

# Application of “Transfer-Free” Suzuki Coupling Protocols toward the Synthesis of “Unambiguously Linear” Poly(*p*-phenylenes)

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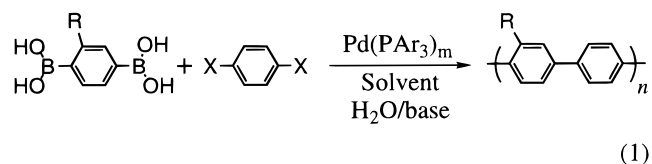
**ABSTRACT:** Soluble derivatives of poly(*p*-phenylene) of high molecular weight were synthesized via Suzuki coupling reactions catalyzed by palladium(0) precursors in the presence of either triphenylphosphine (TPP) or tri(*o*-tolyl)phosphine (TOTP). Syntheses involving the former ligand resulted in the formation of polymers in which the incorporation of phosphine was clearly observable by <sup>31</sup>P NMR. However, polymers formed utilizing the latter ligand in a hydrophobic solvent such as CH<sub>2</sub>Cl<sub>2</sub> exhibited no signals in the <sup>31</sup>P NMR spectrum, even after 20 000 scans. Analyses by tandem GPC–light scattering and tandem GPC–light scattering–viscometry showed that polymers synthesized by utilizing a large amount of TPP-based catalyst (2%) possessed a considerably lower molecular weight than did the other samples and exhibited markedly different dependencies of the radius of gyration and intrinsic viscosity on molecular weight. From these studies, it does appear that the aryl–aryl interchange reaction known to occur in ArPdL<sub>2</sub>I complexes significantly affects the architecture of these polymers.

## Introduction

Although truly rigid-rod macromolecules are rich with potential, their synthesis and processing has proven to be an extremely challenging goal for polymer chemists.<sup>1–8</sup> Synthesizing conjugated, rigid-chain polymers in order to access optical,<sup>9</sup> optoelectronic,<sup>10</sup> and pure electronic<sup>11</sup> properties further compounds the problem. The inherent insolubility and intractability of these structures pose a formidable obstacle, as synthesis, processing, and adequate characterization of high molecular weight materials is dependent upon their maintaining a fluid state by means of either a melt or solution. Furthermore, these polymers gain solubility only by virtue of extensive derivatization through incorporation of flexible side chains to exploit the entropy of solvent-side chain mixing<sup>12</sup> (a strategy that appears to have a detrimental effect on materials properties since the same strong interchain interactions which are the cause of intractability appear to be responsible for mechanical strength in oriented fibers<sup>13</sup>), the generation of a polyelectrolyte (to take advantage of interchain charge repulsion) through protonation,<sup>4–7</sup> complexation with Lewis acids,<sup>14</sup> or functionalization with charged groups.<sup>15</sup> Since the overall architecture of the polymer is critically sensitive to any regiochemical flaws introduced during the polymerization, an additional requirement is that the synthesis of genuinely rodlike polymers must occur through an error-free polymerization reaction. Classical methods<sup>16</sup> for the synthesis of poly(arylenes) are inadequate due to the presence of recalcitrant side reactions that both introduce regiochemical irregularities and limit molecular weight. Electrochemical polymerizations<sup>17</sup> do allow for the fabrication of thin films but the molecular weight of the polymer is limited by its insolubility, and regiochemical flaws again appear to be present.<sup>18</sup> Elegant strategies have been developed for

the synthesis of defect-free high molecular weight samples of underivatized poly(*p*-phenylene)<sup>19</sup> and poly(*p*-phenylene vinylene)<sup>2b–d,f,i,j</sup> using soluble precursor routes. Current methodologies for the direct synthesis of derivatized poly(*p*-phenylene) and other soluble polyarylenes are primarily based upon nickel- and palladium-mediated cross-coupling reactions<sup>20</sup> due largely to their preservation of regiochemistry and nearly quantitative yields.<sup>1b–e</sup>

The cross-coupling of aryl halides and arylboronic acids (Suzuki coupling)<sup>21</sup> is one of the most prevalent methods for the synthesis of polyarylenes (eq 1).<sup>22</sup>

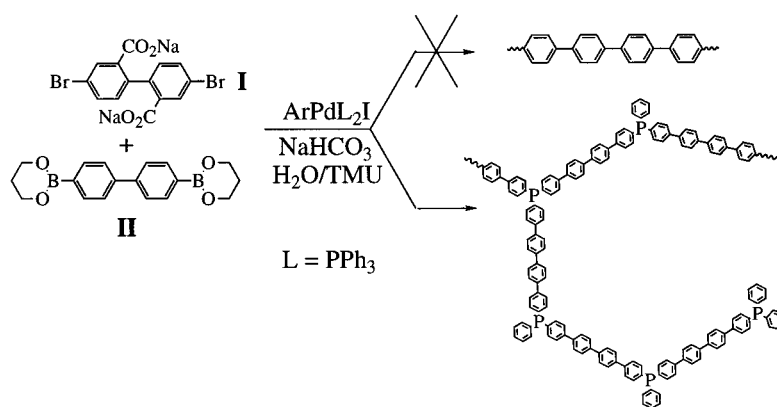


In addition to the advantages listed above, this reaction is tolerant of most functionalities and proceeds under mild conditions.<sup>21</sup> These qualities have made possible the development of water-soluble, water-processable poly(*p*-phenylene) analogues that have been the focus of other research in our group.<sup>15a</sup> Upon further investigation of these materials, however, we have found that they behave not as anisotropic rods, but rather as branched, isotropic materials (Scheme 1)<sup>23</sup> due to an exchange reaction on the ArPdL<sub>2</sub>I (L = triphenylphosphine, TPP, or similar) intermediates. (The concentration of phosphine defects depicted in Scheme 1 is purposely exaggerated in order to include all possible types in a limited space.) This exchange equilibrates the palladium-bound aryl groups with those bound to phosphorus (equilibrium between intermediates **1** and **2**, Scheme 2).<sup>24</sup> Such a side reaction would not only generate end caps (derived from the phosphorus-bound aryl moieties) but also provide for flexible units and branch points at the twice- (**3**) and thrice-substituted (**4**) phosphorus atoms, respectively, as the now func-

