co-polymers over those synthesized by the commonly used Stille co-polymerization by reducing the number of different types of polymer chains that form.

Conjugated polymers of thiophene moieties are synthesized by metal-mediated crosscoupling or, less frequently, by oxidative polymerization (which we will not discuss). The reactive intermediates of metal-mediated polymerizations are thiophene–metal complexes, formed *in situ* from a halogen, and a thiophene bearing a Sn (Stille), Mg (GRIM), Br (Yamamoto), or B (Suzuki).[1–10] Each of these methods is suited to a particular system; GRIM and Yamamoto are typically used for homo-polymerizations and random co-polymerizations of simple monomers. For example, regio-regular poly(3-hexylthiophene) (rrP3HT) is easily prepared using GRIM, which reproducibly leads to high-quality polymers—a major reason for the wide-spread use of rrP3HT. For alternating co-polymers or polymers with labile functional groups, Suzuki or Stille must be used. Unlike GRIM, these two reactions proceed by a step-growth mechanism in which the molecular-weight and polydispersity index (PDI) of the polymer are extremely sensitive to the purity and stoichiometry of the monomers, hindering reproducibility.[11] Homo-coupling and side-reactions exacerbate this problem by uncontrollably affecting the stoichiometry of the monomers during the polymerization reaction.[12,13] These and other side-reactions introduce defects and terminate chains uncontrollably, negatively affecting the electronic properties of the polymer. Janssen *et al.* demonstrated that polymers prepared by Suzuki co-polymerization can be terminated in 11 different ways, producing 11 unique polymer chains per repeating unit.[14–17] This is an inescapable consequence of co-polymerizations which, even in the absence of side-reactions, can initiate from and be terminated by either monomer.

As rrP3HT has shown, if these complex co-polymers are to see commercial success,[18–24] reproducible polymerization techniques that produce well-defined polymers are needed.[25–27] The non-toxic, mild conditions of the Suzuki polymerization make it preferable to the Stille.[28] However, the electron-rich nature of thiophene-based monomers, which are a popular choice because they are easily functionalized to fine-tune their properties,[28,29] slows the catalytic cycle of the Suzuki method. This requires high temperatures and long reaction times, leading to low molecular-weight polymers with poor electronic properties. Additionally, the requisite boronate-functionalized thiophene monomers are notoriously difficult to purify. For both Stille and Suzuki polymerizations, copolymers can be synthesized either by co-polymerizing a bis-halogen, X–Ar_A–X, with a bis-boronate or bis-stanane, Y–Ar_B–Y, or homo-polymerizing an asymmetric co-monomer, X–Ar_AAr_B–Y; both will produce the same co-polymer, $(Ar_AAr_B)_n$. The co-monomer approach is, in theory, preferable because, even though it may require more synthetic steps, it produces a higher degree of polymerization and leads to less variation in end-groups than the equivalent co-polymerization because the chains can only initiate from and terminate with the same monomer. In reality, however, the syntheses and, in particular, the purification of these co-monomers are often very difficult.

We synthesized a series of thiophene-based compounds and polymerized them directly from the bis-bromide by generating the active boronate species for a Suzuki polymerization *in situ* from BiPi *via* the Miyaura reaction.[30–35] We also synthesized identical polymers by the commonly used Stille co-polymerization method

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for comparison. These reactions are summarized in Scheme 2. This "BiPi method" combines the more facile syntheses of the co-polymerization route with the reproducibility and higher-quality polymers of the co-monomer route by enabling the direct homopolymerization of a symmetric co-monomer[36,37] to form a co-polymer. This method obviates the synthesis of Sn- or B-containing monomers and retains the versatility and tolerance for functional groups of the standard Suzuki polymerization. It produces higher-quality polymers in fewer synthetic steps and with less variation in end-groups than the same co-polymers prepared by Stille co-polymerizations.

2. Experimental

2.1 General

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise indicated. NMR were measured using a Varian VXR-300 (300 MHz) or a Varian Gemini-200 (200 MHz) instrument at 25 °C (in $CDCl_3$ with the exception of polymers with overlapping peaks which were performed in CD_2Cl_2). ATR-IR spectra were recorded on a Bruker IFS88. GPC measurements were done on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns (PLGel 5μ mixed-C) (Polymer Laboratories) were calibrated using narrow disperse polystyrene standards (Polymer Laboratories). Samples were made in chloroform at a concentration of 1 mg mL^{-1}. MALDI-TOF measurements were performed on a Biosystems Voyager apparatus. Samples were prepared by mixing the matrix (terthiophene or dithranol, 20 mg mL^{-1} in $CHCl_3$) and the sample (1 mg per 5 mL in $CHCl_3$) in a 1 : 1 ratio. All the samples were measured in negative ion mode.

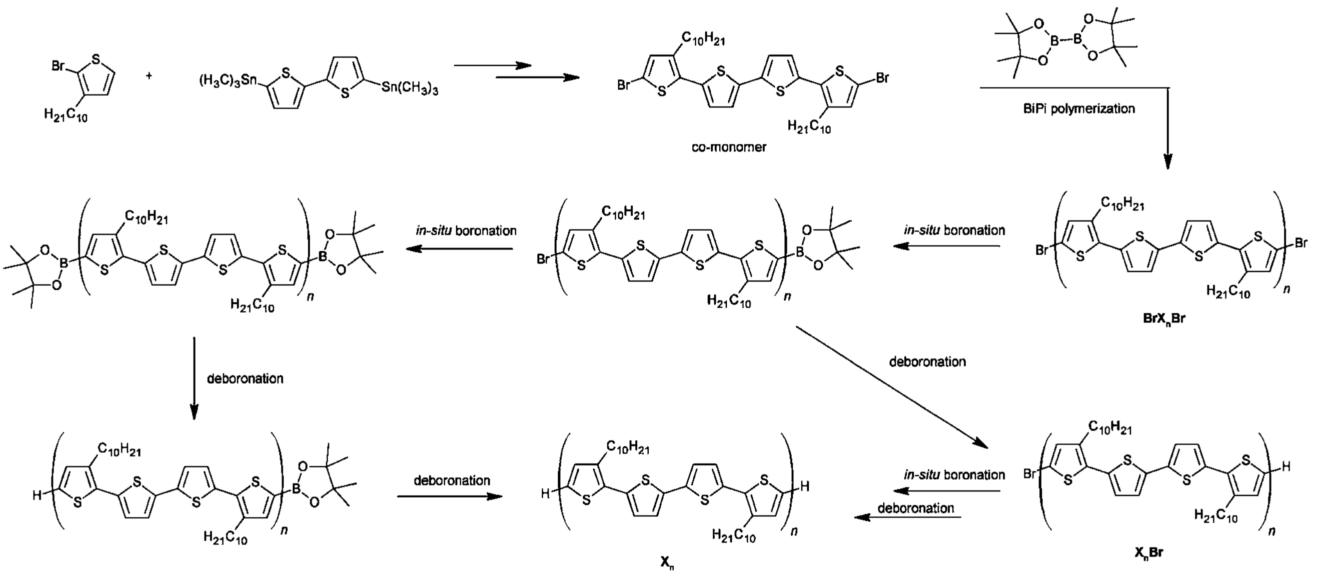
Kumada, Stille and Suzuki coupling reactions were performed under dry conditions and nitrogen atmosphere.

Thieno[2,3-*b*]thiophene,[38] 2,5-bis(trimethylstannyl)thiophene,[39] 2,5-bis(trimethylstannyl)thieno[2,3-*b*]thiophene,[40] 2,7-dibromo-9,9-dihexyl-9*H*-fluorene,[41] 3-decylthiophene,[42] 2-bromo-3-decylthiophene,[43] 1,5-diiodonapthalene,[44] and 4,7-dibromo-2,1,3-benzothiadiazole[45] were synthesized according to the literature procedures; we obtained ^1H-NMR and ^{13}C-NMR spectra that are identical to the reported spectra.

