

Synthesis of Hyperbranched Poly(*m*-phenylene)s via Suzuki Polycondensation of a Branched AB₂ Monomer

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ABSTRACT: An efficient synthesis of hyperbranched poly(m-phenylene)s is achieved by Suzuki polycondensation of a *m*-terphenyl-derived branched AB₂ monomer. The resulting hyperbranched polymers show high molecular weight and relatively low polydispersity and are readily soluble in common organic solvents. A catalyst system composed of Pd(OAc)₂ and S-Phos was found to be highly active in the present Suzuki polycondensation protocol. The molecular weight and polydispersity of the polymer are controllable by varying the catalyst loading and the starting monomer concentration. Experimental results are consistent with a pseudo-chain-growth pathway that involves intramolecular catalyst transfer during polymerization. Furthermore, the triflate end groups of the hyperbranched poly(*m*-phenylene)s can be efficiently converted to other functionalities via *in situ* Suzuki–Miyaura cross-couplings.

Introduction

In hyperbranched polymeric architectures, high branching density leads to compact macromolecular objects with multiple end-functionalities. As a result, hyperbranched polymers (HBPs) offer higher solubility and lower viscosity when compared with their linear counterparts, partly due to their globular shape and decreased degree of interchain entanglement.¹⁻⁶ HBPs are therefore frequently referred to the close analogues to dendrimers, despite that the latter are perfectly branched macromolecules with high structural regularity and monodispersity, whereas HBPs generally have less well-defined structures and broad molecular weight distributions.⁷ Among the wide variety of HBPs that have been synthesized to date, hyperbranched poly(phenylene)s (HB-PPs) exhibit structural rigidity and extraordinary thermal stability.8-11 Our interest in HB-PPs arose from the pursuit of carbon-rich polymeric architectures.^{12,13} In this context, the unique characteristics of HB-PPs coincide with that of the hyperbranched polymers developed in our group—hyperbranched aromatic poly(ether imide)s^{14–17} and poly(phenyleneacetylene)s.^{18–20}

Three methods have dominated the synthetic approaches of HB-PPs. The first, and earliest examples, utilize transition-metalcatalyzed cross-coupling reactions of AB₂-type monomers.^{21–24} Another approach utilizes the Diels–Alder reaction between phenylethynyl and cyclopentadienone functionalities incorporated in multifunctionalized monomers (i.e., AB₂, A₂/B₃, etc.), giving rise to highly branched poly(phenylene)s.^{25,26} A third strategy involves catalytic cyclotrimerization of diynes, wherein newly formed trisubstituted phenyl rings constitute the branch points of the hyperbranched structures.²⁷ While considering the synthetic methods, we were particularly interested in SPC due to the high specificity, good efficiency, and mild reaction conditions that allow for an accurate configuration of the branch points and tolerance of a wide range of functionalities.²⁸ In addition, although SPC was one of the earliest methods utilized to access HB-PPs, there has since been very limited effort devoted to further exploration of this methodology. We present here an efficient SPC protocol by using a branched AB_2 monomer and a highly active palladium catalyst to construct hyperbranched poly(*m*-phenylene)s (HB-PmPs) with high molecular weights and excellent solubility in common organic solvents.

Results and Discussion

Monomer Design and Synthesis. One of the most important characterization parameters associated with HBPs is the degree of branching (DB).²⁹ For HBPs synthesized by polymerization of AB₂ monomers, DB may vary from 0 to 100% according to Frey's definition^{30–32}

