Mechanistic Aspects of the Suzuki Polycondensation of Thiophenebisboronic Derivatives and Diiodobenzenes Analyzed by MALDI−TOF Mass Spectrometry

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ABSTRACT: Thiophenebisboronic derivatives (acids and esters) have been successfully utilized for the first time in palladium-catalyzed Suzuki polycondensations to prepare well-defined alternating thiophene−phenylene copolymers. 2,5-Thiophenebis(boronic acid) and its corresponding 1,3-propanediol and pinacol diesters have been synthesized and polymerized with 2,5-dialkoxy-1,4-diiodobenzenes in the presence of $Pd(OAc)_2$ or $Pd(PPh_3)_4$ catalysts. SEC analysis showed that the polymers have moderate molecular weight with a polydispersity of 1.2 to 2.4. The role of the boronic derivatives and the catalyst on the yield and molecular weight of the resulting polymers have been investigated in detail. MALDI−TOF mass spectrometry has been used to elucidate the limiting steps in the polymerization and to assess the end groups. The results suggest that hydrolytic deboronation limits the formation of high molecular weight polymers. The polymers prepared using $Pd(OAc)_2$ possess various end groups and contain macrocycles, whereas $Pd(PPh_3)_4$ produces much cleaner polymers. However, the use of $Pd(PPh_3)_4$ introduces phenyl end groups via aryl−aryl exchange between the catalytic palladium intermediate and the triphenylphosphine ligand. We found that this aryl−aryl exchange can be suppressed by the introduction of side chain branching in the 2,5-dialkoxy-1,4-diiodobenzene, and as result defect-free, perfectly alternating, chains with mainly thiophene end groups have been obtained in monomodal molecular weight distribution.

Introduction

In alternating conjugated copolymers, the nature of the two monomers affords a novel means to design materials with functional, optical, and electrical properties that add to the scope of applications for π-conjugated polymers. Alternating copolymers are generally prepared via palladium-catalyzed polycondensations by reacting either arylbis(boronic acid) derivatives (Suzuki method) or aryldistannyl derivatives (Stille method) with dihaloarenes.[1−11] The Suzuki route has attained more importance and is potentially more versatile than the Stille reaction mainly because the boronic derivatives are easy to handle, the reaction tolerates a large number of functional groups, and nontoxic byproducts are formed.

Surprisingly, no successful attempt has been reported for using 2,5-thiophenebisboronic derivatives in a Suzuki polycondensation to prepare alternating conjugated copolymers. Alternating thiophene−phenylene copolymers have previously been synthesized in a Suzuki polycondensation by reacting 1,4-benzenebisboronic esters with 2,5-dibromothiophenes in moderate molecular weights.[8−11] Efforts to obtain the same copolymers by using 2,5-thiophenebis(boronic acid) derivatives and 1,4-phenylene dihalides were unsuccessful.[11] Synthetically, reactive 2,5-thiophenebis(boronic acid) derivatives would be very useful because they would add to the use of Suzuki polycondensations in the synthesis of a larger variety of alternating conjugated copolymers. It is well understood in the literature that side reactions such as deboronation prior to aryl−aryl coupling in thiopheneboronic acid derivatives limit the formation of desired product in Suzuki condensation.[11−15] Recently, Guillerez et al. reported the successful synthesis of high molecular weight poly(3-octylthiophene) via a Suzuki polycondensation using a thiophene monomer bearing iodine and a boronic ester derivative in the 2- and 5-positions, respectively. By using a $Pd(OAc)_2$ catalyst instead of $Pd(PPh_3)_4$, hydrolytic deboronation could be suppressed, thereby increasing the molecular weight.[16]

Here, we report the successful application of the Suzuki polycondensation reaction to obtain thiophene−phenylene copolymers in moderate molecular weights starting from a 2,5-thiophenebis(boronic acid) derivative and a palladium catalyst. We show that the success of the polymerization reaction strongly depends on the type of catalyst and the type of boronic acid derivative used. The polymers are analyzed in detail using MALDI−TOF mass spectrometry to identify various types of end groups and to afford a deeper insight in the reaction mechanism and the limiting side reactions. While, in principle, the copolymers may contain up to 10 different types of chains due to a various combinations of end groups (not including macrocycles or products in which an aryl−aryl exchange occurred), we have been able to synthesize a perfectly alternating thiophene−phenylene copolymer containing essentially one type of chain with predominantly hydrogen terminated thiophene end groups. Both the catalyst and the monomers involved in the reaction control this selectivity.

Experimental Section

Materials. 2,5-Dibromothiophene, trimethyl borate, 1,3-propanediol, pinacol, $Pd(OAc)_2$, and $Pd(PPh_3)_4$ were purchased from Aldrich Chemical Co. and used without further purification. 2,5-Bis(2-ethylhexyloxy)-1,4-diiodobenzene and 2,5-dioctyloxy-1,4-diiodobenzene were prepared following reported procedures.[17,18]

General Procedures. The monomers and polymers were characterized by ^1H and ^{13}C NMR using a 300 MHz Varian

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NMR spectrometer in deuterated solvents and TMS was used as internal reference. For samples recorded in 1,2-dichlorobenzene-d_4 (ODCB-d_4), the upfield solvent resonance was set to 7.00 ppm and all other signals were referred with respect to this peak. The molecular weights were determined by size exclusion chromatography (SEC) in chloroform at 25 °C. The polymers were dissolved in chloroform and filtered prior to the SEC measurements. A 20 μL aliquot of the polymer solution was injected and the flow rate of chloroform was maintained at 1 mL/min. An online UV−vis detector (λ = 440 nm) was used and the instrument was calibrated using polystyrene standards. Absorption spectra of the polymers were recorded in $CHCl_3$ at 25 °C using a Perkin-Elmer Lambda 900 UV−vis−near-IR spectrophotometer. MALDI−TOF mass spectra were recorded on a PerSeptive Biosystems Voyager-DE PRO instrument in linear mode. Polymers were dissolved either in chloroform or ODCB (0.5 mg/mL) depending upon their solubility and mixed with a matrix solution of α-cyano-4-hydroxycinnamic acid in tetrahydrofuran (THF) (20 mg/mL), and 0.3 μL of the resultant mixture was used for the analysis. Alternatively, dithranol and norharman were used to check the influence of the matrix on fragmentation in the MALDI−TOF spectra. The mass spectra were calibrated with oligothiophene standards prior to further analysis.