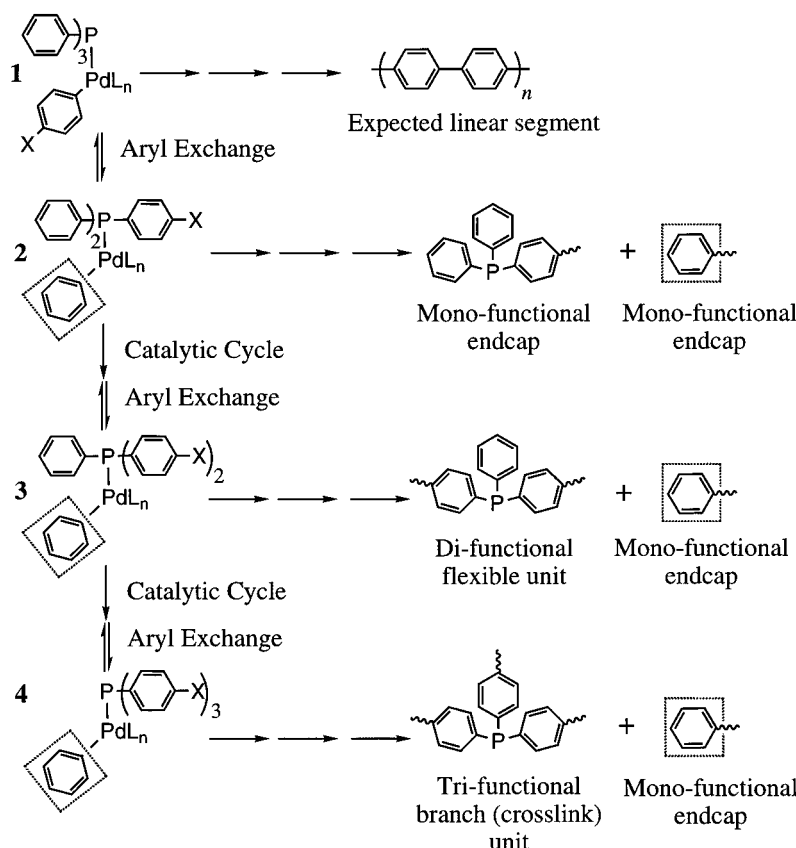
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Scheme 1



Scheme 2



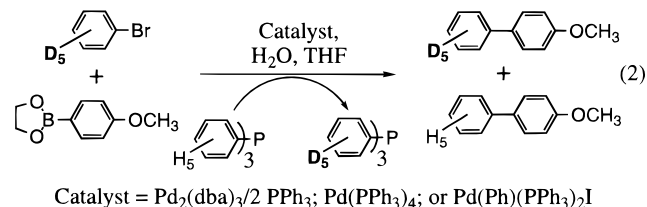
tionalized phosphines themselves are consumed in the polymerization reaction (Scheme 2).

In a previous report,<sup>25c</sup> we discussed that the aryl–aryl interchange could be eliminated in Suzuki coupling reactions through the use of a “ligandless” catalyst.<sup>25</sup> It was also found that byproducts due to the interchange could be reduced to less than 0.4% through the use of the bulky tri(*o*-tolyl)phosphine (TOTP) ligand in THF, or reduced to less than 0.003% with this phosphine when the reaction was performed CH<sub>2</sub>Cl<sub>2</sub>.<sup>26</sup> In this paper, we will discuss the implementation of these methodologies toward the synthesis of “unambiguously linear” poly(*p*-phenylenes). Then, from the results obtained from these endeavors, we will assess the impact of the interchange reaction on the properties of the polymers described here and elsewhere.

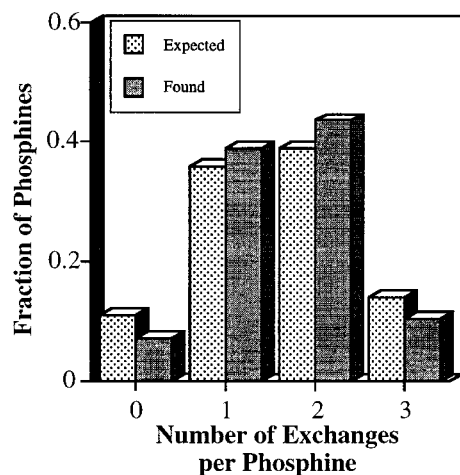
## Results and Discussion

Suzuki coupling protocols can call for up to 5% Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst.<sup>22</sup> To determine whether aryl

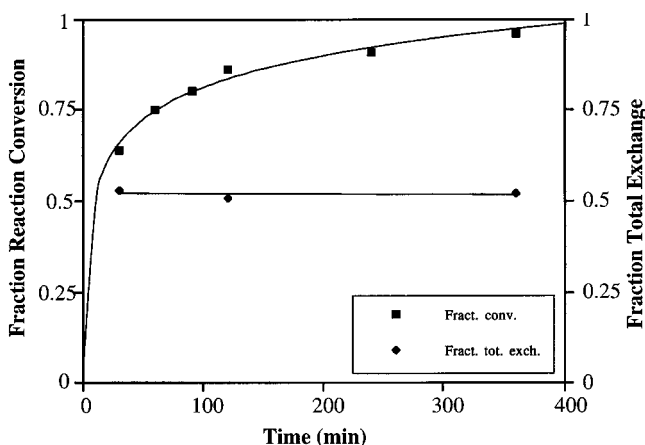
exchange occurs under *catalytic* conditions relevant to polymerizations, deuterium labeling was conducted using bromobenzene-*d*<sub>5</sub> as the aryl halide substrate and nondeuterated phosphines on the catalyst (eq 2).



Product distributions (both the biphenyls and deuterated phosphines) were measured using GC–MS. The results obtained clearly show that aryl exchange is a ubiquitous and facile process under typical polymerization conditions. For the coupling shown in eq 2, in THF/H<sub>2</sub>O at 65 °C using the benzene adduct of tris-



**Figure 1.** Observed deuterated phosphine distributions (GC-MS) for a reaction exhibiting 52% total exchange compared to the values predicted from a binomial frequency function. Reaction temperature 50 °C. Catalyst: Pd(Ph)(PPh<sub>3</sub>)<sub>2</sub>I.

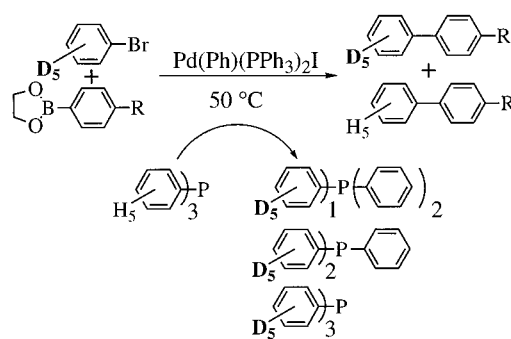


**Figure 2.** Time-course graph simultaneously showing the evolution of coupling product (solid squares) and exchange product (diamonds). See text for experimental conditions.

(dibenzylideneacetone)dipalladium(0) (**1**) in the presence of 2 equiv of TPP, greater than 99.9% conversion can be obtained (as measured by GC-MS). As expected, mixtures of deuterated and nondeuterated biphenyls were obtained. During a series of runs varying temperatures, solvents, and catalysts, the total number of <sup>1</sup>H-phenyl rings on the phosphines varied from 12% to 65% if all of the moieties in the phosphine ligands were exchanged for phenyl-*d*<sub>5</sub> moieties. Furthermore, product distributions (mono-, di-, and triexchanged phosphines) were found to fit a simple statistical binomial distribution. An example is shown in Figure 1 for a reaction carried out at 50 °C using Pd(Ph)(PPh<sub>3</sub>)<sub>2</sub>I as the catalyst. These results, which conclusively demonstrate that aryl exchange occurs during relevant catalytic conditions, together with the fact that these reactions have been optimized to yield quantitative conversion of functional groups, lead to the conclusion that the halogenated phosphines formed by this side reaction are ultimately incorporated into the polymeric structures.