$$DB = \frac{2D}{2D+L} \tag{1}$$

where D and L denote the mole fractions of dendritic and linear units in the HBP structure, respectively. Theoretical studies predict that the maximum DB for the HBP obtained from an AB₂ monomer is only 50%, assuming that the reactivities of the terminal groups remain constant through-out the course of the reaction.³² Hyperbranched polymers with high DB require increasing the number of dendritic units (D) and/or reducing the amount of linear units (L). Examples of HBPs up to 100% DB have been reported but are limited to only a small number of monomers and methods.^{33–36} A more general approach to increase DB is to incorporate one or more branch points within the mono-mer struture.^{37,38} Considering the structural rigidity and relatively low solubility of unsubstituted poly(phenylene)s, we designed a branched AB_2 monomer M that is built upon a *m*-terphenyl scaffold composed of one focal point A, two terminal units **B**, and two solubilizing groups **R**, as shown in Figure 1, where functional groups **A** and **B** are reacting partners in the polycondensation reactions. In addition to the built-in branch point, the increased distance between the reactive termini may facilitate the coupling of monomers. Upon polymerization, each terminus is converted to a linear unit that forms the connection between two dendritic units,

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Figure 1. Calculation of the degree of branching (DB) for the hyperbranched poly(m-phenylene)s synthesized from *m*-terphenyl AB₂ monomer M. In the structure, "A" and "B" denote generic reactive sites, $\mathbf{R} =$ solubilizing group, and $\mathbf{Ar} =$ aryl group.

and two new termini are generated in the meanwhile. This reaction pattern will eventually lead to *n* dendritic, (n - 1) linear, and (n + 1) terminal units, where *n* is the degree of polymerization (DP). The DB of the resulting polymer is calculated to become essentially constant at 67% when n > 27.

The monomer was synthesized by adopting a strategy of iterative C-H activation/borylation followed by Suzuki-Miyaura cross-coupling sequence as we recently reported for the construction of 1,3,5-polyphenylene dendrons.³⁹ As depicted in Scheme 1, using iridium-catalyzed C-H bond functionalization, tert-butyldimethylsilyl (TBS)-protected 3-*tert*-butylphenol 1 was borylated regioselectively at the *meta* position with respect to the two substituents. 40,41 The resulting boronate ester 2 was then coupled with 1,3-dibromobenzene in the presence of a catalyst system composed of $Pd(OAc)_2$ and 2-dicyclohexylphosphino-2',6'-dimethoxy-biphenyl (S-Phos),⁴² providing *m*-terphenyl **3** in quantitative yield.⁴³ The *meta* position of the internal benzene ring in 3 was then borylated, again by using iridium-catalyzed C-H activation/borylation to give the *m*-terphenyl boronate ester 4.44 Deprotection of the TBS groups was carried out in THF with tetrabutylammonium fluoride (TBAF) to provide bisphenol 5.45 Subsequent esterification with triflic anhydride provided the branched AB_2 monomer 6 in good yield.

Polymerization Conditions: Catalyst, Temperature, and Solvent. The synthesis of polyarylenes via SPC has been extensively studied.^{46,47} Most commonly these preparations involved the use of difunctionalized aryl boronic acids/esters and aryl halides. Examples with aryl triflates remain rare,⁴⁴ despite that these starting materials are easily accessed from a wide range of phenolic precursors. Another advantage of using aryl triflates is that, unlike halides, phenols are readily masked by various protecting groups if orthogonal reactivities need to be realized, resulting in a more facile synthetic protocol. To test the performance of the branched AB_2 monomer in SPC, we subjected 6 to various conditions to a screening of catalysts and solvents. A relatively mild base, K_3PO_4 , was applied in each case due to its extensive uses in Suzuki-Miyaura cross-couplings and to minimize potential hydrolysis of the triflate end groups.