2.2 Monomers

General bromination procedure. The bromination resulting in the co-monomers **1**, **2**, **3**, **4**, **5** and **6** was performed using a modified literature procedure under a nitrogen atmosphere in the dark.[46] To a cooled (0 °C) mixture of co-monomer (1.0 g) in 50 mL of THF was added drop-wise a solution of NBS (2.10–2.25 equivalents) in 15 mL of THF. The resulting mixture was allowed to warm up to RT overnight and poured into 200 mL of 0.1 M HCl followed by extraction with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed by rotary evaporation and the crude product purified by column chromatography (silica, hexane or heptane), followed by recrystallization from isopropanol/methanol (3 : 1).

3,3‴-Didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene. 3,3‴-Didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene was prepared according to modified literature procedures.[47,48] 2-Bromo-3-decyl thiophene (4.0 g, 13 mmol) was dissolved in 15 mL dry THF and added drop-wise to activated magnesium (380 mg, 15 mmol) at reflux. After complete addition the mixture was refluxed for an additional 5 h. The mixture was cooled to RT and cannulated to a second flask containing 5,5′-dibromo-2,2′-bithiophene (1.5 g, 5 mmol), Ni(dppp)Cl_2 (46 mg), and 40 mL of dry THF/toluene (4 : 3) before refluxing overnight. The reaction was cooled to RT, quenched with saturated NH_4Cl, extracted with CH_2Cl_2, and washed with brine. The combined organic layers were dried over



Scheme 1

Na_2SO_4 and the solvent removed by rotary evaporation. The crude product purified by column chromatography (silica) using hexanes as the eluent, followed by recrystallization from isopropanol/methanol (3 : 1) to give 3,3‴-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene (1.87 g, 60%) as a fluorescent-yellow solid. δ_H (300 MHz, $CDCl_3$) 7.16 (d, J = 5.2, 2H), 7.11 (d, J = 3.7, 2H), 7.00 (d, J = 3.8, 2H), 6.92 (d, J = 5.2, 2H), 2.85–2.67 (m, 4H), 1.62 (d, J = 7.6, 4H), 1.24 (s, 28H), 0.85 (t, J = 6.6, 6H). δ_C (50 MHz, $CDCl_3$) 140.08, 136.99, 135.50, 130.51, 130.30, 126.72, 124.06, 124.02, 32.14, 30.89, 29.85, 29.83, 29.75, 29.68, 29.57, 29.48, 22.92, 14.36. HRMS (APCI) calculated for $[M + H]^+$ 611.2868, found 611.2866.

5,5‴-Dibromo-3,3‴-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene 1. 3,3‴-Didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene (1.0 g, 1.6 mmol) was brominated with NBS (637 mg, 3.6 mmol) according to the general bromination procedure to give **1** (1.1 g, 88%). δ_H (200 MHz, $CDCl_3$) 7.08 (d, J = 3.7, 2H), 6.94 (d, J = 3.8, 2H), 6.88 (s, 2H), 2.69 (t, J = 7.9, 4H), 1.53 (s, 6H), 1.24 (s, 28H), 0.84 (t, J = 6.5, 6H). δ_C (50 MHz, $CDCl_3$) 140.74, 137.25, 134.26, 132.92, 131.89, 127.17, 124.20, 110.87, 32.13, 30.74, 29.83, 29.78, 29.62, 29.56, 29.41, 22.91, 14.36. HRMS (APCI) calculated for $[M + H]^+$ 769.1057, found 769.1058.

3,3″-Didecyl-2,2′:5′,2″-terthiophene. 3,3″-Didecyl-2,2′:5′,2″-terthiophene was prepared according to modified literature procedures.[49,50] To a mixture of 120 mL dry toluene and 40 mL dry DMF in a three-necked flask were added 2,5-bis(trimethylstannyl)thiophene (1.7 g, 4.1 mmol), 2-bromo-3-decylthiophene (2.5 g, 8.1 mmol), and $Pd(PPh_3)_4$ (150 mg, 0.13 mmol). The mixture was sparged with dry nitrogen, heated to 110 °C for 16 h, and then cooled to RT, poured over ice, and extracted with $CHCl_3$. The combined organic layers were washed with 2 M HCl solution, brine, and dried over Na_2SO_4 followed by removal of the solvent by rotary evaporation. The crude product was purified by column chromatography (silica) with petroleum ether (40–60 °C) as the eluent followed by recrystallization from isopropanol/methanol (3 : 1) to give 3,3″-didecyl-2,2′:5′,2″-terthiophene (1.4 g, 65%) as a yellow oil. δ_H (300 MHz, $CDCl_3$) 7.15 (d, J = 5.2, 2H), 7.03 (s, 2H), 6.92 (d, J = 5.2, 2H), 2.76 (t, J = 7.6, 4H), 1.71–1.56 (m, 4H), 1.24 (s, 28H), 0.85 (t, J = 6.6, 6H). δ_C (50 MHz, $CDCl_3$) 139.92, 136.26, 130.61, 130.29, 126.25, 123.93, 32.14, 30.99, 29.86, 29.80, 29.73, 29.58, 29.52, 22.92, 14.36.

5,5″-Dibromo-3,3″-didecyl-2,2′:5′,2″-terthiophene 2. 3,3″-Didecyl-2,2′:5′,2″-terthiophene (1.0 g, 1.9 mmol) was brominated with NBS (707 mg, 3.9 mmol) according to the general bromination procedure affording **2** (940 mg, 74%) as a light yellow powder. δ_H (200 MHz, $C_2D_2Cl_4$) 6.96 (s, 2H), 6.88 (s, 2H), 2.78–2.52 (m, 4H), 1.71–1.41 (m, 4H), 1.41–1.03 (s, 28H), 0.82 (t, J = 6.7, 6H). δ_C (50 MHz, $C_2D_2Cl_4$) 140.42, 134.88, 132.81, 131.46, 126.31, 110.41, 31.82, 30.46, 29.55, 29.51, 29.36, 29.35, 29.27, 29.19, 29.11, 22.65, 14.18. HRMS (APCI) calculated for $[M + H]^+$ 687.1181, found 687.1180.

2-[9,9-Dihexyl-7-(2-thienyl)-9*H*-fluoren-2-yl]thiophene. 2-[9,9-Dihexyl-7-(2-thienyl)-9*H*-fluoren-2-yl]thiophene was prepared according to modified literature procedures.[51] To 40 mL of dry DMF were added 2,7-dibromo-9,9-dihexyl-9*H*-fluorene (2.5 g, 5 mmol) and 2-thiopheneboronic acid (1.29 g, 10 mmol). To this was added crushed and dried K_3PO_4 (2.14 g, 10 mmol) to form a white suspension. The mixture was sparged with dry nitrogen three times, followed by the addition of $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and additional sparging. The reaction mixture was stirred at 110 °C overnight in the absence of light, cooled to RT, poured into ice water, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and removed by rotary evaporation. The crude product was purified by short column chromatography (silica) using petroleum ether/CH_2Cl_2 (10 : 1) as the eluent and recrystallized from isopropanol/methanol (4 : 1) to give 2-[9,9-dihexyl-7-(2-thienyl)-9*H*-fluoren-2-yl]thiophene (2.0 g, 84%) as green crystals. δ_H (300 MHz, $CDCl_3$) 7.67 (dd, 4H, J = 7.7, J = 15.4), 7.56 (s, 2H), 7.38 (d, 2H, J = 2.2), 7.29 (d, 2H, J = 5.1), 7.12 (t, 2H, J = 3.6), 2.02 (m, 4H), 1.10 (m, 12H), 0.73 (m, 10H). δ_C (200 MHz, $CDCl_3$) 151.66, 145.14, 140.17, 133.23, 128.04, 124.95, 124.51, 122.87, 120.11, 120.06, 55.26, 40.42, 31.44, 29.65, 23.70, 22.56, 13.99. HRMS (APCI) calculated for $[M + H]^+$ 499.2488, found 499.2479.

2-bromo-5-[7-(5-bromo-2-thienyl)-9,9-dihexyl-9*H*-fluoren-2-yl]thiophene 3. 2-[9,9-Dihexyl-7-(2-thienyl)-9*H*-fluoren-2-yl]-thiophene (900 mg, 1.8 mmol) was brominated with NBS (705 mg, 4.0 mmol) according to the general bromination procedure to give **3** (1.724 g, 88%) as yellow, slightly green crystals; mp 100–110 °C. δ_H (300 MHz, $CDCl_3$) 7.66 (dd, 4H, J = 7.7, J = 42.1), 7.45 (s, 2H), 7.12 (dd, 4H, J = 3.7, J = 15.0), 1.99 (m, 4H), 1.12 (m, 12H), 0.75 (t, 6H, J = 6.6), 0.65 (b, 4H). δ_C (200 MHz, $CDCl_3$) 151.82, 146.50, 140.39, 132.61, 130.85, 124.67, 123.04, 120.28, 119.79, 111.11, 73.72, 55.32, 40.35, 31.43, 29.62, 23.70, 22.55, 13.99. HRMS (APCI) calculated for $[M + H]^+$ 657.0678, found 657.0685.