Mechanistic information can also be obtained by simultaneously monitoring product formation and the appearance of exchange products. The time-course plot for the coupling reaction shown in Figure 1 is shown in Figure 2.

Interestingly, using the palladium(0) precursor catalysts, all of aryl-aryl exchange occurs during the initial



burst of catalytic activity and then halts, although the coupling process proceeds unimpeded. These observations strongly suggest a change in mechanism must be present although the details of this are yet to be elucidated. What is certain is the fact that during the bulk of the coupling reaction, there are mono-, di-, and triexchanged phosphines present.

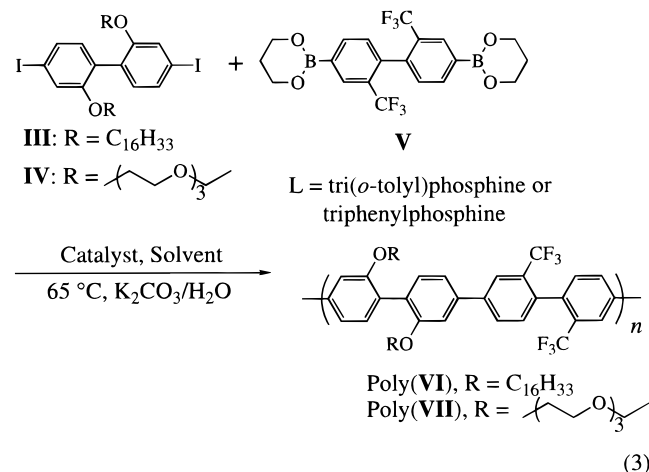
The questions now become, can we get direct evidence of phosphine incorporation into these polymers and how does this incorporation affect their properties? Initial attempts at synthesizing "unambiguously linear" poly(*p*-phenylenes) of **I** and **II** using our ligandless methodology<sup>25</sup> proved futile, as employing the cesium, sodium, or potassium salts of **I** all resulted in the formation of insoluble polymers. Although initially discouraging, this result did give an indication of the potential magnitude of the effect that the aryl-aryl interchange reaction could have on the polymer structure. Polymerizations performed with TPP catalysts (where the interchange reaction was documented to occur)<sup>23</sup> resulted in polymers of **I/II** that were freely soluble in water/DMF mixtures.<sup>15a</sup> Molecular weight turned out not to be the delineating factor (vide infra).

At this point, emphasis was switched from the aqueous polymerizations to more conventional organic solvent systems. To obtain soluble polyphenylenes, diiodide monomers **III** and **IV** were synthesized in four steps from 3-nitroanisole. Similarly, bis(boronic ester) monomer **V** with -CF<sub>3</sub> groups on the 2 and 2' positions (again to improve solubility<sup>1h,27-29</sup>), was also prepared. Polymerization of **V** with **III** or **IV** using the benzene adduct of tris(dibenzylideneacetone)dipalladium(0) (**1**) as the catalyst in the presence of TOTP<sup>26</sup> resulted in poly(**VI**) and poly(**VII**), respectively (eq 3). Polymers with two different side chains were targeted in order to show the generality of this approach. Although both polymers were freely soluble in THF, toluene, benzene, chloroform, and methylene chloride, which allowed for their purification (successive precipitations and lyophilizations), full characterization via NMR, GPC, viscometry and light scattering was conducted on poly(**VI**).

Aryl exchange between the palladium and phosphines is highly dependent on the phosphine (TPP ≫ TOTP), its concentration (i.e., the catalyst concentration), and the solvent used (THF > CH<sub>2</sub>Cl<sub>2</sub>).<sup>26</sup> To determine the effect of aryl interchange on the structure of soluble poly(*p*-phenylenes), samples of poly(**VI**) were synthesized under a variety of conditions (Table 1), and the

**Table 1. Polymerization Conditions and GPC–LS Results Obtained in THF for Poly(VI) Samples Prepared Using Different Phosphines**

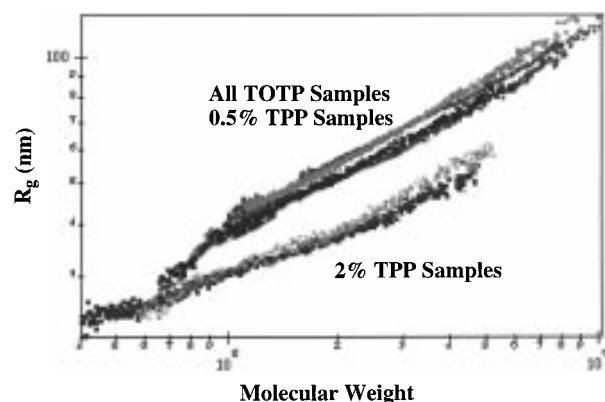
sample	ligand (% catalyst content)	$M_n$	$R_g$ (nm)	$R_g$ (calc) <sup>a</sup> (nm)	slope <sup>b</sup>
1	TOTP (0.5)	195 000	60 ± 2	118	0.449
2	TPP (0.5)	97 000	40 ± 1	59	0.417
3	TOTP (2.0)	96 000	39 ± 2	58	0.428
4	TPP (2.0)	47 000	25 ± 3	28	0.320

<sup>a</sup> Radius of gyration calculated from eq 4. <sup>b</sup> See text.

resulting polymer samples were analyzed by tandem gel permeation chromatography–light scattering (GPC–LS).<sup>30</sup> Although CH<sub>2</sub>Cl<sub>2</sub> is the preferred solvent for exchange minimization, comparative polymerizations utilizing TPP in CH<sub>2</sub>Cl<sub>2</sub> were not included in this study since it was found that this protocol did not produce quantitative results in model experiments.<sup>26</sup> The GPC–LS data obtained in THF for the polymer samples are listed in Table 1.