Among the catalyst systems tested, Pd(OAc)₂ combined with Buchwald's S-Phos ligand was most active.⁴⁹ The catalyst was preformed by stirring a THF solution of 0.5 mol % Pd(OAc)₂ and 1 mol % S-Phos (molar ratio with respect to the AB₂ monomer) for 30 min under argon. The reaction mixture containing the monomer (starting monomer concentration $[M]_0 = 50$ mM), the catalyst, and 2 M K₃PO₄ solution was then stirred in an argon-filled sealed container. At 65 °C, the monomer was consumed within 20 min, by which time the molecular weight $(M_{\rm p})$ of the polymer portion reached ca. 35.8 kDa relative to polystyrene (PS) standards and remained essentially constant thereafter. The polydispersity index (PDI) was 1.5 as determined by gel permeation chromatography (GPC). At room temperature, the reaction also showed high efficiency in that consumption of the monomer and formation of high molecular weight polymer ($M_n = 35.1 \text{ kDa}$, PDI = 1.8) occurred within 20 min, as shown in Figure 2a. The polymer obtained after 4 h showed only a slight increase in both M_n (36.1 kDa) and PDI (1.9) compared to the 20 min sample. When the polymerization was conducted at 0 °C and monitored by GPC analysis (Figure 2b), polymer formation was observed after 30 min, and the M_n of the polymer slowly increased to 48 kDa with a PDI of 2.4 after 5 h, by which time the monomer conversion was about 50% and no obvious low molecular weight oligomers were observed. Mechanistically, this result is in sharp contrast to what is expected for a step-growth polycondensation, wherein high molecular weight polymers generally form only at a high monomer conversion.50

Furthermore, the molecular weight distribution of the polymer was relatively narrow, especially at the initial stage of the reaction. Therefore, a pseudo-chain-propagation process seems more plausible than a random condensation of low molecular weight oligomers. Examples of chain-growth Suzuki polycondensation have been recently reported,^{34,51,52} wherein an intramolecular catalyst transfer process was believed to be operative leading to polymers with relatively narrow molecular weight distributions. In our case, during polymerization, the Pd⁰ center may migrate from the growing chain end to a vicinal aryl triflate group that will





Figure 2. GPC chromatograms of Suzuki polycondensation of 6 at (a) room temperature and (b) 0 °C. Reaction conditions: 0.5 mol % Pd(OAc)₂; 1 mol % S-Phos; 6 equiv K_3PO_4 (2 M aq); THF; $[M]_0 = 50$ mM.



Scheme 1. Synthesis of Branched AB₂ Monomer 6

become the new chain end and generate the branch points in hyperbranched polymers. This explanation also correlates well with the catalyst-dependent preferential oxidative addition process (*vide infra*). On the other hand, however, a gradual increase in PDI was observed in our case as the reaction progressed, suggesting that coupling of oligomers may also have occurred to some extent.

Other phosphine-based catalysts, such as $Pd(PPh_3)_4$, $Pd(OAc)_2/dppf$, and $Pd(OAc)_2/P(o-tolyl)_3$, or a commercial *N*-heterocyclic carbene-based catalyst, PEPPSI,⁵³ were tested, but all appeared to be less efficient than the combination of $Pd(OAc)_2$ and S-Phos, as evidenced in each case by the relatively lower molecular weight and higher PDI of the product (Figure S1 and Table S1).

It is worth noting that the polymer remained completely soluble during the entire course of the reaction, and the products were isolated by simple extraction. The polymer was further purified by dissolving it in a minimum amount of THF or DCM and then precipitating it from methanol, resulting in yields ranging from 83% to 95% for different runs. The white powdery product is readily soluble in a wide range of solvents such as THF, DCM, chloroform, ethyl acetate, toluene, and benzene. The polymers are partially soluble in cyclohexane, diethyl ether, acetone,1,4-dioxane, and DMF but insoluble in methanol, ethanol, acetonitrile, DMSO, and water.

In comparison to the HB-PmPs obtained from branched monomer 6, HB-PmPs obtained from simple AB₂-type

monomers based on trisubstituted benzene only polymerizes to relatively low molecular weights in most of the cases.²² For example, in great contrast to monomer 6, when 3,5-dibromophenyl boronate ester 7 was subjected to the optimized polymerization conditions, precipitation occurred almost instantly after the reaction started, whereas the soluble part only comprised a small amount of low molecular weight polymers. The high molecular weight and excellent solubility of our HB-PmPs may be attributed to the more active catalyst used and the structural characteristics of the branched monomer M. Moreover, the presence of regularly spaced branch points and tert-butyl-substituted linear and terminal units in the polymer may contribute to the increased solubility and hence the high molecular weights that can be achieved. The SPC conditions we employed also contribute to the successful polymerization of 6. For example, when $Pd(PPh_3)_4$ or $Pd(OAc)_2/dppf$ was used with 6, a bimodal distribution of the molecular weight was obtained in both cases, which may be attributed to the decreased rate of the Pd(0) oxidative addition step, as seen in other SPC reactions 34,54,55 and related studies. 56,57



