Effect of Core Reactivity on the Molecular Weight, Polydispersity, and Degree of Branching of Hyperbranched Poly(arylene ether phosphine oxide)s

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ABSTRACT: Synthesis of hyperbranched poly(arylene ether phosphine oxide)s, HB PAEPOs, from bis-(4-fluorophenyl)(4-hydroxyphenyl)phosphine oxide, **1a**, in the presence of a series of core molecules with systematically altered reactivity of the aryl fluoride groups provides polymers with molecular weights, MWs, controlled by the concentration of the core molecule, and narrow polydispersity indices, PDIs. Polymers with number-average molecular weights ranging from 3270 to 8100 Da, and PDIs as low as 1.25 have been prepared. The core molecules utilized in this work consist of a series of fluorinated triarylphosphine oxides, tris(4-fluorophenyl)phosphine oxide, tris(3,4-difluorophenyl)phosphine oxide, and tris(3,4,5-trifluorophenyl)phosphine oxide, **2a**, **2b**, and **2c**, respectively. The most highly activated core, **2c**, provides the best control over the final MW and the lowest PDIs. The degree of branching, DB, for the HB PAEPOs decreases from 0.57 with no core to below 0.40 at higher concentrations of **2b** and **2c**.

# Introduction

Hyperbranched polymers have received considerable attention over the past decade due to their interesting properties such as large numbers of end groups, low intrinsic viscosities, and three-dimensional structures.<sup>1–9</sup> The physical properties and final applications of hyperbranched polymers depend on the chemical composition, the molecular weight (MW), the polydispersity index (PDI), and the degree of branching (DB). Hyperbranched polymers including alkyl<sup>10</sup> and aryl<sup>11,12</sup> esters and amides<sup>13,14</sup> to siloxanes<sup>15</sup> have been prepared, and the subject has been extensively reviewed.<sup>3–9</sup>

Several theoretical studies have described the structural development in terms of MW, PDI, and DB as the polymerization reaction of an AB<sub>2</sub> monomer proceeds. As first predicted by Flory,<sup>1</sup> rather high PDIs are expected at high conversions of the Å functional groups.  $^{16-22}$  Because of the difficulty in determining accurate structure-property relationships with illdefined systems, the high polydispersity indices are considered to be one of the main drawbacks of hyperbranched systems. Contributing to the high PDI values in many of the more flexible systems, such as alkyl esters and ethers, is the propensity for intramolecular cyclization.<sup>23-25</sup> Recently, attempts to prepare highly branched polymers with low PDIs and controlled molecular weights have utilized multifunctional core mol-ecules in conjunction with slow<sup>26,27</sup> or batchwise<sup>10</sup> monomer addition to the respective cores. The "core dilution/slow monomer addition" method has been exploited to prepare hyperbranched polyglycerols<sup>26</sup> and poly(phenyl acetylene)s<sup>27</sup> with controlled MWs and narrow PDIs (<1.5).

Other than the experimental examples of core systems that have been described above, most studies involving the addition of core molecules have been theoretical treatments.<sup>28–32</sup> All of the theoretical studies indicate that the addition of a core molecule provides access to hyperbranched polymers with narrower PDIs than polymers prepared in the absence of a core as long as the reactivity of the functional groups in the core is comparable to the reactivity of the functional groups in



the monomer. Of particular interest for our project is a theoretical paper by Cheng and Wang<sup>28</sup> where the effect of core reactivity on the MW, PDI, and DB of hyperbranched polymers is studied using AB<sub>2</sub> monomers and multifunctional cores (B'<sub>3</sub>) with varying reactivities of B'. They have defined the reactivity ratio,  $\beta$ , as the ratio of rate constants  $k_{AB'}/k_{AB}$  (Scheme 1). They indicate that, at high conversions of functional groups, the final PDI is decreased significantly with an increase in the ratio of reactivity of B' to B or when  $\beta \gg 1$ . In addition, it should be possible to control the final MW of the polymer by altering the concentration of the core. To the best of our knowledge, no experimental work that systematically alters the reactivity of the core functional groups to study the effect on MW, PDI, and DB has been reported.