These samples were also analyzed by <sup>31</sup>P NMR (20 000 scans) in order to determine whether phosphorus was incorporated into their backbones via aryl interchange during the polymerization reactions (Supporting Information). After rigorous purification, samples 2 and 4, formed using TPP (i.e., conditions that facilitate exchange) showed strong phosphorus signals at  $\delta$  = 28.5 ppm (phosphine oxide region), indicating a substantial amount of phosphine was incorporated into the polymer backbone. Samples formed using TOTP, a ligand with, at best, minimal propensity to exchange, showed no phosphorus signal at all. This corresponds well with the data obtained from the analytical small-molecule coupling experiments outlined in the previous disclosure.<sup>26</sup>

Again, in all cases, the synthetic protocols employed were previously optimized to give quantitative conversion of the functional groups (i.e., differences in molecular weights cannot be ascribed to differing levels of conversion). One immediately noticeable difference between samples polymerized with the TPP-based catalysts (samples 2 and 4) and those polymerized with the TOTP-based catalysts (samples 1 and 3) is that the former suffer from a severe molecular weight depression with respect to the latter (e.g., 195 000 vs 97 000 for samples 1 and 3). While the depression trend can be explained by the end capping caused by the aryl–aryl interchange reaction,<sup>31</sup> the magnitude of the depression results from counterbalancing end capping, branching, and the slight degree of cross-linking (Scheme 2).

**Figure 3.** Logarithmic plots of radius of gyration vs molecular weight for poly(VI) samples prepared using TOTP- and TPP-based catalysts.

Another notable observation from these tables is the fact that even for the TOTP entries, the molecular weights for the 2% examples are considerably lower than those for the corresponding 0.5% samples: an observation that is again consistent with an increased number of end cap groups emanating from the catalyst.<sup>32</sup>

For an ideal rod, the radius of gyration<sup>33</sup> ( $R_g$ ) is related to the length of the rod ( $L$ ) by eq 4.<sup>34</sup>

$$R_g^2 = (L^2/12) \quad (4)$$

Assuming a 4.17 Å phenylene unit length (from the 1.39 Å carbon–carbon bond length in benzene<sup>35</sup>), the radii of gyration for the polymers were calculated on the basis of the molecular weight values determined. These values were also determined experimentally by the GPC–LS instrument, and the resulting data are included in Table 1. The experimental values are noticeably smaller than the calculated values, and the discrepancy is worse for the larger polymer samples. We attribute this to the fact that polyphenylene chains do not behave as rigid rods.<sup>1g</sup> Indeed, the solution behavior of other “rigid-chain” polymers<sup>36</sup> displays quite a bit of flexibility and they are better described as wormlike<sup>37</sup> or even coil<sup>38</sup> polymers. This inherent flexibility of the phenylene backbone may mask any contributions due to low levels of incorporated phosphine units. Branching, however, which increases the average segmental density, can be detected even in the presence of flexibility.

For linear and branched polymers of the same molecular weight, one would expect the branched polymer to have a much smaller radius of gyration since the chains have three dimensions over which to distribute their mass, whereas the chains of the linear polymer have only one. Since the probability of branching increases with higher molecular weight, one would expect this discrepancy to become magnified for larger molecular weights. Plots of  $\log(M_n)$  versus  $\log(R_g)$  measured in THF for several samples of poly(VII) are shown in Figure 3.

Under minimal exchange conditions (0.5% TPP catalyst or TOTP catalyst) small amounts of phosphine incorporation does not noticeably affect the solution properties of these polymers. However, at a fixed size (i.e., radius of gyration), samples of poly(VII) synthesized with 2% TPP catalysts clearly have much larger molecular weights than samples prepared with TOTP catalysts. In all cases, the values for this slope are

**Table 2. Poly(VI) Sample Analysis by GPC-LS-Viscometry**

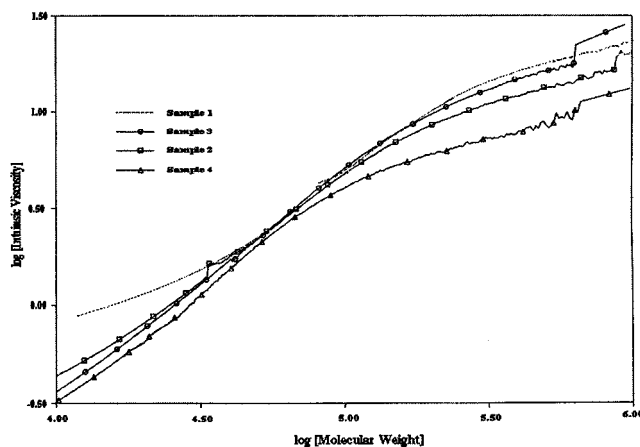
sample	$M_n$ ( $\times 10^4$ )	$M_w$ ( $\times 10^4$ )	PDI	$[\eta]$ (dL/g)	$r_G$	log $K$	$\alpha$
1	14.01	20.99	1.50	9.212	39.18	-3.620	0.868
2	7.23	12.58	1.74	5.724	27.79	-4.522	1.041
3	6.30	12.18	1.93	4.826	25.70	-4.107	0.952
4	3.15	6.18	1.96	2.184	15.63	-4.851	1.092
5	10.32	15.73	1.52	7.008	32.25	-4.467	1.029
6	8.72	14.48	1.66	5.684	28.99	-4.650	1.055

smaller than expected and are more consistent with coil structures rather than rods. A polydisperse sample of polystyrene measured under identical conditions displayed a slope of 0.567, a value in line with what would be expected for a random-coil polymer, suggesting that these aberrant results are not artifacts of the GPC-LS instrument.

Aggregation in solution is always a concern in evaluating solution properties of polyarylenes. This phenomenon has been observed in other "rigid" polymer samples,<sup>39</sup> even where the polymer exhibited a unimodal GPC chromatogram.<sup>39c</sup> However, it should be noted that unexpected flexibility and short persistence lengths have been measured for poly(*p*-phenylenes) under conditions in which aggregation is eliminated.<sup>1g</sup> In chloroform, samples 1 and 2 did show a slightly high molecular weight shoulder in the light-scattering trace, an occurrence indicative of possible aggregation.<sup>30e</sup> Furthermore, for the high molecular weight samples, the low molecular weight fractions displayed a great deal of curvature in the logarithmic plots of radius of gyration vs molecular weight. This type of curvature has been seen in samples of polystyrene where gelation has taken place;<sup>30e</sup> conceivably, aggregation could produce this effect as well. Fortunately, the curvature was found to be dependent upon both the columns used for the GPC and the solvent, suggesting that this effect is not due to chemical cross-links in the polymer and that it could be minimized. We found that aggregation could be suppressed by running GPC-LS measurements in THF, on Ultrastaygel columns (Column Resolution), or in  $\text{CHCl}_3$ , on PL-Gel columns (Polymer Laboratories).

Due to the uncertain slope data and the inherent flexibility of these chains, we cannot conclusively state that even under fully optimal conditions (TOTP catalysts in  $\text{CH}_2\text{Cl}_2$ ) have we successfully synthesized "unambiguously linear" poly(*p*-phenylenes). However, from this comparative data, it is clear that there is a significant difference in the overall solution behavior between polymers synthesized under conditions where the interchange reaction has been all but eliminated (e.g., TOTP catalysts), and those synthesized under conditions where the interchange is noticeably present (2% TPP catalysts). These differences suggest that aryl exchange reactions on the catalyst center do indeed play a key role in determining the structure of the polymer. This position is bolstered by the  $^{31}\text{P}$  NMR data: only samples with detectable  $^{31}\text{P}$  NMR resonances show decreased molecular weights and diminished hydrodynamic radii.