2,5-Bis(3-decylthiophen-2-yl)thieno[2,3-*b*]thiophene. To a mixture of 120 mL dry toluene and 40 mL dry DMF in a dry three-necked flask were added 2,5-bis(trimethylstannyl)-thieno[2,3-*b*]thiophene (1.9 g, 4.1 mmol), 2-bromo-3-decylthiophene (2.5 g, 8.1 mmol), and $Pd(PPh_3)_4$ (150 mg, 0.13 mmol) under an atmosphere of dry nitrogen. The mixture was sparged with dry nitrogen, heated to 110 °C for 17 h, and then cooled to RT, poured over ice, and extracted with $CHCl_3$. The combined organic layers were washed with 2 M HCl, brine, and then dried over Na_2SO_4 and followed by removal of the solvent by rotary evaporation. The crude product was purified by column chromatography (silica) with petroleum ether as the eluent, followed by recrystallization from isopropanol/methanol (3 : 1) to give the product (1.3 g, 51%) as a white powder. δ_H (300 MHz, $CDCl_3$) 7.20 (d, J = 6.1, 4H), 6.94 (d, J = 5.2, 2H), 2.85–2.66 (m, 4H), 1.63 (s, 4H), 1.24 (s, 28H), 0.85 (t, J = 6.6, 6H). δ_C (50 MHz, $CDCl_3$)146.54, 140.64, 138.67, 130.75, 130.70, 130.08, 124.60, 119.21, 32.13, 31.12, 29.83, 29.76, 29.70, 29.57, 29.36, 22.92, 14.36. HRMS (APCI) calculated for $[M + H]^+$ 585.2712, found 585.2712. Calc. for $C_{34}H_{48}S_4$: C, 69.81; H, 8.27; S, 21.92. Found: C, 69.52; H, 8.26; S, 22.22%.

2,5-Bis(5-bromo-3-decylthiophen-2-yl)thieno[2,3-*b*]thiophene 4. 2,5-Bis(3-decylthiophen-2-yl)thieno[2,3-*b*]thiophene (1 g, 1.7 mmol) was brominated with NBS (640 mg, 3.6 mmol) according to the general bromination procedure affording **4** (807 mg, 65%)

as an off-white powder. δ_H (200 MHz, $CDCl_3$) 7.13 (s, 2H), 6.91 (s, 2H), 2.64 (t, $J = 7.7$, 4H), 1.76–1.42 (m, 4H), 1.42–1.00 (m, 28H), 0.83 (t, $J = 6.6$, 6H). δ_C (50 MHz, $CDCl_3$) 146.02, 141.17, 137.14, 132.58 (2×), 131.59, 119.32, 111.03, 31.82, 30.62, 29.52, 29.47, 29.33, 29.25, 29.01, 22.65, 14.18. HRMS (APCI) calculated for $[M + H]^+$ 743.0901, found 743.0898. Calc. for $C_{34}H_{46}Br_2S_4$: C, 54.98; H, 6.24; S, 17.27. Found: C, 54.49; H, 6.23; S, 17.39%.

2.3 Polymers

General BiPi polymerization procedure. All reactions were performed under anhydrous conditions under a nitrogen atmosphere. To a three-necked flask of stirring solvent were added equal molar quantities of monomer and bis(pinacolato)diboron. The solution was then sparged with dry nitrogen for 10 min before the addition of 5 mol% 1,1′-bis(diphenylphosphino)-ferrocenepalladium(II)dichloride dichloromethane complex ($Pd(dppf)Cl_2$; Fig. S4†) and 5 eq. of crushed K_3PO_4 and an additional 10 min of sparging. The mixture was heated to 110 °C and stirred for 24 h, cooled to RT, and the solvent removed by rotary evaporation. The remaining residue was dissolved in a minimal amount of $CHCl_3$ and precipitated by pouring slowly into 1 L of CH_3OH. To facilitate the precipitation, 1 mL of concentrated HCl was then added. The resulting slurry was stirred for an hour and the precipitate collected by centrifugation at 4000 rpm for 10 min and dried *in vacuo*. The crude polymer was then purified in a Soxhlet extractor using CH_3OH, acetone, and $CHCl_3$, in which the purified polymer dissolved before being re-precipitated into cold CH_3OH and dried *in vacuo*.

General Stille polymerization procedure.[52] All reactions were performed under anhydrous conditions under a nitrogen atmosphere. To a three-necked flask of stirring solvent were added equal molar quantities of both monomers. The solution was then sparged with dry nitrogen for 10 min before the addition of 5 mol% $Pd(PPh_3)_4$ and an additional 10 min of sparging. The mixture was heated to reflux and stirred for 24 h, cooled to RT, and the solvent removed by rotary evaporation. The remaining residue was treated identically as the general BiPi polymerization procedure.

Poly(3,3′-didecyl-quaterthiophene) PQT-BiPi. K_3PO_4 (552 mg, 2.6 mmol), **1** (400 mg, 0.52 mmol), BiPi (132 mg, 0.52 mmol), $Pd(dppf)Cl_2$ (7 mg, 0.008 mmol) were reacted in 25 mL of dry DMF according to the general BiPi polymerization procedure. Pure **PQT-BiPi** (128 mg, 37%) was obtained as a dark red powder. δ_H (300 MHz, CD_2Cl_2) 7.45–6.73 (b, 6H), 2.98–2.60 (b, 4H), 1.93–1.52 (b, 4H), 1.52–1.03 (b, 28H), 1.03–0.72 (b, 6H). ATR-IR (cm^{-1}): 3062, 2951, 2918, 2848, 1495, 1455, 1375, 1260, 1065, 821, 780, 720.

Poly(3,3′-didecyl-quaterthiophene) PQT-BiPi-2. K_3PO_4 (550 mg, 2.6 mmol), **1** (400 mg, 0.52 mmol), BiPi (132 mg, 0.52 mmol), $Pd(dppf)Cl_2$ (7 mg, 0.008 mmol) were reacted in a mixture of 8 mL dry DMF and 17 mL dry toluene according to the general BiPi polymerization procedure. Pure **PQT-BiPi-2** (268 mg, 77%) was obtained as a dark red powder. δ_H (300 MHz, CD_2Cl_2) 7.35–6.85 (b, 6H), 2.97–2.56 (b, 4H), 1.87–1.53 (b, 4H), 1.53–1.05 (b, 28H), 1.01–0.72 (b, 6H). ATR-IR (cm^{-1}): 3062, 2918, 2849, 1495, 1456, 1375, 1189, 1067, 821, 780, 720.

Poly(3,3′-didecyl-terthiophene) PTBT-BiPi. K_3PO_4 (223 mg, 1.5 mmol), **2** (150 mg, 0.22 mmol), BiPi (56 mg, 0.22 mmol), $Pd(dppf)Cl_2$ (5 mg, 0.006 mmol) were reacted in 20 mL of dry DMF according to the general BiPi polymerization procedure. Pure **PTBT-BiPi** (56 mg, 48%) was obtained as a dark red powder. δ_H (300 MHz, CD_2Cl_2) 7.45–6.70 (b, 4H), 3.04–2.56(b, 4H), 1.89–1.52 (b, 4H), 1.51–1.11 (b, 28H), 1.04–0.73 (b, 6H). ATR-IR (cm^{-1}): 3062, 2952, 2918, 2849, 1497, 1456, 1376, 1187, 1065, 821, 782, 720.