For the solvents screened, THF was found to be optimal. Other solvents such as DCM, toluene, cyclohexane, and 1, 4-dioxane resulted in decreased molecular weights and relatively broad PDIs in most of the cases (Figure S2 and Table S2). Precipitation of the products from the reaction mixture occurred in the case when cyclohexane or 1, 4-dioxane was used.

Effects of Catalyst Loading and Starting Monomer Concentration. The amount of catalyst used was found to have a drastic effect on the molecular weight and PDI of the polymer (entries 1-5 in Table 1, Figure S3). First, the standard polymerization conditions were chosen (65 °C, Pd(OAc)₂/ S-Phos, THF, and 2 M K₃PO₄ at a starting monomer concentration of 50 mM). Use of 4 and 2 mol % catalyst (entries 1 and 2, Table 1) resulted in polymers with a much lower molecular weight ($M_{\rm n} = 12$ kDa and 16 kDa, respectively) compared to the case with 0.5 mol % catalyst (entry 3, Table 1), although the PDI of the corresponding polymer was lower. In contrast, decreasing the catalyst loading by an order of magnitude to 0.05 mol % (entry 4, Table 1) led to an increase in molecular weight ($M_n = 54$ kDa) without any significant decrease in efficiency. More strikingly, use of only 0.01 mol % catalyst (entry 5, Table 1) led to nearly complete monomer conversion and a high molecular weight polymer $(M_{\rm n} = 57.3 \text{ kDa})$. The molecular weight dependence upon catalyst loading also reveals that SPC of this AB2 monomer is more consistent with a pseudo-chain-growth rather than a step-growth mechanism. On the other hand, as the catalyst loading decreased from 4 to 0.01 mol %, the corresponding PDI increased from 1.3 to 1.9.

The starting monomer concentration, $[M]_0$, also has a significant effect on the molecular weight and PDI of the polymer (entries 6–11 in Table 1, Figure S4). For instance, under otherwise identical conditions, as the monomer concentration increased, both the molecular weight and PDI increased. The same trend was observed with a lower catalyst

Table 1. Effect of Catalyst Loading and Starting Monomer Concentration [M]₀ on the Molecular Weight and PDI of the HB-PmPs

entry	catalyst (mol %)	$\left[M\right]_{0}\left(mM\right)$	$M_{\rm n}({\rm kDa})^a$	DP^b	PDI ^a
1	4	50	12.0	24	1.3
2	2	50	16.0	32	1.4
3	0.5	50	35.8	73	1.5
4	0.05	50	54.0	110	1.9
5	0.01	50	57.3	117	1.9
6	0.5	100	46.2	94	3.0
7	0.5	20	31.9	65	1.3
8	0.5	10	27.1	55	1.3
9	0.05	100	59.6	122	2.1
10	0.05	20	48.5	99	1.6
11	0.05	10	44.7	91	1.6

^{*a*} Molecular weights and PDI were determined by GPC with respect to polystyrene standards. ^{*b*} Degree of polymerization (DP) was calculated based on the M_n values determined by GPC.



Figure 3. Selected regions of (a) ¹H NMR (CDCl₃) and (b) ¹³C NMR (CDCl₃) spectra of hyperbranched poly(*m*-phenylene) with a molecular weight (M_n) of 35.8 kDa.

loading (0.05 mol %), wherein the molecular weight and PDI decreased upon dilution. Thus, these reaction parameters can be readily altered to allow for easy control over the molecular weight of the polymer.