2,5-Thiophenebis(boronic acid) (1). *n*-Butyllithium (64 mL, 1.6 M in hexane, 0.10 mol) and dry THF (40 mL) were cooled to −78 °C under an atmosphere of dry argon. Subsequently 2,5-dibromothiophene (10.0 g, 0.041 mol) dissolved in dry THF (40 mL) was added dropwise over 30 min, followed by stirring for 3 h at −78 °C. The resulting 2,5-dilithiothiophene was treated with trimethyl borate (32 mL) and stirred for 1 h at −78 °C. The reaction mixture was warmed to room temperature and stirred for 30 min before pouring onto crushed ice containing concentrated HCl (40 mL). After extraction into diethyl ether, the organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to afford a white solid. The solid was washed with *n*-hexane to remove unreacted materials and recrystallized from hot water to give **1** (4.0 g, 56%): mp 262−265 °C;[19] ^{1}H NMR (DMSO-d_6) δ 7.63 (s, Th−H(3)); ^{13}C NMR (DMSO-d_6) δ 136.6 (Th−C(3)).

2,2′-(2,5-Thiophene)bis[1,3,2-dioxaborinane] (2). 1,3-Propanediol (0.44 g, 5.8 mmol) and 2,5-thiophenebis(boronic acid) (**1**) (1.00 g, 5.8 mmol) were refluxed in dry dichloromethane (25 mL) for 12 h under an atmosphere of dry argon using a Dean−Stark trap. After the reaction the organic layer was dried over anhydrous Na_2SO_4 and solvent was removed in vacuo to afford a light brown solid. Recrystallization from *n*-hexane/$CHCl_3$ afforded **2** (0.95 g, 65%): mp 193−194 °C; ^{1}H NMR ($CDCl_3$) δ 7.56 (s, 2H, Th−H(3)), 4.17 (t, 8H, OCH_2, J = 5.2 Hz), 2.08 (m, 4H, OCH_2CH_2, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$) δ 136.1 (Th−C(3)), 62.2 (OCH_2), 27.4 (OCH_2CH_2). Anal. Calcd for $C_{10}H_{14}B_2O_4S$: C, 47.68; H, 5.60. Found: C, 47.64; H 5.98. GC−MS (MW = 252) m/z = 252 $[M]^{+\bullet}$.

2,2′-(2,5-Thiophene)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (3). 2,5-Thiophenebis(boronic acid) (**1**) (1.00 g, 5.8 mmol) was reacted with pinacol (0.69 g, 5.8 mmol) as described for **2**. After workup, the ester was purified by recrystallization from *n*-hexane/$CHCl_3$ to afford **3** (1.36 g, 70%): mp 217−218 °C;[20] ^{1}H NMR ($CDCl_3$) δ 7.68 (s, 2H, Th−H(3)), 1.33 (s, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ 137.8 (Th−C(3)), 84.2 (C−CH_3), 24.9 (−C−CH_3). Anal. Calcd for $C_{16}H_{26}B_2O_4S$: C, 57.18; H 7.80. Found C, 57.32; H, 7.46. GC−MS (MW = 336) m/z = 336 $[M]^{+\bullet}$.

Synthesis of Polymers. The polymerization was carried out by mixing the thiophene monomer (**1**, **2**, or **3**) (0.45 mmol) and the appropriate 2,5-dialkoxy-1,4-diiodobenzene (0.45 mmol) in the presence of 3 mol % of catalyst ($Pd(OAc)_2$ or $Pd(PPh_3)_4$) in THF (9 mL) under an atmosphere of dry argon. The mixture was stirred and degassed for 10 min at 25 °C. K_2CO_3 (0.19 g, 1.35 mmol) dissolved in water (1 mL) was degassed and added to the polymerization mixture. The mixture was degassed again and refluxed under an atmosphere of dry argon for 18 h. Ethanol (0.5 mL) was added as a cosolvent when the $Pd(OAc)_2$ was used as catalyst.[16] The polymers were purified by precipitating into methanol, dissolving the residue after filtration in $CHCl_3$ (by warming), and again precipitating into acetone. The final precipitate was washed with acetone until the filtrate became colorless. Finally, the purification procedure was repeated to remove all oligomers. The yields of polymers are reported in Table 1.

Table 1. Yield, Molecular Weight, and Optical Absorption of Polymers

polymer	monomer	catalyst	yield[a] (%)	M_w[b] (g/mol)	PD[c]	λ_{max}[d] (nm)
P-1	**1**	$Pd(PPh_3)_4$		1600	1.1	431
P-2	**1**	$Pd(OAc)_2$	31	3500	1.2	453
P-3	**2**	$Pd(PPh_3)_4$		1600	1.2	421
P-4	**2**	$Pd(OAc)_2$	43	3200	1.2	455
P-5	**3**	$Pd(PPh_3)_4$	76	3600	1.2	453
P-6	**3**	$Pd(OAc)_2$	90	3700	1.2	456
P-7	**3**	$Pd(PPh_3)_4$	22	7300	2.1	468
P-8	**3**	$Pd(OAc)_2$	39	11 600	2.3	468

[a] For the polymers precipitated from acetone during purification. [b] Determined by SEC in $CHCl_3$ at 25 °C against polystyrene standards. Values pertain to the $CHCl_3$-soluble fraction of the polymer. [c] Polydispersity M_w/M_n. [d] At 25 °C in $CHCl_3$.

Polymers **P-1**−**P-6**: ^{1}H NMR (ODCB-d_4) δ 7.86 (br, 2H, Ph−H), 7.50 (br, 2H, Th−H), 4.18 (br, 4H, OCH_2), 2.0 (br, 4H, OCH_2CH_2), 1.6 (br, 4H, $OCH_2CH_2CH_2$), 1.5−1.1 (br, 16H, $(CH_2)_4CH_3$), 0.92 (br, 6H, CH_3); ^{13}C NMR (ODCB-d_4) δ 149.9, 139.7, 126.5, 123.4, 112.4, 69.5, 32.3, 30.1, 29.9, 29.8, 26.8, 23.2, 14.5.