Poly[2,7-(9,9-dihexylfluorene)-*alt*-bithiophene] PFBT-BiPi. K_3PO_4 (806 mg, 3.8 mmol), **3** (500 mg, 0.76 mmol), BiPi (193 mg, 0.76 mmol), $Pd(dppf)Cl_2$ (14 mg, 0.017 mmol) were reacted in 25 mL of dry DMF according to the general BiPi polymerization procedure. Pure **PFBT-BiPi** (279 mg, 74%) was obtained as a yellow/green powder. δ_H (300 MHz, CD_2Cl_2) 8.02–7.47 (b, 6H), 7.47–6.98 (b, 4H), 2.38–1.74 (b, 4H), 1.40–0.91 (b, 12H), 0.91–0.45 (b, 10H). ATR-IR (cm^{-1}): 3064, 2922, 2850, 1888, 1748, 1606, 1464, 1416, 1375, 1257, 1196, 1134, 1065, 1005, 878, 815, 788, 742, 722.

Poly(2,5-bis(3-decylthiophen-2-yl)thieno[2,3-b]thiophene) PDTT-BiPi. K_3PO_4 (551 mg, 2.6 mmol), **4** (400 mg, 0.53 mmol), BiPi (134 mg, 0.53 mmol), $Pd(dppf)Cl_2$ (7 mg, 0.008 mmol) were reacted in 25 mL of dry DMF according to the general BiPi polymerization procedure. Pure **PDTT-BiPi** (208 mg, 67%) was obtained as a red powder. δ_H (300 MHz, CD_2Cl_2) 7.31–7.12 (b, 2H), 7.12–6.87 (b, 2H), 2.96–2.52 (b, 4H), 1.87–1.52 (b, 4H), 1.52–0.98 (b, 28H), 0.98–0.68 (b, 6H). ATR-IR (cm^{-1}): 3068, 2951, 2917, 2848, 1628, 1512, 1455, 1376, 1260, 1158, 821, 719.

Poly(3,3′-didecyl-quaterthiophene) PQT-Stille. 5,5′-Bis-(trimethylstannyl)-2,2′-bithiophene (492 mg, 1.0 mmol), 5,5′-dibromo-4,4′-didecyl-2,2′-bithiophene (605 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) were reacted in a mixture of 17 mL dry DMF and 80 mL dry toluene according to the general Stille polymerization procedure. Pure **PQT-Stille** (552 mg, 90%) was obtained as a dark red powder. δ_H (300 MHz, CD_2Cl_2) 7.85–6.61 (b, 6H), 3.18–2.31 (b, 4H), 1.91–1.52 (b, 4H), 1.52–1.04 (b, 28H), 1.00–0.72 (b, 6H). ATR-IR (cm^{-1}): 3061, 2951, 2917, 2848, 1493, 1455, 1435, 1375, 1309, 1158, 1120, 820, 779, 722.

Poly(3,3′-didecyl-terthiophene) PTBT-Stille. 2,5-Bis-(trimethylstannyl)thiophene (410 mg, 1.0 mmol), 5,5′-dibromo-4,4′-didecyl-2,2′-bithiophene (605 mg, 1.0 mmol), $Pd(PPh_3)_4$ (59 mg, 0.05 mmol) were reacted in a mixture of 16 mL dry DMF and 80 mL dry toluene according to the general Stille polymerization procedure. Pure **PTBT-Stille** (160 mg, 30%) was obtained as a dark red powder. δ_H (300 MHz, CD_2Cl_2) 6.68–6.15 (b, 4H), 2.42–1.61 (b, 4H), 1.20–0.84 (b, 4H), 0.84–0.33 (b, 28H), 0.33–0.02 (b, 6H). ATR-IR (cm^{-1}): 3061, 2951, 2916, 2848, 1497, 1456, 1434, 1375, 1260, 1183, 1066, 817, 776, 719.

Poly[2,7-(9,9-dihexylfluorene)-*alt*-bithiophene] PFBT-Stille. 5,5′-Bis(trimethylstannyl)-2,2′-bithiophene (491 mg, 1.0 mmol), 2,7-dibromo-9,9-dihexyl-9*H*-fluorene (492 mg, 1.0 mmol),

$Pd(PPh_3)_4$ (58 mg, 0.05 mmol) were reacted in a mixture of 17 mL dry DMF and 83 mL dry toluene according to the general Stille polymerization procedure. Pure **PFBT-Stille** (356 mg, 71%) was obtained as a dark orange powder. δ_H (300 MHz, CD_2Cl_2) 8.29–6.62 (b, 10H), 3.31–2.60 (b, 2H), 2.63–1.78 (b, 2H), 1.49–0.93 (b, 12H), 0.93–0.21 (b, 10H). ATR-IR (cm^{-1}): 3064, 2922, 2850, 1888, 1748, 1602, 1455, 1375, 1256, 1195, 1134, 1066, 1005, 979, 877, 816, 788, 752.

Poly(2,5-bis(3-decylthiophen-2-yl)thieno[2,3-*b*]thiophene) PDTT-Stille. 2,5-Bis(trimethylstannyl)thieno[2,3-*b*]thiophene (600 mg, 1.0 mmol), 5,5′-dibromo-4,4′-didecyl-2,2′-bithiophene (774 mg, 1.0 mmol), $Pd(PPh_3)_4$ (75 mg, 0.06 mmol) were reacted in a mixture of 25 mL dry DMF and 75 mL dry toluene according to the general Stille polymerization procedure. Pure **PDTT-Stille** (659 mg, 87%) was obtained as a dark orange powder. δ_H (300 MHz, CD_2Cl_2) 7.42–7.14 (b, 2H), 7.14–6.91 (b, 2H), 3.01–2.41 (b, 4H), 1.98–1.52 (b, 4H), 1.52–1.13 (b, 28H), 1.05–0.73 (b, 6H). ATR-IR (cm^{-1}): 3068, 2918, 2849, 1648, 1536, 1456, 1375, 1302, 1159, 1100, 1063, 963, 898, 818, 720.

3. Results and discussion

3.1 Nomenclature

For brevity, we use “X” to denote a generic monomer or repeat-unit, omitting H end-groups. Thus, X_n refers to bis-H-terminated polymer chains and, for example, SnX_n, and BrX_nBr refer to mono-Sn-terminated and bis-Br-terminated polymer chains, respectively. When necessary, the two monomers of a co-polymerization are distinguished with superscripts, *e.g.*, X^A and X^B; in these cases X_n is equivalent to $(X^AX^B)_n$. We refer to all boronate end-groups as “B” (boronate esters are hydrolyzed during the work-up). We use “Y” to refer to variable end-groups (*e.g.*, either B or Br). We abbreviate “MALDI-TOF” as “MT.” We abbreviate molecular-weight as “MW” (not to be confused with M_w).