Another method by which the solution structure of a polymer can be studied is by tandem GPC-LS-viscometry.<sup>40</sup> Six samples were analyzed by a triple detector system consisting of a GPC apparatus equipped with an in-line viscometer and a light-scattering detector. The data for all six are presented in Table 2, and an overlay Mark-Houwink plot displaying four representative curves is shown in Figure 4.

**Figure 4.** Overlay Mark-Houwink plot for poly(VI) samples determined by tandem GPC-LS-viscometry.

A random coil will typically produce a slope ( $\alpha$ ) of 0.5–1.0,<sup>41</sup> while a rigid-rod will exhibit a significantly higher slope (e.g.,  $\alpha = 1.7$  for poly( $\gamma$ -benzyl L-glutamate),<sup>42</sup> a helical rodlike polymer). At a molecular weight of 40 000, the poly(VI) samples exhibit slopes of about 1.35, indicative of a wormlike polymer (one with a structure between that of a rod and a random coil). At higher molecular weights, the slope decreases dramatically, suggesting a worm-coil transition commonly observed with other wormlike polymers.<sup>36</sup> Since the samples of higher molecular weight materials contain a larger proportion of more "coil-like" polymer, the sample-wide  $\alpha$  values listed in Table 2 are not indicative of the stiffness of the structure when comparing one sample with another. However, as can be seen from Figure 3, sample 4, synthesized with 2% of the triphenylphosphine-based catalyst, clearly undergoes the worm-coil transition at a significantly lower molecular weight, in agreement with the results obtained above.

Finally, it should be emphasized that poly(phenylenes) synthesized under conditions optimized to yield the linear structure are still surprisingly flexible. These measurements are in agreement with published reports of unexpectedly short persistence lengths (13 nm) for substituted poly(phenylenes).<sup>1g</sup> Consistent with a rod-to-coil continuum, shorter poly(phenylenes) display stiffer chain characteristics in solution, as evidenced by the previously reported Mark-Houwink coefficients for lower molecular weight poly(phenylenes) (5 000–35 000) between 1.58 and 1.60.<sup>1h</sup>

## Conclusions

From the experiments presented in this paper, we have shown that by utilizing TOTP-based palladium catalysts and nonhydrophilic solvents such as methylene chloride, soluble poly(*p*-phenylenes) with no signals observable by  $^{31}\text{P}$  NMR can be synthesized. Polymers synthesized via TPP-based catalyst systems, on the other hand, clearly show a single phosphine signal in the phosphine oxide region of the  $^{31}\text{P}$  NMR spectrum. From GPC-LS and tandem GPC-viscometry techniques, we were able to determine that polymer samples in which significant exchange had taken place exhibited notably lower molecular weights and showed dependencies of viscosity and radius of gyration upon molecular weight different than those exhibited by polymers synthesized under interchange-free conditions. This suggests that the aryl-aryl interchange is having a

fundamental impact on the structure of the polymers formed from this Suzuki coupling methodology when TPP based catalysts are employed.

As far as the impact of aryl-aryl exchange on other polymerization systems is concerned, this assessment should be considered on a case by case basis. For the water soluble poly(*p*-phenylenes) discussed earlier,<sup>15a</sup> the monomer substituents are relatively small, located in the meta positions relative to the aryl halide bond, and the polymerization proceeds in a highly polar medium. As a result, one would expect the interchange reaction to have a large effect on polymer structure, and this is borne out by the difference in solubility between the polymers formed by the traditional<sup>15a</sup> and transfer-free catalyst systems (vide supra). For the majority of the organic systems, however, the polymerizations are carried out in aqueous emulsions using relatively non-polar cosolvents (benzene, toluene, chlorinated hydrocarbons) and the monomers contain bulky substituents ortho to the carbon-halogen bond.<sup>43</sup> Since it was established in our previous disclosure that ortho substituents severely hinder aryl-aryl interchange,<sup>26</sup> this side reaction probably does not have a significant effect on these latter polymerization systems. For intermediate cases, such as the one presented in this paper, where the substituents are in the meta position and the cosolvent is of moderate polarity, synthetic polymer chemists should be mindful of the interchange reaction and take steps to avoid it, such as by using the TOTP/methylene chloride protocol discussed here.

## Experimental Section

**General Information.** Schlenk-line or drybox (MBraun Labmaster 100 series; maintained under positive argon pressure) techniques were used for all air-sensitive manipulations. <sup>1</sup>H NMR spectra were acquired at 200, 300, 400, or 500 MHz using Bruker AC series, AM series, MSL series, and AMX series spectrometers; proton-decoupled <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P spectra were obtained at corresponding frequencies. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported relative to internal TMS; <sup>31</sup>P chemical shifts are reported relative to an external standard of triphenyl phosphite ( $\delta = 127.0$  ppm); <sup>19</sup>F chemical shifts are reported relative to an external standard of fluorobenzene ( $\delta = -113.1$  ppm). THF, toluene, diethyl ether, dimethoxyethane, benzene, and hexanes were purified by distillation from sodium/benzophenone and used immediately. CH<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub> and vacuum-transferred prior to use. Triphenylphosphine was purchased from Aldrich, recrystallized from degassed ethanol, and sublimed under vacuum prior to use. 2,2'-Bis(trifluoromethyl)-4,4'-diiodobiphenyl was synthesized by Marshalltown Research Laboratories, Inc. (Winston Salam, NC) and purified via sublimation under reduced pressure prior to use. The benzene adduct of tris(dibenzylideneacetone)dipalladium(0),<sup>44</sup> bis[tri(*o*-tolyl)phosphine]palladium(0),<sup>32b</sup> and phenylboric anhydride<sup>25c</sup> were all prepared via known procedures. Other chemicals were used as received from commercial suppliers. The polydisperse sample of polystyrene was synthesized from styrene in toluene initiated by AIBN. Listed melting point values are uncorrected. DSC measurements were performed on quenched samples with a DuPont Instruments Model 2000, while thermogravimetric analyses were performed with a Perkin-Elmer 7 Series Thermal Analysis System. Analytical data were obtained by the elemental analysis facilities at the University of California at Berkeley and the University of Massachusetts at Amherst.