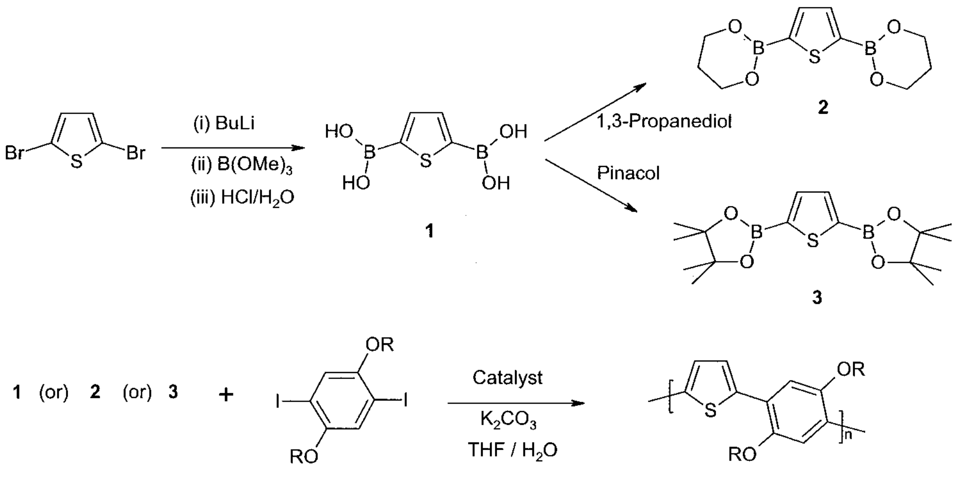
Polymers **P-7** and **P-8**: ^{1}H NMR ($CDCl_3$) δ 7.65 (br, 2H, Ph−H), 7.36 (br, 2H, Th−H), 4.08 (br, 4H, Ph−OCH_2), 2.0−1.2 (br, 24H, $CH_2(CH_2)_6$); 1.05−0.8 (br, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 149.7, 139.2, 126.3, 122.9, 112.4, 71.7, 39.8, 30.8, 29.3, 24.2, 23.5, 14.2, 11.0.

Results and Discussions

Synthesis and Characterization. The synthesis of the three monomers, 2,5-thiophenebis(boronic acid) (**1**) and its corresponding diesters of 1,3-propanediol (**2**) and pinacol (**3**), is outlined in Scheme 1. Bis(boronic acid) **1** was synthesized from 2,5-dibromothiophene by lithiation followed by reaction with trimethyl borate at −78 °C and acidic workup. Refluxing of bis(boronic acid) **1** with an equimolar amount of either 1,3-propanediol or pinacol and using a Dean−Stark trap afforded **2** and **3**, respectively. The monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy, GC−MS, and elemental analysis.

Poly(thiophene−phenylene) **P-1** (Scheme 1) was prepared by reacting bis(boronic acid) **1** with 2,5-dioctyloxy-1,4-diiodobenzene using $Pd(PPh_3)_4$ as a catalyst. The polymer did not precipitate from acetone as it completely dissolved during the purification. ^{1}H and ^{13}C NMR spectra of the polymer in $CDCl_3$ confirmed the formation of low molecular weight oligomers containing 1 to 3 repeating units only. It is well-established that phosphine inhibition may limit the catalytic efficiency of Suzuki aryl couplings.[21] In fact, efficient palladium-mediated reactions can be achieved in the presence of phosphine-free palladium sources such as $Pd(OAc)_2$.[21,22] Following these studies, polymer **P-2** was prepared under identical conditions by using $Pd(OAc)_2$ instead of $Pd(PPh_3)_4$ as a catalyst and precipitated from acetone as a red material. **P-2** was partially soluble in $CHCl_3$ and THF at 25 °C and completely dissolved at high temperatures. It was freely soluble in toluene and ODCB at 25 °C. The ^{1}H and ^{13}C NMR spectra of **P-2** (in ODCB-d_4) revealed the loss of the peaks corresponding to the end groups and confirmed the formation of higher molecular weight polymers.[3] The molecular weights of **P-1** and the fraction of **P-2** soluble in $CHCl_3$ were determined by SEC in $CHCl_3$ at 25 °C using

Scheme 1



R = n-octyl (for Polymers **P-1** to **P-6**)

R = 2-ethylhexyl (for Polymers **P-7** and **P-8**)

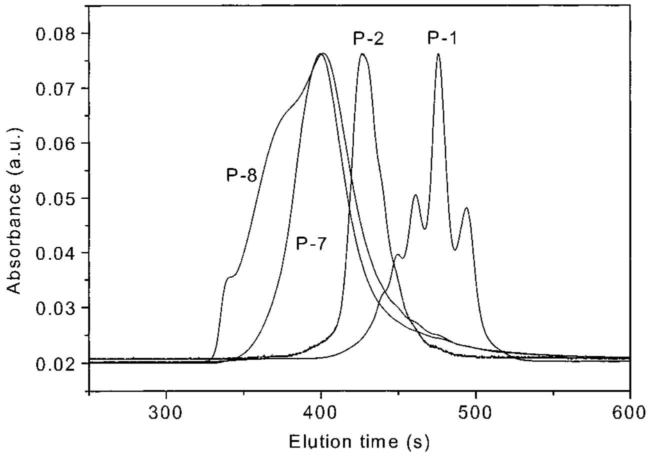


Figure 1. Normalized SEC traces of polymers **P-1**, **P-2**, **P-7**, and **P-8** in CHCl$_3$ at 25 °C.

polystyrene standards. The SEC plots are shown in Figure 1 and the values are reported in Table 1. While the SEC trace of **P-1** shows multiple peaks corresponding to different oligomers, a monomodal distribution is found for the chloroform-soluble fraction of **P-2** with a lower elution time. The data in Table 1 indicate that this fraction of **P-2** has a higher molecular weight with a narrow polydispersity corresponding to an average number of repeating units of $n = 8-9$, whereas **P-1** only consists of oligomers up to $n = 3$. In addition, the absorption maximum (λ_{max}) of **P-2** also showed a 20 nm red shift compared to **P-1,** indicative of an increased conjugation length. These results suggest that Pd(OAc)$_2$ enhances the Suzuki coupling in 2,5-thiophenebis(boronic acid)s and increases the molecular weight compared to Pd(PPh$_3$)$_4$.

As reported earlier, deboronation of acids could be limiting the formation of high molecular weight polymers in Pd(PPh$_3$)$_4$-catalyzed Suzuki polycondensations.[11] Thiopheneboronic esters are more stable than the corresponding acids in simple Suzuki couplings. Reports are known in the literature where Suzuki couplings were achieved in 60–70% yield using thiophene boronic 1,3-propanediol esters and Pd(PPh$_3$)$_4$ as a catalyst.[13,23] In an attempt to improve the molecular weight of the Pd(PPh$_3$)$_4$-catalyzed Suzuki polymerization, bisboronic diester **2** was polymerized with 2,5-dioctyloxy-1,4-diiodobenzene (for **P-3**) using Pd(PPh$_3$)$_4$. However, similar to **P-1**, **P-3** completely dissolved in acetone during purification and the SEC molecular weight confirmed the formation of low molecular weight oligomers (Table 1). Replacing the Pd(PPh$_3$)$_4$ with Pd(OAc)$_2$ again enhanced the Suzuki coupling and gave a higher molecular weight polymer, **P-4**, in 43% yield. The molecular weight and other characteristics of **P-3** and **P-4** are almost similar to **P-1** and **P-2**, respectively. Guillerez et al. reported a similar trend in the poly(3-octylthiophene) synthesis when Pd(OAc)$_2$ was used instead of Pd(PPh$_3$)$_4$.[16]