We have been interested in synthesizing hyperbranched polymers containing triarylphosphine or triarylphosphine oxide groups at every repeat unit for use as macromolecular ligands and rheological modifiers, respectively. Our approach involves the preparation of several AB<sub>2</sub> monomers (Figure 1) and the subsequent polymerization under nucleophilic aromatic substitution conditions.<sup>33</sup> Hyperbranched poly(arylene ether phosphine oxide)s (HB PAEPOs) with number-average molecular weights ranging from 9500 to 14600 Da and molecular weight distributions from 2.44 to 3.43 have been achieved. The degree of branching for these polymers is approximately 0.57. Lee et al. have also reported the polymerization of **1a**.<sup>34</sup>

The polymerization of **1a** is an ideal system to study the effect of core reactivity on MW, PDI, and DB because



Figure 1.  $AB_2$  monomers utilized for the preparation of hyperbranched PAEPOs via nucleophilic aromatic substitution.

the preparation of core molecules with varied reactivity of the aryl fluoride moieties is relatively straightforward. We now wish to present our results from polymerizations of **1a** in the presence of three triarylphosphine oxide core molecules, **2a**, **2b**, and **2c** (Figure 2), in which the reactivity of the aryl fluorides in the para positions has been systematically altered by the presence of adjacent fluorine atoms, to study the effect of  $\beta$ on MW, PDI, and DB.

#### **Experimental Section**

All reactions were performed under a nitrogen atmosphere, and all transfers were done using syringes or cannula as necessary. All of the chemicals were purchased from Aldrich Chemical Co., with the exceptions of 1-bromo-3,4-difluorobenzene and 1-bromo-3,4,5-trifluorobenzene which were purchased from Fluorochem USA. All reagents were distilled or otherwise purified prior to use. Tetrahydrofuran and toluene were dried over and distilled from sodium/benzophenone prior to use. *N*-Methylpyrrolidinone was dried over CaH<sub>2</sub> and distilled prior to use. Monomer **1a** was prepared according to a previously reported procedure.<sup>33</sup> The phosphine precursor to core **2a** is available from Aldrich.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were obtained using a Bruker Avance DMX 300 MHz instrument operating at 300, 75.5, and 121.5 MHz, respectively. Samples were dissolved in CDCl<sub>3</sub>. GPC analysis was performed using a Viscotek model 300 TDA system equipped with refractive index, viscosity, and light scattering detectors operating at 70 °C. Polymer Laboratories  $5 \,\mu$ m PL gel columns (guard column, 10<sup>3</sup> and 10<sup>4</sup> Å) were used with NMP (with 0.5% LiBr) as the eluent and a Thermoseparation model P1000 pump operating at 0.8 mL/min.

**Synthesis of Tris(3,4-difluorophenyl)phosphine Oxide, 2b.** A 100 mL round-bottom flask, equipped with an addition funnel and reflux condenser, was charged with 1.26 g of magnesium turnings. A solution of 9.75 g (50.5 mmol) of 1-bromo-3,4-difluorobenzene in 50 mL of anhydrous THF was added dropwise over a period of 1 h to maintain a gentle reflux. After complete addition, the reaction mixture was allowed to stir at room temperature for 6 h, at which time it was cooled to 0 °C using an ice bath. A solution of 1.40 mL (16.0 mmol) of PCl<sub>3</sub> in 25 mL of anhydrous THF was slowly added to the stirred mixture. The resulting mixture was allowed to stir overnight and finally heated to reflux for 4 h. Excess Grignard reagent was quenched with saturated aqueous ammonium chloride. The resulting mixture was poured into a separatory funnel, and 100 mL of ether was added. The layers were separated; the organic layer was washed with water, dilute sodium hydroxide, and distilled water, then dried over magnesium sulfate, and filtered. The solvents were removed under reduced pressure to afford 4.92 g (83%) of a yellow oil that was used without further purification. GC/MS: m/z 369.

The yellow oil was dissolved in a mixture of 30 mL each of ether and acetone. To the rapidly stirred mixture was slowly added 3.0 mL of 30% hydrogen peroxide, and the reaction was allowed to stir overnight. The reaction mixture was poured into a separatory funnel, and 100 mL of toluene was added. The layers were separated, and the organic layer was washed with sodium thiosulfate and water and dried over magnesium sulfate. The solvents were removed to afford a yellow solid that was recrystallized from toluene to provide 4.32 g of **2b** (84%) as a white solid (mp = 93–95 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.25–7.55 (m, 3H, Ar–H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 118.9 (m), 121.6 (m), 128.0 (m), 129.3 (m), 149.3 (dd), 152.1 (dd), 152.7 (dd), 155.3 (dd). Elem. Anal. Calcd for C<sub>18</sub>H<sub>9</sub>F<sub>6</sub>OP: C, 55.98%; H, 2.35%. Found: C, 55.96%; H, 2.42%.