Polymer Characterization. In the ¹H NMR spectra of the HB-PmP with a molecular weight (M_n) of 35.8 kDa, the aromatic region showed complex overlapping signals, whereas the upfield region showed three broad signals from δ 1.58 to δ 0.25, corresponding to the *tert*-butyl groups of different types. In Figure 3a, the broad signals from δ 1.58 to δ 1.25 (region 1) are assigned to the *tert*-butyl groups attached to the peripheral terminal units, as the tert-butyl groups in the monomer resonate at δ 1.34. The other two broad signals spanning from δ 1.25 to δ 0.25 (region 2) are attributed to the tert-butyl groups attached to the linear units, for which the difference in chemical shift may indicate the presence of different environments for the linear units nearer to the peripheral units compared to those located in the inner tiers of the HB-PmP. When DP is sufficiently high, the ratio of the terminal versus linear units is expected to be ca. 1:1 based on their relationship, that is, T = L + 2. However, because of the broadness of the signals, it was not possible to obtain an accurate integration ratio of "region 1" versus "region 2". In the ¹³C NMR spectra, the *tert*-butyl –CH₃ groups show two relatively narrow lines at δ 31.5 and δ 31.1 that overlap with a broad signal centered at δ 30.9 (Figure 3b). The ¹⁹F NMR spectra (not shown) of the HB-PmP only display one broad signal centered at δ -73.3, indicating that hydrolysis of the triflate termini does not appear to occur to any great extent.

The HB-PmPs were also examined by MALDI-TOF spectroscopy. For a polymer sample with a M_n (GPC) of 16 kDa, a series of oligomers up to 18mer were detected (Figure S6).⁵⁸ For each of these oligomers, the presence of one pinacol boronate ester and (n + 1) triflate end groups was confirmed by comparing the results with the calculated values. This observation suggests that cyclization at the focal point is not a significant reaction pathway.

The UV-vis absorption spectra for HB-PmPs with different molecular weights ($M_n = 27.0$, 35.8, and 57.3 kDa) show very similar profiles with a strong absorption at $\lambda_{max} =$ 255 nm, exhibiting a slight red shift as compared to that of the monomer ($\lambda_{max} = 249$ nm). As expected, the long-range conjugation in the 1,3,5-terphenyl-based polymer backbone is disrupted and confined within discrete biphenyl units. As a result, these three polymer samples with the same weightvolume percentage in THF solution showed essentially the same magnitude of absorbance per mole of repeat unit (Figure S7).

The thermal stability of the HB-PmPs was examined by thermal gravimetric analysis (TGA) under N₂ from room temperature to 900 °C at a constant increment rate of 10 °C/ min (Figure S8). Two mass loss steps were present with the onset temperature of 330 and 490 °C. Each step corresponds to approximately 22–24% loss of the original polymer mass, for which we attribute the first stage to the loss of triflate groups and the second to the *tert*-butyl groups according to our previous results obtained for the *tert*butyl-substituted 1,3,5-polyphenylene dendrons.³⁹ Differential scanning calorimetry (DSC) experiments carried out under N₂ from room temperature to 400 °C did not show detectable phase transition before decomposition of the polymer (Figure S10).