Recently, pinacol derivatives have been found to be more stable and are used frequently in Suzuki coupling to prepare biaryls and polymers.[20,24–28] To understand the role of the pinacol esters over monomers **1** and **2**, bisboronic diester **3** was polymerized under identical conditions using of Pd(PPh$_3$)$_4$ and Pd(OAc)$_2$ to prepare polymers **P-5** and **P-6**, respectively. Interestingly, the pinacol ester proved to be more stable under the polymerization conditions, and **3** gave high molecular weight polymers, in very good yields, for both Pd(OAc)$_2$ and Pd(PPh$_3$)$_4$. The molecular weights and λ_{max} of the fractions of **P-5** and **P-6**, soluble in chloroform are similar to **P-2** (Table 1). It is important to note that Pd(OAc)$_2$ increases the molecular weights for both boronic acids and esters unlike Pd(PPh$_3$)$_4$. The reasons for the different catalytic activity of Pd(PPh$_3$)$_4$ may be that excess phosphine inhibits both the oxidative addition and the transmetalation steps in the Suzuki cross-coupling reactions.[29–31] However, the pinacol ester **3** is found promising for producing high molecular weight thiophene copolymers in good yields, irrespective of the catalyst used. One possible explanation may be that the methyl groups induce noncoplanarity in the ester **3**, which reduces the influence of sulfur atom on the carbon–boron bond and makes it more stable in the Suzuki coupling compared to the planar **1** and **2**. The SEC number-average molecular weights and λ_{max} values of the chlorofrom-soluble fractions of polymers **P-2**, **P-4**, **P-5**, and **P-6** (containing 8–9 repeating units) are comparable with that of the same polymer prepared by Stille coupling (10 repeating units and $\lambda_{max} = 458$ nm).[3] Unlike the Stille route, the Suzuki polycondensation also produced high molecular weight polymer chains that are insoluble in chloroform. The low polydispersity of **P-2**, **P-4**, **P-5**, and **P-6** (Table 1) has to be considered as being the result of the fractionation that results from the limited solubility in chloroform.

It is well-known in the literature that one can easily increase the solubility of the polymers by introducing branching in the solubilizing side chains. To prepare completely soluble polymers with the same structure, pinacol ester **3** was polymerized with 2,5-bis(2-ethylhexyloxy)-1,4-diiodo benzene under identical conditions using both $Pd(PPh_3)_4$ and $Pd(OAc)_2$. The resulting polymers **P-7** and **P-8** (Scheme 1) were freely soluble in $CHCl_3$ and THF at 25 °C. The calculated yields were much lower than for **P-5** and **P-6**, due to the partial solubility of **P-7** and **P-8** in acetone during purification. The structure of the polymers was confirmed by ^1H and ^{13}C NMR spectroscopy. The molecular weights of **P-7** and **P-8** were determined by SEC in $CHCl_3$ at 25 °C (Table 1 and Figure 1). **P-7** has a monomodal distribution, similar to the soluble fraction of **P-2**, but the SEC trace of **P-8** reveals shoulders corresponding to much higher molecular weight polymers. It is clear from the plots that $Pd(OAc)_2$ increases the molecular weight of polymers for both boronic acid **1** and its ester **3** compared to $Pd(PPh_3)_4$. The increase in polydispersity of **P-7** and **P-8** is expected due to the difference in the SEC retention volume for branched-side chain polymers compared to the linear-side chain polymers (**P-2**, **P-4**, **P-5** and **P-6**).[32] In addition **P-7** and **P-8** showed a 10 nm red shift in the absorption spectrum (Table 1) due to the solubility of higher molecular weight fractions.

These results suggest that Suzuki polycondensations of 2,5-thiophenebisboronic pinacol diester derivatives are indeed very effective in producing moderate molecular weight polythiophene copolymers. An important advantage of the bisboronic pinacol diester derivatives is that they are less sensitive to air and easier to purify and to handle than the moisture sensitive thiophene-distannyl compounds employed in the Stille synthesis of the same thiophene−phenylene copolymers.

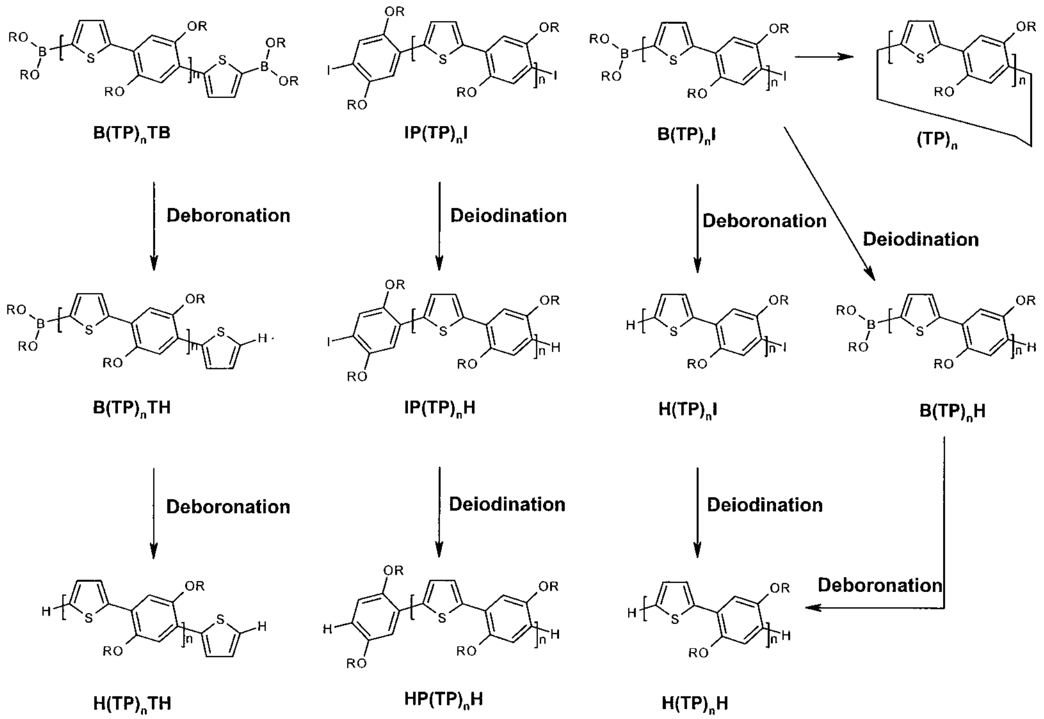
End Group Analysis by MALDI−TOF Mass Spectrometry. In a typical polycondensation of A−A and B−B type monomers, the polymer chain is expected to have the same functional groups at both the ends. For the Suzuki polycondensation investigated here $\mathbf{B(TP)_{\mathit{n}}TB}$ and $\mathbf{IP(TP)_{\mathit{n}}I}$ will be present (in this notation the symbols **T** and **P** represent 2,5-thienylene and 2,5-dialkoxy-1,4-phenylene repeating units, while **B** and **I** represent boronic and iodo end groups, respectively). At any instance reactive chain end groups can further react with each other to produce higher molecular weight polymer chains bearing boronic derivatives (**B**) and iodo (**I**) at both ends such as $\mathbf{B(TP)_{\mathit{n}}I}$. $\mathbf{B(TP)_{\mathit{n}}I}$ polymer chains are normally produced in the self-condensations of A−B type monomers. In the absence of side reactions, only these three types of polymer chains are expected to be present in the resultant polymer. However, side reactions such as deboronation and dehalogenation may terminate the growing polymer chains by introducing nonreactive end groups. Thus, polymer chains having boronic derivative end groups ($\mathbf{B(TP)_{\mathit{n}}TB}$ and $\mathbf{B(TP)_{\mathit{n}}I}$) may undergo stepwise deboronation and leave their corresponding products such as $\mathbf{B(TP)_{\mathit{n}}TH}$, $\mathbf{H(TP)_{\mathit{n}}TH}$, and $\mathbf{H(TP)_{\mathit{n}}I}$ in the polymers, where **H** represents a hydrogen atom. Similarly, the dehalogenation of phenyl iodides ($\mathbf{IP(TP)_{\mathit{n}}I}$ and $\mathbf{B(TP)_{\mathit{n}}I}$) may also leave their corresponding products such as $\mathbf{IP(TP)_{\mathit{n}}H}$, $\mathbf{HP(TP)_{\mathit{n}}H}$, and $\mathbf{B(TP)_{\mathit{n}}H}$ in the polymer. Either the dehalogenation of $\mathbf{H(TP)_{\mathit{n}}I}$ or the deboronation of $\mathbf{B(TP)_{\mathit{n}}H}$ may also give $\mathbf{H(TP)_{\mathit{n}}H}$ type chain ends. As a consequence 10 different types of chains may be expected. A further complication arises because it is well-known in the literature that polymer chains having reactive A and B type end groups may react intramolecularly to form macrocycles instead of reacting with another polymer chain to increase the molecular weight of polymers. In the present case macrocycles $\mathbf{(TP)_{\mathit{n}}}$ are expected to occur by the cyclization of $\mathbf{B(TP)_{\mathit{n}}I}$. The MALDI−TOF technique is extensively used to identify such macrocycles in various polymers such as polyesters and polyethers.[33,34] The various possible end groups of the polymers (**P-1**−**P-8**) prepared from different boronic derivatives (**1**, **2**, and **3**) are shown in Scheme 2.