**Synthesis of Tris(3,4,5-trifluorophenyl)phosphine Oxide, 2c.** Core **2c** was prepared according to the procedure used for **2b** to afford 2.37 g (97%) of **2c** as a white solid (mp = 219– 221 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.23–7.31 (m, 2H, Ar–H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 116.9 (m), 126.0 (m), 127.5 (m), 141.7 (dt), 145.2 (dt), 150.5 (m), 153.9 (m). Elem. Anal. Calcd for C<sub>18</sub>H<sub>6</sub>F<sub>9</sub>-OP: C, 49.11%; H, 1.37%. Found: C, 49.09%; H, 1.41%.

**General Procedure for Polymerization Reaction of 1a** with 2b Core. A 100 mL round-bottom flask was charged with 1.32 g (4.10 mmol) of 1a, 0.15 g (0.4 mmol) of core 2b, 0.61 g (4.4 mmol) of potassium carbonate, 14 mL of NMP, and 12 mL of toluene. The reaction was heated to reflux for 4 h, during which time any water was azeotropically removed to ensure dryness. The toluene was distilled, and the temperature of the reaction mixture was raised to ca. 202 °C and held there for 4 h. The reaction mixture was cooled to room temperature, filtered to remove any salts, and precipitated into 300 mL of 10% acetic acid to afford the polymer as an off-white solid. The polymer was dissolved in THF and reprecipitated from water to provide a low-density, white solid that was filtered, washed with water, and dried under vacuum to yield 1.10 g of polymer. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.08-7.25 (b, 4 H), 7.60-7.64 (b, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 116.6 (m), 119.4 (m), 127.1 (m), 127.9 (m), 128.6 (m), 129.3 (m), 134.9 (m), 159.8 (s), 163.9 (s), 167.2 (s). <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): 28.5 (s), 28.7 (s), 28.9 (s).

#### **Results and Discussion**

In order for the core to effectively control the MW and PDI in the polymerization of **1a**, similar, if not better, reactivity of the aryl fluoride moieties toward nucleo-



Figure 2. Phenoxide derivative, 1d, of 1a and the core molecules for the polymerization of 1a.



philic aromatic substitution is required. Core **2a** provides aryl fluorides with reactivities toward nucleophilic aromatic substitution that are slightly greater than those in the phenoxide derivative of **1a** (Figure 2, **1d**) due to the decreased electron-withdrawing capability of the phosphoryl group in the presence of phenoxide (i.e.,  $\beta > 1$ ). Derivatives **2b** and **2c** provide core molecules with  $\beta \gg 1$  since substitution of the para fluorine atom should be highly activated by the presence of the additional fluorine atoms. We have previously shown that substitution reactions of the methoxy protected analogues of **1b** and **1c** occur exclusively at the para positions, and identical behavior is expected in this study.<sup>33</sup>

core

The synthesis of core molecules **2a**, **2b**, and **2c** is shown in Scheme 2. Reaction of 3.15 equiv of the appropriate Grignard reagent with phosphorus trichloride provides the precursor phosphines. Oxidation to the desired phosphine oxides, **2a**, **2b**, and **2c**, is achieved by reaction with an excess of 30% hydrogen peroxide. Washing with sodium thiosulfate removes any residual hydrogen peroxide. After removal of the solvents, recrystallization from toluene provides the phosphine oxides in analytically pure form in good to excellent yields (69.9–95.5%).

Polymerization reactions of **1a** in the presence of 3, 5, and 10 mol % of **2a**, **2b**, and **2c** have been carried out under typical nucleophilic aromatic substitution



**Figure 3.** GPC traces of the polymers prepared with no core and 3% of core **2a**, **2b**, and **2c**.



Figure 4. GPC traces of the polymers prepared with 5% of core 2a, 2b, and 2c.

conditions ( $K_2CO_3$ , NMP at reflux) with reaction times of 8 h (see Scheme 3). To ensure that no oligomeric species are lost during precipitation, slightly acidic water has been used as the nonsolvent. GPC traces of the products from the polymerization reactions are displayed graphically for the 3, 5, and 10% core reactions in Figures 3, 4, and 5, respectively, and the results are listed in Table 1. It should be kept in mind that the number-average molecular weights given in Table 1 are reported relative to linear polystyrene standards and, as such, cannot be taken as absolute values, but only used for comparison purposes in the following discussion.