3.2 The proposed mechanism of the BiPi method

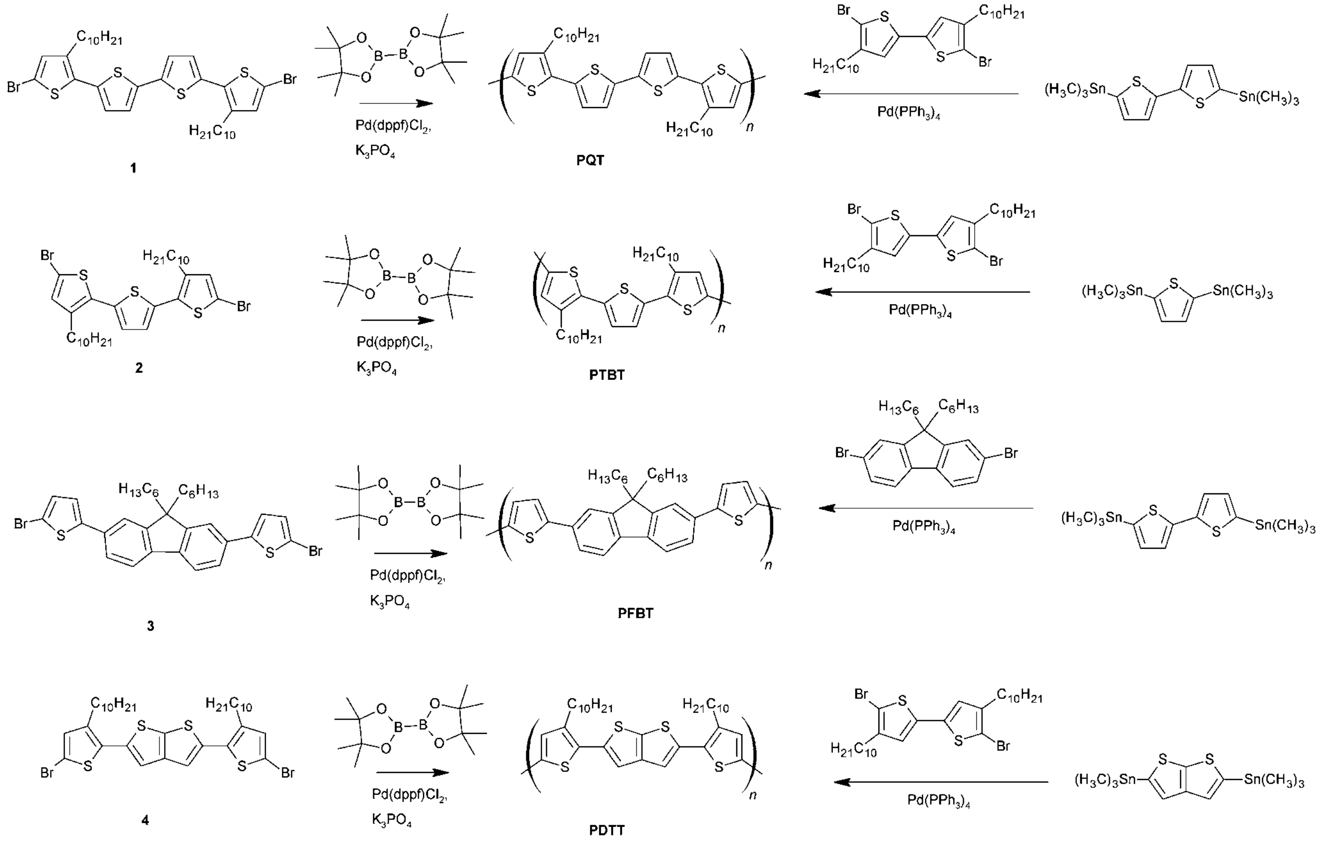
The likely mechanism of the BiPi method is that of two palladium-mediated catalytic cycles (Fig. S5†). In one cycle (Miyaura), the active Pd^0 species oxidatively inserts into a C–Br bond and exchanges Br^- for $K_2PO_4^-$ (from the base). The resulting K_2PO_4PdXBr complex then transmetallates with BiPi and the Pd^{II} reductively eliminates, forming the asymmetric BXBr monomer *in situ* (and inert K_2PO_4B). This monomer can then either undergo a second palladium-mediated bromine–boron exchange or enter the other catalytic cycle (Suzuki) and react with another YXBr (where Y = Br, B, or a growing polymer chain). The rate-limiting steps for entry and exit in both cycles are oxidative insertion and transmetallation, respectively. It does not matter which specific monomers react (*e.g.*, BrXBr with BrXB, BXB with BrXB, *etc.*) because the absolute stoichiometry is set by the co-monomer and the BiPi. However, since oxidative insertion is slower for BrXB than for BrXBr, we assume that BXB is not present in significant quantities. The equilibrium stoichiometry will be dictated by the relative rates of transmetallation in the two cycles. It has been demonstrated that treating aryl halides with KOAc and BiPi in the presence of a palladium catalyst produces boronated products, while a stronger base (*e.g.*, K_2CO_3) produces symmetric biaryls.[53] This result indicates that the cross-coupling step is the rate-determining step overall in the BiPi method (*i.e.*, that the Suzuki cycle is slower than the Miyaura) because bases specifically activate the transmetallation step of the Suzuki reaction, meaning that the polymerization is sensitive to the stoichiometry of BiPi. However, unlike the *ex situ* generation of co-monomers discussed above, BiPi is easy to obtain in high purity, as well as the bis-bromo co-monomers.

The presence of a strong base also promotes deboronation, where $B(OR)_2$ is lost and then replaced by H during the work-up. Regardless of the exact mechanism of deboronation, we make the assumption that the longer the boronated compounds persist in the reaction mixture, the more likely they are to deboronate. Thus, if the Suzuki cycle is sufficiently fast, the equilibrium concentration of BrXB will remain low because it will be quickly captured by the Suzuki cycle and either initiate or propagate a polymer chain. If, however, the Suzuki reaction is decelerated, BrXB will persist (and some BXB may form) and we will observe more deboronated products. Conversely, if the Suzuki is accelerated, we will observe more Br-terminated products. These pathways are summarized in Scheme 1.

3.3 Comparison of the BiPi and Stille GPC data

To compare the BiPi method to the Stille method, we divided the “quality” of a polymer into four observables: (i) MW, (ii) PDI (M_w/M_n), (iii) yield, and (iv) uniformity (*i.e.*, distribution of endgroups). We then synthesized the four thiophene-based, symmetric co-monomers shown in Scheme 2. We prepared two sets of four polymers: one by directly polymerizing these bis-bromo comonomers using the BiPi method (homo-polymerization) and the other by co-polymerizing the appropriate bis-bromo and bis-stannyl monomers (Scheme 2). We chose the Stille copolymerization as a fair comparison to the BiPi homopolymerization for three reasons: (i) the well known tendency of thiophene-based monomers to deboronate under standard Suzuki copolymerization conditions, (ii) to compare the composition of polymers from tin-based crosscouplings to that of boron-based, and (iii) because Stille co-polymerizations are more commonly used for thiophene-based monomers.[54] We chose $Pd(PPh_3)_4$ over more sophisticated (and possibly better) Pd catalysts because it is the most widely used. We adapted the specific conditions for the BiPi method from Bräse *et al.*[55] and Wu *et al.*[56] We characterized the resulting polymers by NMR, FT-IR, GPC, and MT mass-spectrometry.[6,9] The NMR data (see Experimental) confirmed the connectivity of the polymers, but were not sensitive enough to differentiate the end-groups. Similarly, FT-IR data confirmed the presence/absence of expected/unexpected functional groups in the polymers. Neither revealed any abnormalities with either method. Although GPC is known to over-estimate the MW of conjugated polymers,[6] we are, in principle, comparing structurally identical polymers that differ only by how they were prepared. Table 1 summarizes these GPC data.

The BiPi method, in all cases, gave a slightly (within one unit) higher PDI than the Stille method. This may be because of the relatively slow propagation step (which is limited by transmetallation) of the Suzuki cycle, leading to a higher frequency of



Scheme 2

chain-terminating (and monomer-consuming) deboronation reactions. Monomers **1** and **2** both gave approximately the same M_n for the Stille and BiPi methods (**PQT-BiPi/PQT-Stille**), while the M_w was somewhat higher for the BiPi method. This means that the BiPi method produces, on average, higher MW chains than the Stille (presumably because it is a homo-polymerization and does not suffer from chain-terminating reactions due to imbalances in stoichiometry). Initially, **PQT-BiPi** was also obtained in a significantly lower yield than **PQT-Stille**, suggesting that not all of **1** was converted to the active co-monomer (*i.e.*, BrXB) *in situ*, leading to fewer, longer polymer chains. We thought that solubility may be playing a role and polymerized **1** by the BiPi method, but using the same solvents as the Stille, producing **PQT-BiPi-2** not only in a similar yield to **PQT-Stille**, but also with almost an identical M_n, M_w, M_z, and PDI. The same did not hold true for **2**, which, despite the structural similarity to **1**, produced **PTBT-BiPi** in a higher yield, M_n, M_w, M_z, and PDI than **PTBT-Stille**.