To identify the end groups and the different types of chains that are formed, the polymers were subjected to MALDI−TOF MS analysis using α-cyano-4-hydroxycinnamic acid as matrix. The polymers **P-1**, **P-3**, **P-7**, and **P-8** were dissolved in THF and mixed with the matrix in THF. Polymers **P-2**, **P-4**, **P-5**, and **P-6** were dissolved in 1,2-dichlorobenzene and mixed with the matrix in THF. A small amount of the mixture was evaporated on the target plate, and the mass spectra were recorded in linear mode. The polymers formed radical cations in the MALDI instead of cationized (e.g., $[M + Na]^+$ or $[M + K]^+$) species, in accordance with previous studies on poly(*p*-phenylenes)[35] and polythiophenes.[36] In MALDI−TOF mass spectrometry on polymers, there is a discrimination against higher molecular weight species in samples with a polydispersity of more than 1.1−1.2, and an accurate determination of the molecular weight distribution from MALDI−TOF can only be obtained in combination with a SEC fractionation to analyze low-dispersity samples.[37−40] Therefore, the molecular weight values from MALDI−TOF probably do not represent the actual molecular weight distribution but do allow to assess the mechanism of the different polymerization reactions.

The mass spectra of the polymers **P-1** and **P-3** were similar to each other having mass peaks below $m/z = 2100$ corresponding to the oligomers of $n = 1−3$. On the other hand the polymers **P-2**, **P-4**, and **P-5**−**P-8** mainly have mass peaks in the higher molecular weight range corresponding to oligomers up to $n = 16$. The low molecular weight polymers **P-1** and **P-3** are not used for further discussions.

To understand the role of the boronic derivatives in the $Pd(OAc)_2$-catalyzed Suzuki polycondensation, the mass spectra of polymers **P-6**, **P-4**, and **P-2** were compared (Figure 2). All three spectra show mass peaks with up to $n = 16$ repeating units. Expanded mass regions ($m/z = 3600−4000$, corresponding to the repeating unit of $n = 9$) are shown in the insets (Figure 2). The mass values for all types of end groups and polymer chains corresponding to $n = 8$ and $n = 9$ are listed in Table 2. On the basis of previous work on oligo and polythiophenes, we do not expect that fragmentation is significant in the MALDI−TOF analysis.[36,41] To further exclude the possibility that MALDI−TOF analysis of the end groups is hampered by presence of fragmentation, we employed dithranol and norharman matrices which are known to reduce fragmentation as compared to α-cyano-4-hydroxycinnamic acid. Using

Scheme 2



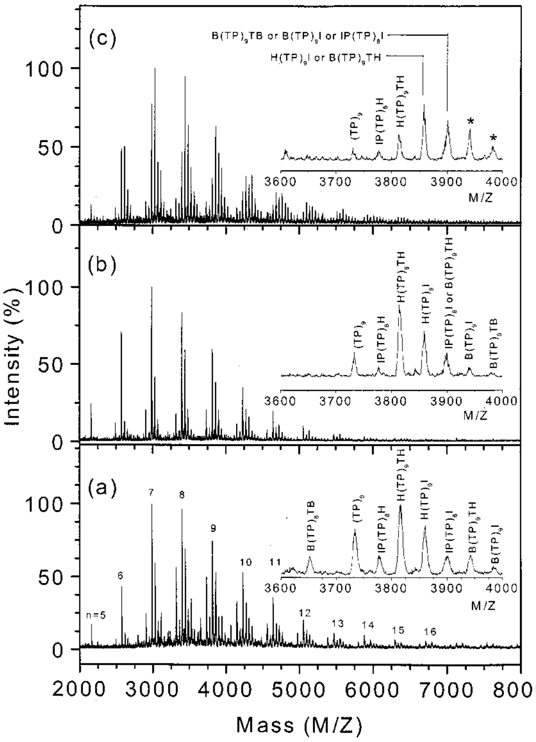


Figure 2. MALDI−TOF mass spectra of polymers **P-6** (a), **P-4** (b), and **P-2** (c).

these matrices, no significant differences were found.