As expected from the theoretical predictions, the presence of the core molecules decreases the numberaverage molecular weights of the polymers with a concurrent reduction in the molecular weight distributions. It is noted that, in stark contrast to previous examples of narrow molecular weight distribution polymers prepared by the core dilution/slow monomer addition method,<sup>26,27</sup> the current work involves addition of all of the monomer at the onset of the reaction.

In principle, if monomer reacts exclusively with core molecules or growing polymeric species rather than with another monomer, polymers will be prepared with approximately 33 repeat units per macromolecule when 3% core is used, 20 repeat units when 5% core is used, and 10 repeat units when 10% core is used. The theoretical  $M_n$  is calculated according to eq 1. In our case the repeat unit formula mass is 310 Da.

 $\frac{\text{theor. # of repeat units}}{\text{molecule}} \times \text{repeat unit formula mass} \quad (1)$ 



Figure 5. GPC traces of the polymers prepared with 10% of core 2a, 2b, and 2c.

Table 1. Molecular Weight and Polydispersity IndexResults from Polymerization Reactions of 1a in thePresence of Core Molecules

polymer	core	amount (mol %)	time (h)	M <sub>n</sub> (theor) (Da)	$M_{\rm n}{}^a$ (Da)	PDI
3a	none	N/A	8		12500	2.64
3b	2a	3	8	10400	6720	2.28
3c	2a	5	8	6220	6370	2.10
3d	2a	10	8	3110	4470	1.62
3e	2b	3	8	10400	7910	1.83
3f	2b	5	8	6220	6740	1.93
3g	2b	10	8	3110	4360	1.38
3ĥ	2c	3	8	10400	8100	1.55
<b>3i</b>	2c	5	8	6220	5840	1.39
3j	2c	10	8	3110	3270	1.25

 $^{a}\,\mathrm{Molecular}$  weights are reported relative to polystyrene standards.

Core **2a** decreases the molecular weight compared to the control polymer with no core and provides a significant decrease in PDI from 2.64 down to 1.62 with 10% of **2a**. This indicates that the reactivity of the fluorine atoms in **2a** is slightly higher than that of the fluorine atoms in **1d** but that the PDI cannot be sufficiently lowered when **2a** is used at lower concentrations. The polymer that is formed using 3% of **2a** shows a slightly lower MW than the theoretical value. This may be explained by a change in the reactivity of the aryl fluorides upon the initial reaction of **1d** as shown in Scheme 4.

The reaction of **1d** with another **1d** would lead to a dimeric species, **1f**, in which the reactivity of the aryl fluorides ( $\mathbf{F}_a$ ) of the "end group" is similar to that of the aryl fluorides in **2a** (i.e.,  $\beta$  is close to one; see Scheme 4). If the rate of formation of **1f** is comparable to the reaction of **1d** with **2a** to form **2f**, the result is essentially an increased number of growing polymer species giving rise to an "apparent" concentration of core higher than 3% with the end result being lower molecular weight polymers. The effect is less noticeable at higher concentrations of **2a**, and the MWs are much closer to the predicted values.

Polymerizations in the presence of **2b** provide hyperbranched polymers with MWs much closer to what has been predicted and with considerably narrower PDI values compared to those with **2a**. The additional activation that is provided by the adjacent fluorine atoms in **2b** is sufficient to provide a polymerization process closer to the ideal case where the reaction of **1d** with **2b** is preferred (i.e.,  $\beta \gg 1$ ).

With **2c**, polymers with low PDI values are produced, with as little as 3% of the core present. Using 3% of **2c**,



the PDI is only 1.55 and decreases to 1.25 when 10% of **2c** is added. The MWs that are observed approach the theoretical values for the 3, 5, and 10% levels, indicating that **2c** is the ideal core for the polymerization of **1a** by providing a reactivity ratio,  $\beta$ , much greater than 1.

**Degree of Branching.** It has been predicted that higher percentages of core molecules (i.e., lower MW) should lead to a slight decrease in the observed degree of branching.<sup>28,31,32</sup> This is observed experimentally as a decrease in the number of dendritic units relative to linear units present in each macromolecule and can be quantified using NMR spectroscopy. The degree of branching, DB, for hyperbranched systems can be calculated using two different methods. Hawker and Frechet<sup>12</sup> have defined the degree of branching as

$$DB_{(Hawker)} = (NT + ND)/(total number of units)$$
 (2)

where NT is the number of terminal units, ND is the number of dendritic units, and the total number of units includes the linear units. The second method has been proposed by Holter and Frey<sup>17</sup> and is defined as

$$DB_{(Holter)} = (2ND)/(2ND + NL)$$
(3)

where NL is the number of linear units.