Table 1 GPC data and yields of polymers comparing BiPi and Stille

Monomer/ reaction	Polymer	Solvent	Yield (%)	M_n	M_w	M_z	PDI
1/BiPi	**PQT-BiPi**	DMF	37	6709	17 557	49 153	2.62
1/BiPi	**PQT-BiPi-2**	Tol/DMF (3 : 1)	77	5204	9555	17 262	1.84
1/Stille	**PQT-Stille**	Tol/DMF (3 : 1)	90	5875	9488	14 184	1.61
2/BiPi	**PTBT-BiPi**	DMF	48	8921	22 870	63 272	2.56
2/Stille	**PTBT-Stille**	Tol/DMF (3 : 1)	30	8733	16 142	25 991	1.85
3/BiPi	**PFBT-BiPi**	DMF	74	9464	25 800	79 697	2.73
3/Stille	**PFBT-Stille**	Tol/DMF (3 : 1)	71	3976	8758	15 760	2.20
4/BiPi	**PDTT-BiPi**	DMF	67	5718	16 349	44 590	2.86
4/Stille	**PDTT-Stille**	Tol/DMF (3 : 1)	87	10 092	20 169	33 811	1.99

The polymerization of **3** using the BiPi method produced **PFBT-BiPi** in about the same yield as **PFBT-Stille**, but with a much higher M_n and almost the same PDI. This is likely because fluorenes are more electron-withdrawing than thiophenes and therefore increase the rate of the Suzuki cycle. (Reynolds *et al.* recently showed that fluorene-based polymers, lacking thiophenes, can be prepared in very high yields by a fluoride-promoted BiPi homo-polymerization in the absence of base.[34]) We found exactly the opposite for the cross-conjugated monomer **4**, obtaining **PDTT-BiPi** in lower yield, M_n, M_w, M_z, and higher PDI than **PDTT-Stille**. This means that either the Suzuki or Miyaura cycle (or both) is inhibited significantly for **4**. (Thienothiophene is also more electron-withdrawing than thiophene.[57]) To directly probe the relative rates of the two cycles, we prepared the BXB co-monomer of **4** and reacted it with **4** under the same conditions, but encountered difficulties in isolating and purifying BXB and were unable to isolate any polymer.

3.4 Comparison of BiPi and Stille MALDI-TOF data

Of the four measures of quality, the most telling is the uniformity, which we probed by MT analysis. Unlike GPC, MT tends to underestimate the MW of polydisperse polymers because higher MW chains do not desorb easily.[58,59] Effective ionization and desorption are necessary to obtain high quality MT spectra and the choice of matrix and optimized sample preparation for each individual type of polymer is critical.[60] This includes the manual adjustment of laser power, affecting the ability to resolve higher MW chains. We partially offset this using a low-mass gate (LMG), which blocks low-mass ions from reaching the sensor, improving the signal-to-noise ratio (SNR).[61] What MT does provide is an accurate picture of the distributions of chains in terms of end-groups (*i.e.*, uniformity).[6]

In analyzing MT data, we must take into account the possibility of side-reactions (*i.e.*, reactions that do not form the desired polymer structure). For example, although the use of Stille co-polymerizations to form thiophene-based polymers is well established, side-reactions are prevalent.[12,14,49] The homo-coupling of stannanes is the most common, leading to defects in the backbone of the polymer and a stoichiometric imbalance of monomers. Less pronounced is the transfer of methyl groups (from the tin center) and phenyl groups (from the Pd center) to the polymer and destannylation by trace acids, all of which compete with the co-polymerization. The side reactions of the Suzuki cycle are similar:[16,62] homo-coupling, phenyl transfer, and deboronation. This can not only deplete monomers and terminate growing chains, but also leads to more uniform endgroups. Homocoupled products cannot be distinguished from hetero-coupled products because we used symmetric monomers. We did not observe any products of phenyl-transfer. Direct debromination is not likely under the BiPi conditions, and it is more likely that Br is lost *via* deboronation after the Miyaura cycle. (And in the transmetallation step of the Stille.[63]) This means that for the BiPi method, the three most probable end-groups are $B(OH)_2$ (boronate esters are hydrolyzed during the workup), Br, and H. The analysis of the possible end-groups produced by Stille co-polymerizations is much more complicated. As discussed above, Janssen *et al.* found that standard Suzuki co-polymerizations produce 11 combinations of end-groups, excluding side reactions.[14–17] We found approximately the same number for Stille co-polymerizations. However, because the BiPi method is a homo-polymerization of symmetric co-monomers, it can produce at most six. An important difference between the BiPi and Stille methods is that the chains of the copolymers prepared using the BiPi method initiate and terminate with the same monomer, while those from the Stille method can initiate or terminate with either of the two monomers (Fig. S2†). The distribution of these end-groups will appear as clusters around $n \times M$ where n is the number of monomers in the chain and M is the mass-to-charge ratio (*m*/*z*) of the most prevalent chain.

Fig. 1 is a comparison of the MT spectra for polymers **1–4**, comparing the BiPi and Stille methods. The calculated mass of the X_n chains is indicated. The two most obvious features of the polymers prepared by the BiPi method are that they contain higher MW chains (with the exception of PDTT) and much more clearly defined distributions of these chains. By contrast, all of the polymer chains prepared by the Stille method contain three pronounced peaks corresponding to X^BX_n, X_n, and X_nX^A—a result of co-polymerizing two monomers. The distribution of smaller peaks comprises various combinations of these chains terminated with Br, H, CH_3, and Sn endgroups. We did not observe any boronate-terminated chains. (They are likely lost through deboronation after the polymerization is complete and then converted to H during the work-up.) Thus, the BiPi method generates only three of the six possible types of chains: X_n, BrX_n, and BrX_nBr.

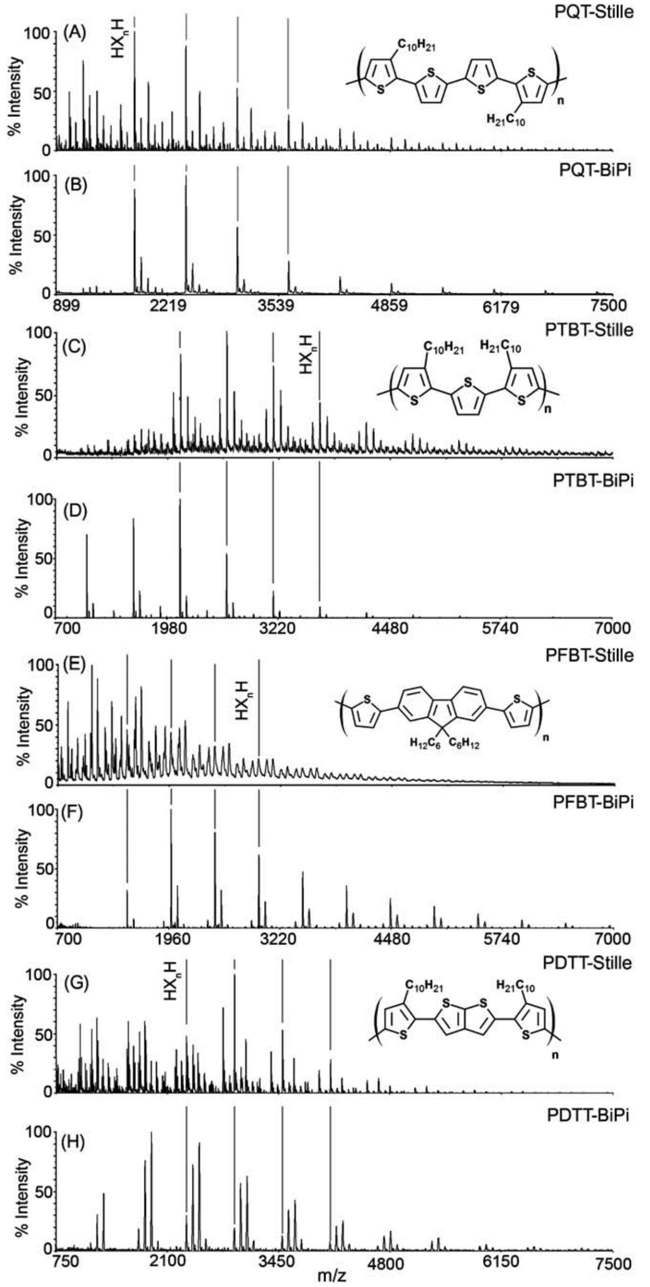


Fig. 1 A comparison of the MALDI-TOF spectra for polymers prepared using the BiPi and Stille methods from monomers **1** (A and B), **2** (C and D), **3** (E and F), and **4** (G and H). The vertical lines are the calculated masses for polymer chains that are H-terminated (where X is the repeat unit).