Comparison of Table 2 and Figure 2a reveals that in **P-6** all possible polymers chains with **B**, **I**, and **H** end groups seem to be present. However, because **HP(TP)$_8$H** and **B(TP)$_8$TB** chains have small mass differences (<2 amu, Table 2, for **P-6**) and the former are absent in the samples **P-4** and **P-2** prepared by the other boronic derivatives (Figure 2b,c), we propose that **HP(TP)$_n$H** chains are not formed in the Suzuki polycondensation. The mass difference between the polymer chains **H(TP)$_9$H** and **(TP)$_9$** is only 2 amu, which leaves some ambiguity in the assignment. In our view, however, the probability for the formation of the **H(TP)$_9$H** is less compared to the cyclization process to **(TP)$_9$**, which implies that **H(TP)$_9$H** is probably absent in **P-6**. Similarly, **B(TP)$_9$H** chains also have a small mass difference compared to **H(TP)$_9$I** in Figure 2a, **H(TP)$_9$TH** in Figure 2b, and **IP(TP)$_8$H** in Figure 2c, respectively. Although their absence is not completely unambiguous, we assume that the formation of a **B(TP)$_9$H** chain from **B(TP)$_9$I** is not a main side reaction because the deboronation of thiophene boronic derivatives is generally more favorable under the standard Suzuki coupling reactions compared to deiodination.[14,15] The mass spectrum of **P-4** (Figure 2b) is similar to that

Table 2. Various Types of End Groups and Their Corresponding Mass Values

end groups	mol wt	MW $n = 8$	MW $n = 9$
B[TP]$_n$TB	171.8 + [414.7]n^a	3489.4	3904.1
	252.0 + [414.7]n^b	3569.6	3984.3
	336.1 + [414.7]n^c	3653.7	4068.4
B[TP]$_n$TH	128.0 + [414.7]n^a	3445.6	3860.3
	168.0 + [414.7]n^b	3485.6	3900.3
	210.1 + [414.7]n^c	3527.7	3942.4
H[TP]$_n$TH	84.1 + [414.7]n	3401.7	3816.4
IP[TP]$_n$I	586.3 + [414.7]n	3903.9	4318.7
IP[TP]$_n$H	460.4 + [414.7]n	3778.0	4192.7
HP[TP]$_n$H	334.6 + [414.7]n	3652.2	4066.9
B[TP]$_n$I	171.7 + [414.7]n^a	3489.3	3904.0
	211.8 + [414.7]n^b	3529.4	3944.1
	253.9 + [414.7]n^c	3571.5	3986.2
H[TP]$_n$I	127.9 + [414.7]n	3445.5	3860.2
[TP]$_n$	[414.7]n	3317.6	3732.3
H[TP]$_n$H	2 + [414.7]n	3319.6	3734.3
B[TP]$_n$H	45.8 + [414.7]n^a	3363.4	3778.1
	85.9 + [414.7]n^b	3403.5	3818.2
	128.0 + [414.7]n^c	3445.6	3860.3
B[TP]$_n$T−Ph	276.1+ [414.7]n^c	3593.7	4008.4
H[TP]$_n$T−Ph	160.2 + [414.7]n	3477.8	3892.5

[a] For polymer **P-2**. [b] For polymer **P-4**. [c] For polymers **P-5** to **P-8**.

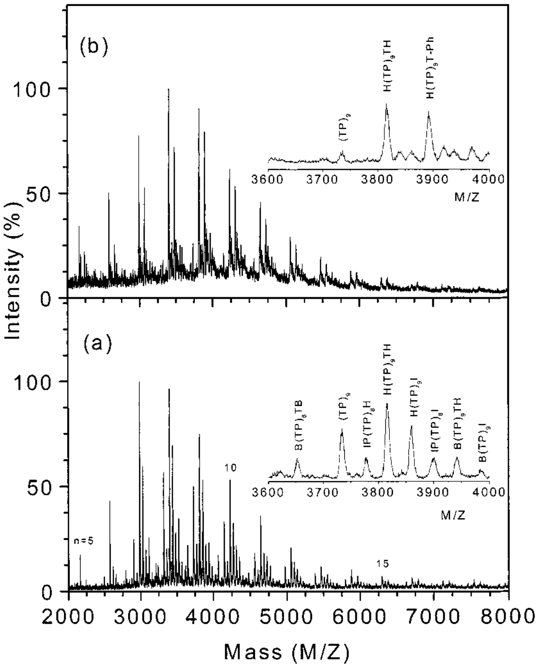


Figure 3. MALDI–TOF mass spectra of polymers **P-6** (a) and **P-5** (b).

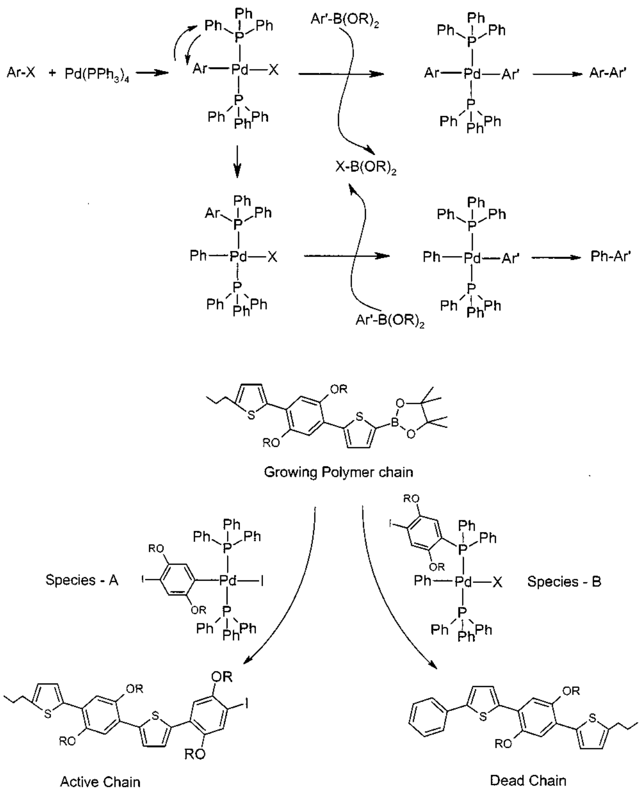
of **P-6**, having all possible end groups as shown in Scheme 2. For **P-4**, polymer chains **IP(TP)$_8$I** and **B(TP)$_9$TH** have only a small difference in mass and are difficult to distinguish. **P-2** (Figure 2) also contains similar chains as **P-4** and **P6**. In addition, Figure 2c shows peaks at 3942 and 3987 amu, labeled with an asterisk, which could not be assigned to any of the polymers chains shown in Scheme 2 using the mass values collected in Table 2 for polymer **P-2**. These signals might originate from side reactions, which only occur in boronic acids and which are essentially absent in the ester derivatives.