We have previously reported the degree of branching, as defined by Hawker, for the polymer from **1a** to be 0.57 (0.55 by the Holter method) by utilizing model compounds and <sup>13</sup>C NMR spectroscopy.<sup>33</sup> The use of <sup>31</sup>P NMR spectroscopy (Figure 6) provides a more time-efficient estimate of the number of dendritic, linear, and terminal units present in the HB PAEPOs. In agreement with the results from <sup>13</sup>C NMR spectra, the upfield, middle, and downfield resonances from the polymerization of **1a** without a core have been assigned to terminal, linear, and dendritic units, respectively.

Figure 7 displays <sup>31</sup>P NMR spectra for the polymers from **1a** that have been prepared in the presence of 3, 5, and 10% of **2a**, **2b**, and **2c**, respectively. The degree of branching for polymers **3a**–**j** according to eqs 2 and 3 are listed in Table 2. It is readily apparent that the reactivity and percentage of core have a dramatic effect



**Figure 6.** <sup>31</sup>P NMR spectrum in CDCl<sub>3</sub> of the polymer from polymerization of **1a** without a core molecule present.

on the final microstructure of the polymer. Core **2a** has little effect on the resultant DB with only a slight change in DB from 0.55 to 0.50 (Holter method) with an increase in core concentration from 3 to 10% **2a**.

The use of core 2b results in a more significant decrease in DB from 0.51 to 0.38 with an increase in core concentration from 3 to 10%, according to the Holter method. According to the Hawker method, there

Table 2. DB Determinations for Polymers from theReactions of 1a in the Presence of Core Molecules

polymer	core	percent	$DB^{a}$	$DB^b$
3a	none	N/A	0.57	0.55
3b	2a	3	0.55	0.53
3c	2a	5	0.55	0.55
3d	2a	10	0.54	0.50
<b>3e</b>	2b	3	0.55	0.51
3f	2b	5	0.57	0.48
3g	2b	10	0.60	0.38
3ĥ	2c	3	0.56	0.43
<b>3i</b>	2c	5	0.61	0.40
3j	2c	10	N/A	N/A

<sup>*a*</sup> Degree of branching calculated according to Hawker's method (see ref 12). <sup>*b*</sup> Degree of branching calculated according to Holter's method (see ref 17).

is a slight increase in DB of 0.55 to 0.60 with 3 and 10% core concentration, respectively. Core **2c** lowers the DB (Holter) to 0.43 at 3% and 0.40 at 5% while, again, the Hawker method gives a slight increase in DB from 0.56 to 0.61. The DB at 10% of **2c** is not discernible since distinct peaks assigned to dendritic, linear, and terminal units are not present in the <sup>31</sup>P spectrum. While it has been shown that the Hawker method favors an overestimation of DB for low molecular weight structures,<sup>18</sup> it appears that with our system the core reactivity may also play a significant role. For example, **3e** and **3h** have essentially the same molecular weight (7910 and 8100 Da, respectively), yet the difference in DB between the two methods increases significantly with an increase in core reactivity.

### Conclusions

Hyperbranched poly(arylene ether phosphine oxide)s with controlled molecular weights and narrow PDI's have been prepared by the polymerization of **1a** in the



**Figure 7.** <sup>31</sup>P NMR spectra in CDCl<sub>3</sub> of the polymers from polymerization of **1a** in the presence of 3%, 5%, and 10% of cores **2a**, **2b**, and **2c**, respectively.

presence of three core molecules, 2a, 2b, and 2c. The more highly reactive the core is toward nucleophilic aromatic substitution, the more control is provided over the final molecular weight and the resultant PDI. In our case, the most highly fluorinated core, 2c, generates polymers with molecular weights approaching the theoretical values and the narrowest PDIs (as low as 1.25). This work represents the first example of an experimental synthetic study in which the reactivity of the functional groups in the core molecules has been altered systematically to provide hyperbranched polymers with low PDI values without requiring slow monomer addition. These results correlate well with theoretical predications by Cheng<sup>28</sup> based on reactivity ratios of  $k_{AB}/k_{AB}$ . The degree of branching, as defined by Holter and Frey,<sup>17</sup> decreased significantly when high concentrations, 5 and 10%, of core molecules 2b and 2c were added.

**Acknowledgment.** The authors thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Wright State University for financial support. The Ohio NMR Consortium is acknowledged for providing access to high field NMR facilities. The reviewers of this manuscript are thanked for their helpful comments and suggestions.

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MA021510B