The MT spectrum of **PQT-BiPi** (Fig. 1B), which was obtained in a much lower yield than **PQT-Stille** (Fig. 1A), is composed almost entirely of X_n chains. In addition to these chains, there are two smaller peaks corresponding to the BrX_n and BrX_nBr chains in decreasing intensity (Fig. 2B). We observed the same trend for **PQT-BiPi-2** (Fig. 2C). Although **PQT-BiPi-2** has a lower M_w than **PQT-BiPi**, it is composed almost entirely of X_n chains, indicating deboronation as a likely cause of the lower MW. The only difference between **PQT-BiPi** an **PQT-BiPi-2** is that the former was prepared in pure DMF and the latter in 3 : 1 toluene/DMF. It is known that DMF accelerates standard Suzuki polymerizations,[49,64] but that toluene is a better solvent for the resulting polymer. Thus, assuming no direct debromination, the toluene is likely decreasing the relative rate of the Suzuki cycle, which allows more time for chain-terminating deboronation reactions. The yield of **PQT-BiPi-2**, however, is double that of **PQT-BiPi**. These data imply that the dominant pathways in the **PQT-BiPi** polymerization are rapid chain-growth followed by deboronation and debromination immediately after initiation, while the dominant pathway for **PQT-BiPi-2** is (slower) chain-growth followed by deboronation, resulting in a lower M_w and PDI, but higher yield for **PQTD-BiPi-2** than **PQTD-BiPi**.

The MT spectrum of **PQT-Stille**, the GPC data for which are almost identical to those of **PQT-BiPi-2**, reveals a strikingly different MT spectrum comprising a relatively even distribution of end-groups. The two prominent peaks at higher m/z than X_n correspond to the X^BX_n and X_nX^A chains (the MW of X^A and X^B are different) and are much more prevalent than the BrX_n and BrX_nBr chains are for **PQT-BiPi** and **PQT-BiPi-2** (Fig. 2B). The small peaks near the baseline comprise the remaining possible combinations of end-groups (*e.g.*, BrX_n, X_nX^ABr, X_nSn, *etc.*).

The MT spectrum of **PTBT-BiPi** (Fig. 1D) again shows X_n chains, but no chains above $n = 9$ are visible. While it is expected that the intensity of peaks will decay as a function of MW, these data do not agree with the GPC data, which show a higher M_w for **PTBT-BiPi** than **PTBT-Stille**. The MT spectrum of **PTBT-Stille** (Fig. 1C) clearly shows higher MW chains, even though both spectra were acquired using the same conditions. In order to see the higher MW peaks for **PTBT-BiPi**, we had to adjust the LMG. These data are summarized in Fig. 3. With the LMG set at 4000 m/z, chains up to $n = 14$ are clearly visible (Fig. 3A), and chains up to $n = 27$ are visible (Fig. 3B), though with a much lower SNR. Once again, a blow-up of the (un-gated) spectrum shows that there are very few BrX_n chains and almost no BrX_nBr chains present (Fig. 3C). By contrast, the spectrum of **PTBT-Stille** clearly resolves peaks up to $n = 12$, but there is much less uniformity in the chains (Fig. 1C). Peaks corresponding to X^BX_n and X_nX^A chains are clearly visible, in addition to the various Sn-, Br-, *etc.* terminated chains. Qualitatively, **PTBT-BiPi** is similar to **PQT-BiPi** and is much more uniform than **PTBT-Stille**, though we cannot explain why it was necessary to set the LMG to 4000 to see chains of $n > 9$. It may be that **PTBT-BiPi** is more crystalline than **PTBT-Stille** and therefore more difficult to desorb, or simply fluctuations in the laser in the time (days) between measurements.

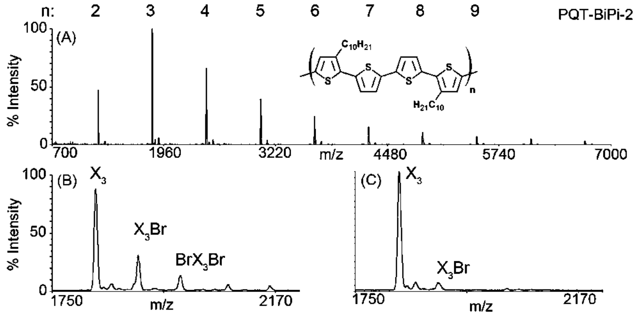


Fig. 2 The MALDI-TOF spectrum of **PQT-BiPi-2** (A), a blow-up of the spectrum of **PQT-BiPi** (B), and a blow-up of the same region of the spectrum of **PQT-BiPi-2** (C). The peaks corresponding to bis-H-terminated (X_n) and Br-terminated chains (X_nBr and BrX_nBr) are labeled.

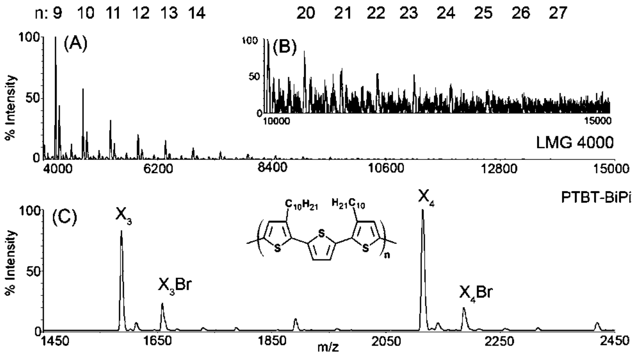


Fig. 3 The MALDI-TOF spectrum of **PTBT-BiPi** with the low-mass gate set at 4000 showing n = 9–14 (A), a blow-up of this spectrum comprising the region n = 20–27 (B), and a blow-up of n = 3–4 (C). The peaks corresponding to bis-H-terminated (X_n) and Br-terminated chains (X_nBr and BrX_nBr) are labeled.

The MT spectrum of **PFBT-BiPi** (Fig. 1F) shows a higher degree of BrX_n chains than for **PQT-BiPi**, **PQT-BiPi-2**, and **PTBT-BiPi**, but essentially no BrX_nBr (Fig. 4). Given the relatively high yield of **PFBT-BiPi**, it is not likely that the fluorene unit is decelerating the Suzuki cycle, causing deboronation of the monomer (thus leaving unreacted BrX_n chains). We postulate that the Suzuki cycle is accelerated for growing chains containing fluorene, meaning that BXBr is coupled to BX_nBr as soon as it is formed, while for the growth of **PQT-BiPi** chains, BrX_nB persists longer, allowing it to be converted to BX_nB, leading to a higher percentage of X_n. It is also possible that **1** and **2** form BXB monomers that couple with YX_nBr. In either case, fluorene is accelerating the Suzuki cycle. What is clear is that, in agreement with the GPC data, **PFBT-Stille** is composed of lower MW chains comprising a nearly equal mixture of every possible combination of end-groups (Fig. 1E).

The MT spectrum of **PDTT-BiPi** (Fig. 1H) shows that the predominant chains are BrX_n and BrX_nBr (Fig. 5D), suggesting

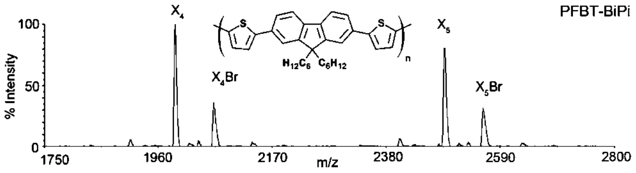


Fig. 4 A blow-up of the MALDI-TOF spectrum of **PFBT-BiPi** with the peaks corresponding to bis-H-terminated (X_n) and mono-Br-terminated chains (X_nBr) labeled.