For **P-6**, **P-4**, and **P-2**, the high intensity of the **H(TP)$_n$TH** peaks in the consecutive patterns for increasing repeating units suggests that the hydrolytic deboronation is the main side reaction in the Pd(OAc)$_2$-catalyzed Suzuki polycondensation. In addition, a small percent of dehalogenation and cyclization can terminate the polymer chains in the Suzuki polycondensation.

To elucidate the differences in the mechanism of Suzuki polycondensation for the Pd(PPh$_3$)$_4$ and Pd(OAc)$_2$ catalysts, the MALDI–TOF mass spectra of polymers **P-5** and **P-6** are compared in Figure 3. In both the spectra, mass peaks corresponding to $n = 16$ are observed confirming the data form SEC that, unlike monomers **1** and **2**, the bisboronic pinacol ester **3** produced similar molecular weight species for both catalysts. Interestingly, the mass spectrum of **P-5** is devoid of most chain types listed in Scheme 2 and Table 2. Instead, two intense peaks dominate the repeating pattern. The maximum intensity mass peak in each repeating unit corresponds to **H(TP)$_n$TH**, while the second peak occurs at **H(TP)$_n$TH** + 76 amu, not matching with any of the end groups as shown in Scheme 2. This signal is essentially absent in the polymers prepared using Pd(OAc)$_2$ (**P-6**, **P-4**, and **P-2**) and suggests that the mechanism of the Suzuki polycondensation of pinacol ester **3** differs for the two catalysts Pd(OAc)$_2$ and Pd(PPh$_3$)$_4$. The Suzuki coupling reaction occurs by three consecutive steps: oxidative additions of aryl halides to the palladium center, transmetalation of aryl boronic derivatives, and reductive elimination of organic partners to yield biaryls (Ar–Ar′) (Scheme 3).[42] Reports in the literature describe the occurrence of aryl–aryl exchange between the triphenylphosphine ligands and palladium center in Ar–Pd[(PPh$_3$)]$_2$-X to produce Ph–Pd[(PPh$_2$Ar)(PPh$_3$)]–X (Scheme 3).[43–49] When the latter species reacts with Ar′-B(OR)$_2$ during transmetalation, it results in the formation of unwanted Ph–Ar′ biaryls instead of Ar–Ar′. O′Keefe et al. reported the formation of 27% phenyl-capped products followed by aryl–aryl exchange in the biaryl synthesis using Pd(PPh$_3$)$_4$ as catalyst.[45] Novak et al. investigated in detail the mechanism and effects of aryl–aryl exchange reactions in the synthesis of linear poly(*p*-phenylenes).[46,47] In the present case, a similar exchange reaction may occur, giving chains with phenyl end groups (Scheme 3). At any instance during the Suzuki polycondensation, a growing polymer chain can react with either of the catalytic palladium intermediates A and B (Scheme 3). Species A results in the normal Suzuki coupling and increases the molecular weight of the growing polymer chain. Species B, on the other hand, transfers the phenyl group to the polymer chain and terminates the polymerization reaction at one end of the chain. In this case, **B(TH)$_n$T-Ph** polymer chains are produced, which may undergo further deboronation to give unreactive **H(TH)$_n$T-Ph** polymer chains. It is evident from Figure 3b that the **H(TP)$_n$T-Ph** peak appears for every repeating unit. Such a ligand transformation is not possible in the Pd(OAc)$_2$-catalyzed Suzuki polycondensation and hence the **P-6** (as well as **P-2** and **P-4**) does not contain **H(TH)$_n$T-Ph** chains. The MALDI–TOF spectra gave no evidence for the incorporation of phosphorus in the polymer backbone as has been found by Novak et al. for the Suzuki polymerization of poly(*p*-phenylene)s.[46]

The MALDI–TOF mass spectra of polydisperse **P-7** and **P-8** are shown in Figure 4. These two polymers

Scheme 3



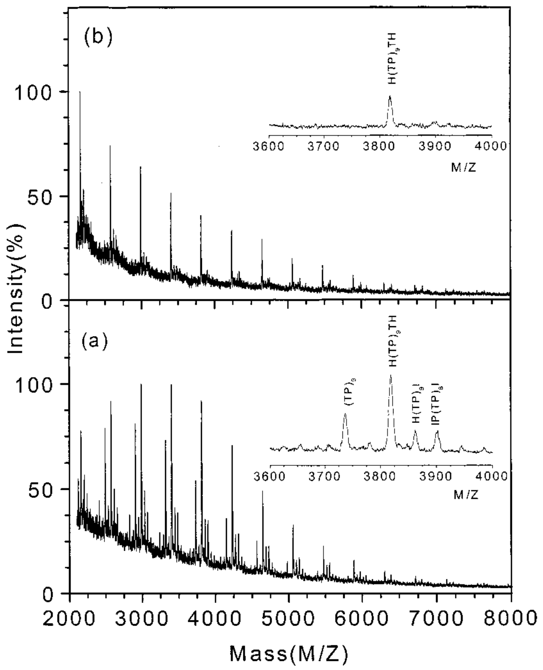


Figure 4. MALDI−TOF mass spectra of polymers **P-8** (a) and **P-7** (b).

were prepared using 1,4-diiodobenzene with branched side chains (2-ethylhexyloxy) in the 2- and 5-positions to increase the solubility. The mass spectrum of **P-8** is almost identical to that of **P-6**, having similar end groups and repeating units up to $n = 16$. The fact that the MALDI−TOF spectra of **P-6** (and also **P-5**) are similar to that of **P-8** shows that the lower molecular weight of **P-6** (and **P-5**) as determined from SEC is an artifact resulting from the poor solubility of these polymers in $CHCl_3$ at ambient temperature. Surprisingly, polymer **P-7** has only single intense mass peaks corresponding to **H(TP)*n*TH** chains. **P-7** is thus essentially devoid of all end groups shown in Scheme 2 and compared to **P-5** (Figure 3b) even peaks corresponding to **H(TH)*n*T-Ph** have almost disappeared in **P-7** (they do appear in small intensities at higher repeating units).