Tandem GPC-LS experiments were performed with a Hewlett-Packard series 1050 HPLC pump equipped with either Ultrastrogel (500, 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, and 10<sup>6</sup> Å) columns (Column Resolution, Inc., San Jose, CA) or PL-Gel columns (Polymer Laboratories, Amherst, MA) in line with a Wyatt Technology (Santa Barbara, CA) DAWN DSP-F Laser pho-

tometer and a Wyatt Optilab 903 interferometric refractometer. Measurements were made at a wavelength of 688 nm. GPC molecular weight determinations were performed with the above pump and columns and a Waters 746 integrator. The listed values are relative to known standards of polystyrene. Refractive index increments for polymers **10** and **11** were measured with an Otsuka Electronics RM-102 differential refractometer at 688 nm and 25.0 °C. The known<sup>45</sup> value of 0.186 mL/g was used for the refractive index increment for polystyrene in THF under the same conditions. Tandem GPC-LS-viscometry measurements were performed by the Viscotek Corp. (Houston, TX), utilizing a Linear Phenomenex GPC column and precolumn in THF in line with a triple detector system consisting of a laser refractometer, viscometer, and light-scattering detector (Viscotek Model LR40 and Viscotek T-60 detector).

**Monitoring Aryl-Aryl Exchange by Deuterium Labeling Using Pd(PPh<sub>3</sub>)<sub>4</sub> as a Catalyst.** A specially designed reaction flask with an isolable sampling port was flushed with argon and charged with 243 mg of bromobenzene-*d*<sub>5</sub> (1.50 mmol), 285 mg of 2-(4'-methoxyphenyl)-1,4,3-dioxaborolane (1.60 mmol), 1.322 g of potassium carbonate sesquihydrate (8.0 mmol), and 18.0 mg of 4,4'-dimethylbiphenyl (0.1 mmol). Water (20 mL) and THF (10 mL) were added, and the mixture was degassed with two freeze-pump-thaw cycles. A solution of Pd(PPh<sub>3</sub>)<sub>4</sub> in degassed THF (1.73 mg/mL; 10 mL gives 1.50 × 10<sup>-5</sup> mol, 1% vs bromobenzene-*d*<sub>5</sub>) was introduced, and the mixture was subjected to two additional freeze-pump-thaw cycles. The flask was immersed in a glycerol bath held at 50 °C and allowed to stir. Aliquots (200 μL) were removed periodically and immediately quenched into prepared Ar-flushed, septum-capped vials containing 200 μL of dilute aqueous KCN (ca. 50 mM). Ether (200 μL) was added to the vials and the aqueous phase was removed via syringe. The organic layer was rinsed twice with 200 μL portions of degassed water and then stored on ice or at -20 °C prior to GC-MS analysis. The data obtained via GC-MS analysis were converted to concentrations (in the case of 4-methoxybiphenyl-*d*<sub>6</sub> and -*d*<sub>5</sub>) to monitor conversion or used as is (in the case of triphenylphosphine mixtures) to assess the degree of aryl interchange.

**4,4'-Diiodo-2,2'-dimethoxybiphenyl.**<sup>46</sup> 3-Nitroanisole (25.0 g, 0.163 mol), of 63.8 g (0.976 mol) of zinc powder, and 125 mL of 95% ethanol were combined in a 250 mL Schlenk flask with a stir bar. In a separate 50 mL Schlenk flask, 6.25 g (94.7 mmol, assuming 85%) of KOH was dissolved in 25 mL of deionized water. Both of these solutions were then degassed via several freeze-pump-thaw cycles, after which the KOH solution was cannula-transferred to the 3-nitroanisole suspension under argon. This flask was fitted with a reflux condenser under an argon backflow, and the reaction was brought to reflux for 1.5 h. An intense orange color developed soon into the reflux and then gradually faded. Afterward, the suspension was allowed to cool and was then cannulated to a Schlenk frit and filtered into a 500 mL Schlenk flask. The residual zinc powder collected in the frit was rinsed with 3 × 100 mL of degassed ethanol. The combined filtrates were concentrated in vacuo to give a slightly yellow biphasic oil, which discolored immediately upon exposure to ambient oxygen. A separate 250 mL Schlenk flask was charged with 23 mL (0.36 mol) of methanesulfonic acid, 85 mL of deionized water, and a stir bar. This solution was then degassed as above and chilled in an ice/water bath. The biphasic oil from above was then suspended in 100 mL of degassed methanol and cannulated into the chilled methanesulfonic acid solution, resulting in the formation of a yellow precipitate. The reaction was allowed to warm to ambient temperature overnight, transferred to a 500 mL round-bottomed flask, and concentrated to half volume with a rotary evaporator. The resulting suspension was chilled in an ice bath to yield a purplish slurry, which was filtered, leaving a lavender powder from a purple filtrate. The filtrate was discarded, and the powder was rinsed with ice-cold water, a couple milliliters at a time. The rinsings were concentrated to yield a second crop, and the combined solids were dried in vacuo to yield 19.0 g (43.6 mmol, 53.5% yield from 3-nitroani-

sole) of 4,4'-diamino-2,2'-dimethoxybiphenyl as the dimesylate salt, which was not further purified. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ 2.35 (s, 3H), 3.69 (s, 3H), 6.87 (dd, *J* = 6.4 Hz, *J* = 1.5 Hz), 6.95 (d, *J* = 1.5 Hz), 7.16 (d, *J* = 6.4 Hz). The 4,4'-diamino-2,2'-dimethoxybiphenyl dimesylate was dissolved in 800 mL of 70:30 water/acetonitrile in a 2 L Erlenmeyer flask equipped with a mechanical stirrer and a low-temperature thermometer. The solution was chilled to 0 °C in an ice/brine bath, 85 mL of methanesulfonic acid was added, causing a rapid warming, and the solution was allowed to cool back to 0 °C. Partial precipitation of the mesylate occurred during cooling. A solution of 6.045 g (87.6 mmol) of NaNO<sub>2</sub> in 400 mL of ice-cold water was added dropwise to the suspension via an addition funnel, while carefully maintaining the reaction temperature at 0 °C, to yield an orange-red solution. A solution of urea (0.992 g, 16.5 mmol) in 40 mL of cold water was then added to destroy any excess nitrous acid. Potassium iodide (166 g, 1.00 mol) in 330 mL of ice-cold water was rapidly introduced to the solution, and the mixture was removed from the ice bath and allowed to warm to ambient temperature. An orange precipitate immediately started to form. An additional 400 g (2.41 mol) of KI was added in portions at intervals during warming. Intense evolution of nitrogen was observed between 10 and 25 °C, and the color of the reaction gradually darkened. Following complete addition, the mixture was rapidly warmed to 60 °C, then chilled to room temperature, and extracted into 2 L of ethyl acetate. The organic layer was separated, washed with 2 × 500 mL of saturated aqueous sodium bisulfite, 2 × 500 mL of water, and 1 × 500 mL of brine and then dried over MgSO<sub>4</sub>. The solvent was then removed with a rotary evaporator to yield a brown solid mass, which was chromatographed on silica with 98:2 petroleum ether/ethyl acetate to yield a yellow solid. This was alternately recrystallized from THF/ethanol and sublimed (150 °C, dynamic 5 mTorr vacuum) until colorless to give 5.49 g (11.8 mmol, 14.5% yield from 3-nitroanisole) of 4,4'-diiodo-2,2'-dimethoxybiphenyl as a waxy white solid: mp 130–132 °C (THF/EtOH); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 3.74 (s, 3H), 6.91 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 7.33 (dd, *J* = 7.9 Hz, *J* = 1.5 Hz, 1H).