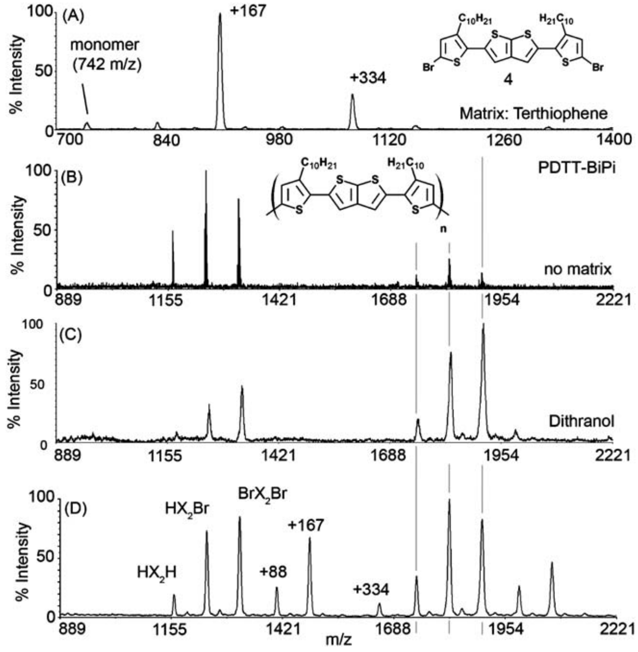


Fig. 5 The MALDI-TOF spectrum of: **4** using a terthiophene matrix (A), **PDTT-BiPi** without a matrix (B), **PDTT-BiPi** in a dithranol matrix and (C), and a blow-up of the spectrum of **PDTT-BiPi** in a terthiophene matrix (D). The peaks corresponding to bis-H-terminated (X_n) and Br-terminated chains (X_nBr and BrX_nBr) are labeled. Peaks labeled +88 and +167 correspond to the addition of one and two terthiophenes, respectively.

that the Suzuki cycle is accelerated. However, **PDTT-Stille** is formed in higher yields and MW than **PDTT-BiPi**—the opposite of what was observed for **PFBT-BiPi** and **PFBT-Stille**. This means that, either the Miyaura cycle for **4** is so slow that the reaction time is not sufficient to convert all of it to BrXB, or that BrXB deboronates too rapidly to efficiently polymerize—we suspect the latter. The lack of X_n means that BrX_nB and BrXB are less reactive towards the Miyaura cycle than for **PFBT-BiPi**. The abundance of BrX_nBr (the dominant product) means that chain-growth occurs mainly between BrX_nBr and BrXB. Thus, the net effect is that entry into the Suzuki cycle is significantly accelerated (*i.e.*, BrXB enters the Suzuki as soon as it is formed), but that deboronation is also disproportionately accelerated compared to **PFBT-BiPi**. We postulate that the active monomer, BrXB is simply unstable such that deboronation (or decomposition) competes with the Suzuki cycle. This could be because thienothiophene groups activate an alternate pathway for deboronation or slow the exit from the Suzuki cycle (*i.e.*, transmetallation). Aside from being more electronegative than thiophene, thienothiophene is crossconjugated. It is possible that the extended conjugation formed by growing polymer chains accelerates the Suzuki cycle and that this effect is absent for **PDTT-BiPi**.

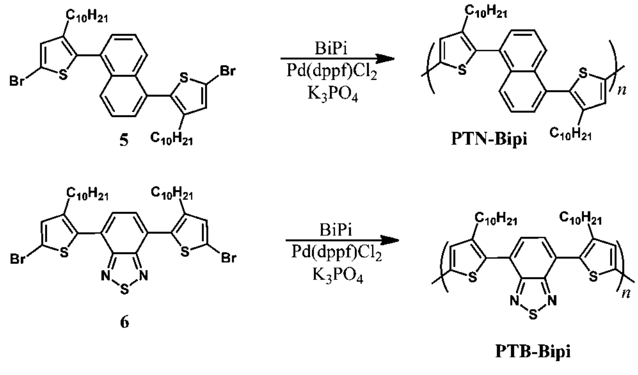
An unexpected feature of the MT of **PDTT-BiPi** are extra peaks at X_n +88 and +167 *m*/*z*, corresponding to the addition of one and two terthiophenes from the matrix, respectively, and in the same relative ratios as BrX_n and BrX_nBr. This is probably due to the higher UV cross-section of **PDTT-BiPi** compared to the other polymers. To ensure that these extra peaks were in fact due to terthiophene, we performed two additional MT measurements, one without a matrix (Fig. 5B) and one in a dithranol matrix (Fig. 5C). We also measured **4** in a terthiophene matrix and found that it reacts almost completely with terthiophene (Fig. 5A).

3.5 Other polymers prepared using BiPi

To help understand the different behaviors of the thiophene-monomers **1** and **2**, *versus* the fluorene-monomer **3** and thienothiophene-monomer **4** towards the BiPi polymerization, we prepared two additional monomers and polymerized them using the BiPi method, forming **PTN-BiPi** (naphthalene-containing) and **PTB-BiPi** (benzothiadiazole-containing; Scheme 3).[65] Monomer **5** is expected to behave similarly to **3** because naphthalene is more similar to fluorene in terms of reactivity and electronegativity than it is to thiophene. Likewise, monomer **6** is expected to behave similarly to **4** because benzothiadiazole is much more electron-withdrawing and reactive than thiophene, fluorene, or naphthalene. Indeed, the MT spectrum of **PTN-BiPi** is almost identical to that of **PFBT-BiPi**—the predominant chains are X_n, with a significant amount of BrX_n, but a complete lack of BrX_nBr (ESI†). The MT spectrum of **PTB-BiPi** is also very similar to that of **PDTT-BiPi**. The predominant chains are BrX_nBr, with a small amount of BrX_n and almost no X_n (ESI†). Like **PDTT-BiPi**, **PTB-BiPi** (and **6**) reacted with the terthiophene matrix (**PTB-BiPi** also incorporated O_2) and was obtained in a lower yield than **PTN-BiPi**. The increasing amount of Br-terminated chains going from **PTN-BiPi** to **PTB-BiPi** again suggests that the Suzuki cycle is activated by electron-withdrawing groups. However, the decreasing yield suggests that at a certain point, this electronegativity accelerates deboronation as well—*i.e.*, that the active monomer, BrXB is unstable.

4. Conclusion

The BiPi method enables the syntheses of thiophene-containing co-polymers *via* the homopolymerization of symmetric Br-terminated monomers. These polymers are of a higher quality and are prepared in less steps than *via* the equivalent Stille co-polymerization. These polymers comprise chains that are initiated and terminated by the same monomer and contain only two different endgroups: Br or H. The relative proportion of BrX_nBr, BrX_n, and X_n polymers can be controlled by



Scheme 3

incorporating different groups into the monomers. Generally, thiophenes give predominantly X_n, aromatic hydrocarbons give a higher fraction of BrX_n, and highly reactive and/or electron withdrawing groups give predominantly BrX_nBr. We interpret these observations as follows: the Miyaura cycle generates the active BrXB monomer, the Suzuki grows the polymer, and deboronation terminates growing chains. The transmetallation steps of the Miyaura and Suzuki involve breaking a B–B bond and a C–B bond respectively, thus the Miyaura is generally faster. Ideally, this leads to the complete conversion of BrXBr to BrXB, followed by the homo-polymerization of BrXB to form BrX_n. Electron-withdrawing groups accelerate the oxidative insertion of Pd, balancing the two cycles and favoring the formation of BrX_n in high yields, which we observed for **PFBT-BiPi** and **PTN-BiPi**. If, however, the rate of one cycle is affected disproportionately, the dominant products will be BrX_nBr (faster Suzuki) or X_n (faster Miyaura). Groups that are too electron-withdrawing also accelerate deboronation (either by simultaneously increasing the oxidative insertion and slowing the transmetallation steps of the Suzuki cycle or creating unstable monomers), leading to lower MWs and yields. This appears to be the case for **PDTT-BiPi** and **PTB-BiPi**, which accelerate the Suzuki cycle disproportionately, forming predominantly BrX_nBr, but in low yields. **PQT-BiPi** and **PTBT-BiPi**, on the other hand, decelerate the Suzuki cycle, forming predominantly X_n in moderate yields. Thus, assuming that the deboronation takes place primarily in the Suzuki cycle and that BrXB is reasonably stable, we conclude that the most relevant factors are the relative rates that monomers/growing-chains enter the Suzuki cycle (limited by oxidative insertion) and exit it (limited by transmetallation).

This means that not only does the BiPi method enable the synthesis of otherwise inaccessible co-polymers, but that the endgroups can be tuned for specific purposes. We hope to further improve this method by better understanding the effect on the relative rates of the Suzuki and Miyaura cycles. All of the molecules we studied were polymerized through thiophenes, with only the adjacent aryl groups differing. From this, we can conclude that relatively small changes in the electronic properties of the monomers used for the BiPi polymerization influence the relative rates of the two catalytic cycles for the monomers as well as the growing chains, leading to substantial changes in the distribution of the end-groups in the resulting polymers.

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