The MALDI−TOF technique has an inherent limitation in analyzing polydisperse polymers.[37−39] In such a case, the combination of SEC and MALDI−TOF is used to characterize the entire range of molecular weights.[37,50,51] To identify the end groups at much higher molecular weights, polymer **P-7** was fractionated in four fractions using preparative SEC in $CHCl_3$. The normalized SEC plot of each fraction is shown in the inset of Figure 5, and the corresponding molecular weights determined using polystyrene standards are reported in Table 3. As expected, the peak molecular weight (M_p), M_n, and M_w decrease with increasing elution time in SEC. All four fractions have a narrow polydispersity in the range of 1.1−1.2. The absorption maximum shows a 4 nm red shift with increasing molecular weight. These results confirmed the good fractionation of **P-7** by SEC. All four fractions were used for MALDI−TOF analysis and the corresponding mass spectra are shown in Figure 5. The molecular weights calculated from the mass peak distribution by the standard methods are reported in Table 3.[37] M_n and M_w calculated from MALDI−TOF show a similar trend and the molecular weights are comparable with that determined by SEC, with the M_n from SEC being 1.05−1.21 times higher than from MALDI−TOF. This correspondence also supports our conjecture that fragmentation is not important in the MALDI−TOF analysis. The mass spectra of fractions 3 and 4 are almost identical to that of the unfractionated polymer **P-7** (Figure 4b) and have mass peaks up to $m/z = 6000$, mainly corresponding to **H(TP)*n*TH** end groups. Interestingly, the relative intensity of the mass peaks corresponding to phenyl end groups, **H(TP)*n*T-Ph** has increased in fractions 1 and 2. In addition, fraction 1 also contains few other end groups such as macrocyclics as shown in Scheme 2. However, the amount of fraction 1 obtained during SEC fractionation is very small compared to other fractions and does not reflect the properties of the entire molecular weight range. The combination of SEC and MALDI−TOF analysis confirmed that a small extent of aryl−aryl exchange reactions also occurred in **P-7**. This aryl−aryl exchange side reaction is favored at higher molecular weight polymers (fractions 1 and 2), and the moderate molecular weight polymers (fractions 3 and 4, repeating units up to 15, $m/z = 6000$) essentially possess only thiophene end groups resulting from deboronation. Polymer **P-8** was subjected to a similar SEC−MALDI−TOF analysis and all the fractions were found to have the same end groups as seen in the unfractionated polymer (Figure 4a). The results on **P-7** show that, unlike polymer **P-5** (prepared using linear side chain diiodide), most of the polymer chains in **P-7** are free from aryl−aryl exchange reactions and the polymer is much cleaner.

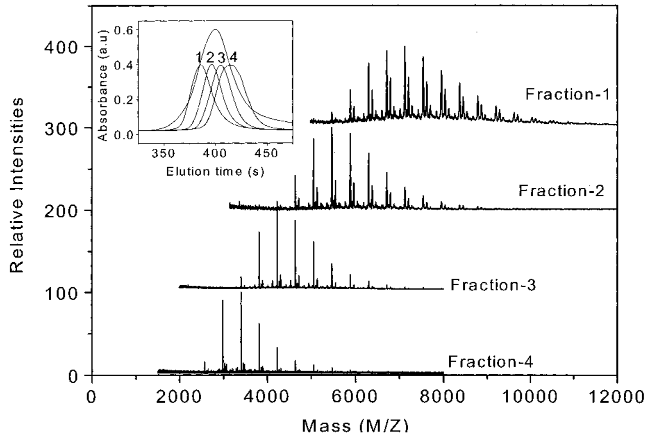


Figure 5. Normalized SEC traces of four fractions of **P-7** (inset) and their corresponding MALDI−TOF mass spectra.

Table 3. SEC and MALDI−TOF Molecular Weights of P-7 and Its Four Fractions

	from GPC[a]				from MALDI−TOF			λ_{max}[b]
sample	M_p	M_n	M_w	PD	M_n	M_w	PD	(nm)
P-7	7350	3550	7300	2.1				468
fraction 1	10 700	8750	10 200	1.2	7800	8400	1.08	470
fraction 2	8050	7200	7900	1.1	6800	7900	1.06	469
fraction 3	6400	5850	6400	1.1	4500	5100	1.13	468
fraction 4	5100	4500	5100	1.1	3700	4400	1.20	466

[a] Determined by SEC in $CHCl_3$ at 25 °C against polystyrene standards. [b] At 25 °C in $CHCl_3$. [c] PD = M_w/M_n

This remarkable result suggests that the aryl−aryl exchange from triphenylphosphine to the palladium center decreased drastically when side chain branching was introduced in the diiodobenzene. We propose that the branching increases the bulkiness in the palladium center and hinders the exchange reaction. O'Keefe et al. and Novak et al. reported a similar observation in their biaryl and poly(*p*-phenylenes) synthesis where there was a decrease in aryl−aryl exchange on using bulky ligands such as tris(2-methoxyphenyl)phosphine and tri(o-tolyl)phosphine, respectively, instead of triphenylphosphine in the palladium catalyst.[45−47] Interestingly, in the present case the exchange reaction is reduced by introducing side chain branching in one of the monomers.

Conclusions

The Suzuki polycondensation of three different 2,5-thiophenebisboronic derivatives and two 2,5-dialkoxy-1,4-diiodobenzenes has been investigated using Pd(PPh_3)$_4$ and Pd(OAc)$_2$ catalysts. While thiophene bis(boronic acid) (**1**) and bis(boronic 1,3-propanediol) diester (**2**) monomers were easily polymerized with Pd(OAc)$_2$ as a catalyst, Pd(PPh_3)$_4$ was not effective under similar conditions. The bisboronic pinacol diester **3** is much more stable in the Suzuki polycondensation and afforded polymers in higher molecular weights and yields compared to **1** and ester **2** using both Pd(OAc)$_2$ and Pd(PPh_3)$_4$ as a catalyst. MALDI−TOF mass spectrometry revealed that polymers obtained using Pd(OAc)$_2$ contain chains with various combinations of boronic, iodo, and hydrogen end groups. The MALDI−TOF analysis confirmed that the main side reaction in the Suzuki polycondensation is hydrolytic deboronation, irrespective of the catalyst and boronic derivatives. Using Pd(PPh_3)$_4$ the number of different end groups and hence, the number of chain types is significantly reduced. However, unlike Pd(OAc)$_2$, Pd(PPh_3)$_4$ induces phenyl−aryl exchange from the triphenylphosphine to the catalytic palladium intermediate and results in polymer chains with phenyl end groups. Surprisingly, this side reaction is effectively suppressed by introducing branching in the side chains present in the diiodobenzene monomer. As a result polymer **P-7** was obtained as a monomodal distribution of perfectly alternating **H(TP)$_n$TH** chains with primarily thiophene end groups and a small amount of phenyl capped chain ends in the high molecular weight chains. While the present investigation emphasizes the subtleties involved in the Suzuki copolymerization of thiophene bisboronic derivatives with aryl dihalides, it demonstrates at the same time that 2,5-thiophenebis(boronic acid) pinacol diester **3** may be a versatile monomer in Suzuki polycondensations. We are currently continuing this work to assess the scope and limitations of these reactions in more detail.

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