Given the high efficiency of the SPC process, we were interested in the feasibility of end group modification of the HB-PmPs via direct Suzuki-Miyaura cross-coupling. Polycondensation of 6 was first conducted under standard reaction conditions in the presence of 0.5 mol % $Pd(OAc)_2$ S-Phos for 1 h, and phenylboronic acid or pyrene-1-boronic acid was then introduced to the reaction mixture without adding more catalyst. When compared to their triflate precursors, the resulting phenyl- and pyrenyl-capped HB-PmPs only showed slightly increased molecular weights and PDIs (Figure S5 and Table S3). However, a significant effect on the solubility is clearly seen for these end-capped HB-PmPs, which showed limited solubility in ethyl acetate, one of the best solvents for triflate-terminated HB-PmPs. TGA curves of the phenyl- and pyrenyl-capped HB-PmPs display less than 4% mass loss before 450 °C, indicating an over 80% efficiency for the end-capping process (Figure S9). The UV-vis absorption and fluorescence spectra of the pyrenyl end-capped (HB-PmP-pyr) and triflate-terminated (HB-PmP-OTf) HB-PmPs are shown in Figure 4. The absorption profile of HB-PmP-pyr displays a strong band peaking at 250 nm along with a small shoulder peak at 281 nm and a broad band centered around 346 nm, indicating the presence of pyrenyl groups. In the fluorescence spectra ($\lambda_{exc} = 346 \text{ nm}$) of HB-PmP-pyr, a strong emission at 460 nm is indicative of pyrene excimer formation.^{59,60} The fluorescence quantum yield measured for HB-PmP-pyr ($M_n = 39.3$ kDa) in THF ($\Phi = 0.74$) is much higher than that for the triflateterminated HB-PmPs ($\Phi = 0.09$) with a comparable molecular weight ($M_n = 35.8$ kDa). Furthermore, it is noteworthy that the strong excimer emission in HB-PmP-pyr was even observed at a submicromolar concentration (0.1 μ M with respect to the pyrene unit),⁶¹ suggesting an intramolecular rather than intermolecular excimer formation as resulted



Figure 4. Normalized absorption and emission spectra of triflate ($\lambda_{exc} = 255 \text{ nm}$) and pyrenyl ($\lambda_{exc} = 346 \text{ nm}$) end-capped HB-PmPs measured in THF. Molecular weight: $M_{n(HB-PmP-OTf)} = 35.8 \text{ kDa}$, $M_{n(HB-PmP-pyr)} = 39.3 \text{ kDa}$.

from the confined spatial arrangement of the pyrenyl groups within the hyperbranched polymer.

Conclusions

In summary, we have developed a Suzuki polycondensation (SPC) protocol of a *m*-terphenyl-based branched AB₂ monomer that efficiently delivers the hyperbranched poly(*m*-phenylene)s (HB-PmPs) with high molecular weights and excellent solubility in common organic solvents. The highly active catalyst system used and the structural characteristics of the branched monomer are believed to be the two main factors that lead to these improvements with respect to the cases where simple trisubstituted benzene-based AB₂ monomers were used. The molecular weight and PDI of the HB-PmPs could be controlled by varving the catalyst loading and the starting monomer concentration. In addition, the degree of branching was expected to be constant (67%) for HB-PmPs obtained from this branched AB₂ monomer. With the strategy described, one should be able to modify the monomer structure by replacing the tert-butyl groups with other functionalities, so that different functional groups could be incorporated within the HB-PmP scaffold. A wide range of available phenolic compounds are therefore potential precursors to the corresponding triflate-based monomer components. We have demonstrated that the triflate end groups of the HB-PmPs can be efficiently replaced in situ by other functional groups via Suzuki-Miyaura cross-coupling. Our current work is focused on these variations that would enable a systematic investigation toward the properties, functions, and implications of functionalized HB-PmPs.

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Supporting Information Available: Experimental details of the monomer and polymer synthesis, characterization data, GPC chromatograms, MALDI-TOF data, UV–vis spectra, thermal analysis data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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- (43) K₃PO₄ was used as the base and THF-H₂O as the solvent. Use of strong bases such as NaOH led to quantitative deprotection of the TBS groups.
- (44) To achieve complete conversion of 3, 3 mol % [Ir(COD)(OMe)]₂ and 6 mol % 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) needed to be added in two portions. See Supporting Information for details.
- (45) Hydrolysis of the boronate ester was observed in this process that resulted in decreased yield. All the pinacol boronate esters, i.e., 2, 4, 5, and 6, are sufficiently stable to the silica gel flash chromatography conditions that we used, although small amounts of decomposition may occur if a prolonged column chromatography process was applied.
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