**2,2'-Dihydroxy-4,4'-diiodobiphenyl.** An oven-dried, argon-flushed 250 mL Schlenk flask was charged with 5.35 g (11.5 mmol) of 4,4'-diiodo-2,2'-dimethoxybiphenyl and 80 mL of dry methylene chloride. The flask was then chilled in an ice bath and fitted with an oven-dried addition funnel to which 38.0 mL (38.0 mmol) of a 1.0 M solution of BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> was then added via a disposable needle and syringe. The BBr<sub>3</sub> solution was then added dropwise over the course of 15 min, causing the reaction immediately to turn orange. The flask was then removed from the ice bath and allowed to warm to room temperature, during which time it turned cloudy, before it was heated at 40 °C overnight in an oil bath. The solvent was removed in vacuo, and the resulting solids were chilled on ice and quenched with an ice-cold saturated aqueous NaHCO<sub>3</sub> solution until slightly basic. The slurry was then extracted into 3 × 100 mL of diethyl ether. The ether layers were combined, washed with 1 × 100 mL of brine, and dried over MgSO<sub>4</sub>. The solvent was removed with a rotary evaporator to give a beige solid, which was recrystallized from MeOH/H<sub>2</sub>O to give slightly off-white strawlike crystals. These were dried in vacuo, yielding 4.82 g (11.0 mmol, 95.9%) of 2,2'-dihydroxy-4,4'-diiodobiphenyl: mp 219–221 °C (MeOH/H<sub>2</sub>O); <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>) δ 6.85 (d, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 7.9 Hz, *J* = 1.7 Hz, 1H), 7.20 (d, *J* = 1.7 Hz, 1H), 9.53 (br, s, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 93.1, 124.0, 124.7, 127.4, 133.0, 155.6. Anal. Calcd for C<sub>12</sub>H<sub>10</sub>I<sub>2</sub>O<sub>2</sub>: C, 32.91; H, 1.84. Found: C, 33.20; H, 1.86. MS (*m/z*) 438.

**4,4'-Diiodo-2,2'-bis(hexadecyloxy)biphenyl (III).** A 50 mL oven-dried, argon-flushed Schlenk flask was charged with 15 mL of dry DMSO, 0.500 g (1.14 mmol) of 2,2'-dihydroxy-4,4'-diiodobiphenyl, 0.288 g (3.00 mmol) of sodium *tert*-butoxide, and a stir bar. The mixture was allowed to stir at room temperature for 5 min, during which time the sodium *tert*-butoxide dissolved and partial precipitation of the diphenoxide occurred, resulting in a straw-colored slurry. A solution of 1-iodohexadecane (1.06 g, 3.00 mmol) dissolved in 5 mL of dry

DMSO and 5 mL of dry THF was then added via cannula, and the reaction was protected from light and heated in a 50 °C oil bath for 24 h under argon. Upon cooling, the mixture was poured into 100 mL of water and extracted into 3 × 50 mL of ether. The ether layers were combined, washed with 1 × 50 mL of water, washed again with 1 × 50 mL of brine, and dried over MgSO<sub>4</sub>. The solvent was removed with a rotary evaporator, and the resulting oil was heated for 2 h at 60 °C under an oil diffusion pump vacuum in a kugelrohr oven to remove residual DMSO. The residual solid was then alternately recrystallized from hexanes and acetone until colorless, and the final material was lyophilized from benzene to yield 0.892 g (1.01 mmol, 88.6% yield) of 4,4'-diiodo-2,2'-bis(hexadecyloxy)biphenyl (III) as a white solid: mp 53–55 °C (hexanes); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 0.87 (distorted t, *J* = 6.6 Hz, 3H), 1.24 (br s, 26H), 1.61 (br m, 2H), 3.85 (br m, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 1.5 Hz, 1H), 7.29 (dd, *J* = 8.2 Hz, *J* = 1.5 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 22.7, 29.0, 29.2, 29.4, 29.6 (multiple resonances), 29.7 (multiple resonances), 31.9, 68.7, 93.1, 121.3, 127.0, 129.2, 132.6, 157.0. Anal. Calcd for C<sub>44</sub>H<sub>72</sub>I<sub>2</sub>O<sub>2</sub>: C, 59.56; H, 8.18. Found: C, 59.66; H, 8.46.

**Triethylene Glycol Monoethyl Ether *p*-Toluenesulfonate [62921-75-9].** A 500 mL round-bottomed flask equipped with an efficient stir bar was charged with 71 g (0.40 mol) of triethylene glycol monoethyl ether, 100 mL of water, and 100 mL of THF. The mixture was cooled to –5 °C, and 28 g (0.43 mol assuming 85% purity) of KOH was added. *p*-Toluenesulfonyl chloride (76 g (0.40 mol) of was added dropwise in 120 mL of THF while the reaction temperature was maintained at less than 3 °C. Following addition, the reaction was stirred for 2 h at 0 °C. The tosylate was separated by adding 150 mL of diethyl ether and washing the combined organic phases once with water and twice with brine. The organic layers were dried over MgSO<sub>4</sub> and concentrated first with the aid of a rotary evaporator and then under vacuum (10 mTorr) in a kugelrohr oven at 65 °C (the tosylate was stabilized with 0.8 g of Na<sub>2</sub>CO<sub>3</sub> prior to the latter drying) to yield 123 g (0.37 mol, 97% yield) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.18 (t, *J* = 7.0 Hz, 3H), 2.43 (s, 3H), 3.50 (q, *J* = 7.0 Hz, 2H), 3.53–3.60 (multiple resonances, 12 H), 3.67 (distorted t, 2 H), 4.14 (distorted t, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 15.0, 21.5, 66.6, 68.6, 69.2, 69.6, 70.7, 127.9, 129.7, 132.9, 144.7; MS (FAB) (*m/z*) 289. Very high purity material suitable for further use was obtained from an additional wash with ice-cold aqueous Na<sub>2</sub>CO<sub>3</sub>. The tosylate was then reisolated by the procedure outlined above. No detectible *p*-toluenesulfonyl chloride remained following this wash.

**4,4'-Diiodo-2,2'-bis[(triethylene glycol monoethyl ether)-oxy]biphenyl (IV).** A 100 mL Schlenk flask was charged with 1.01 g (10.5 mmol) of sodium *tert*-butoxide, 1.50 g (3.42 mmol) of 2,2'-dihydroxy-4,4'-diiodobiphenyl and a stir bar. The flask was then evacuated and heated in a 50 °C oil bath until all volatiles were removed. Dry DMSO (50 mL) was then added via cannula, and the mixture was allowed to stir at room temperature for 5 min, during which time the sodium *tert*-butoxide dissolved and partial precipitation of the diphenoxide occurred, resulting in a straw-colored slurry. Triethylene glycol monoethyl ether *p*-toluenesulfonate (3.70 g, 11.1 mmol) was then added via pipet under argon backflow. The reaction was protected from light and heated at 50 °C for 2 h under argon, after which second aliquots of sodium *tert*-butoxide (0.495 g, 5.10 mmol) and triethylene glycol monoethyl ether *p*-toluenesulfonate (1.83 g, 5.50 mmol) were added under backflow. The reaction at this point was a homogeneous orange solution. It was heated for another 1.5 h, followed by the addition of a third aliquot of sodium *tert*-butoxide (0.900 g, 9.38 mmol) and several drops of methanol to destroy excess tosylate. After a final heating of 1 h, the reaction was poured into 150 mL of water and extracted into 3 × 100 mL of diethyl ether. The ether layers were combined, washed with 2 × 150 mL of brine, dried over MgSO<sub>4</sub>, and concentrated with a rotary evaporator to yield a yellow oil. This was chromatographed on silica with a solvent gradient from 25% to 50% ethyl acetate

in petroleum ether to yield a colorless oil, which was then dissolved in a minimal amount of chloroform. Residual grease was removed by filtering this solution through a 1.5 in. pad of silica in a 150 mL fritted Buchner funnel. After 500 mL of chloroform was rinsed through, the product was eluted with 500 mL of diethyl ether. This solution was concentrated to 10 mL and filtered through a 0.2  $\mu$ m membrane into a 100 mL round-bottomed flask. The solvent was removed with a rotary evaporator, and the resulting oil was heated for 12 h in a kugelrohr oven under oil-diffusion pump vacuum at 65 °C. 4,4'-diiodo-2,2'-bis[(triethylene glycol monoethyl ether)-oxy]biphenyl (**IV**) (2.09 g, 2.76 mmol, 80.7% yield) was isolated as a colorless oil:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.21 (t,  $J$  = 7.1 Hz, 3H), 3.53 (m, 10H), 3.69 (t,  $J$  = 4.7 Hz, 2H), 4.05 (t,  $J$  = 4.7 Hz, 2H), 6.96 (d,  $J$  = 7.9 Hz, 1H), 7.26 (d,  $J$  = 1.3 Hz, 1H), 7.31 (dd,  $J$  = 8.1 Hz,  $J$  = 1.3 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  15.2, 66.6, 68.7, 69.5, 69.8, 70.6, 70.7, 70.8, 93.1, 121.9, 126.9, 129.7, 132.8, 156.7; Anal. Calcd for  $\text{C}_{28}\text{H}_{40}\text{I}_2\text{O}_8$ : C, 44.34; H, 5.32. Found: C, 44.40; H, 5.31.

**4,4'-Bis[2-(1,3,2-dioxaborolane)]-2,2'-bis(trifluoromethyl)biphenyl (V).** An oven-dried, argon-flushed 1 L three-necked flask equipped with a stir bar, addition funnel, stopper, and a septum was charged with 32.0 mL (80.0 mmol) of a 2.5 M solution of *n*-butyllithium in hexanes. Dry ether (200 mL) was added, the septum was replaced with a glass stopper, and the flask was placed in a  $-78$  °C dry ice/acetone bath. A solution of 17.3 g (32.0 mmol) of 4,4'-diiodo-2,2'-bis(trifluoromethyl)biphenyl in 200 mL of dry ether was cannulated into the addition funnel and then added dropwise to the cold *n*-butyllithium solution over 1 h, resulting in a bright orange-yellow solution. A separate, dry, argon-flushed, 1 L three-necked flask was charged with 40.0 mL (175 mmol) of boron triisopropoxide and similarly dissolved in 100 mL of dry ether. This flask was also chilled to  $-78$  °C in a dry ice/acetone bath, and the cold dilithium solution was added via cannula over the course of 20 min. The resulting yellow suspension was allowed to warm to room temperature overnight. It was then poured into a mixture of 45 mL of concentrated HCl and 300 g of ice in a 2 L beaker, and the mixture was stirred for 1 h. The layers were separated with a separation funnel, and the aqueous layer was rinsed with  $2 \times 100$  mL of ether. The ether layers were combined and washed with  $3 \times 100$  mL of brine and dried over  $\text{MgSO}_4$ . The solvent and iodobutane were then removed with a rotary evaporator, and the resulting yellow residue was suspended in 250 mL of benzene and 5.0 mL (70 mmol) of 1,3-propanediol in a 500 mL round-bottomed flask. This was then equipped with a stir bar, a Dean-Stark trap, and a reflux condenser, and the reaction was refluxed for 4 h, or until no additional water was collected in the trap. The solvent was removed with a rotary evaporator, and the residue was recrystallized from degassed acetone until colorless, resulting in clear, cubic crystals. The product was purified further by sublimation (250 °C, 5 mTorr dynamic vacuum) to give 10.23 g (22.34 mmol, 69.8% yield) of 4,4'-bis[2-(1,3,2-dioxaborolane)]-2,2'-bis(trifluoromethyl)biphenyl (**V**) as a white powder: mp 235–237 °C (acetone);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.09 (quint,  $J$  = 5.5 Hz, 2H), 4.20 (t,  $J$  = 5.4 Hz, 4H), 7.24 (d,  $J$  = 7.2 Hz, 1H), 7.91 (d,  $J$  = 7.6 Hz, 1H) 8.13 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  27.4, 62.1, 127.8 (q,  $J$  = 28.1 Hz), 127.8 (q,  $J$  = 259.2 Hz), 130.5, 131.0, 132.8, 135.7, 139.6;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$   $-57.8$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{18}\text{B}_2\text{F}_6\text{O}_4$ : C, 52.45; H, 3.96. Found: C, 52.43; H, 4.11.

**Polymerization of III with V.** A sealable 20 mL ampule was charged with 171.8 mg (0.193 mmol) of **III**, 88.7 mg (0.193 mmol) of **IV**, 159.0 mg (0.937 mmol) of potassium carbonate sesquihydrate, 1.8 mL of THF, 2.1 mL of water (HPLC grade), and a stir bar. The mixture was degassed via several freeze–pump–thaw cycles, after which 150  $\mu\text{L}$  (3.86  $\mu\text{mol}$ ) of a 0.0258 M stock solution of tri(*o*-tolyl)phosphine in THF and 150  $\mu\text{L}$  (1.93  $\mu\text{mol}$ ) of a 0.0129 M (in Pd) stock solution of the chloroform adduct of tris(dibenzylideneacetone)dipalladium-(0) in THF were added via syringe. The ampule was degassed once more and sealed under vacuum, and the polymerization was stirred in a 65 °C oil bath for 1 week, during which time the solution gelled. The ampule was cracked, and the gelled

polymer plug was isolated with a pair of tweezers and stirred with 200 mL of boiling chloroform until completely dissolved. This solution was allowed to cool, transferred to a separatory funnel, shaken vigorously with  $1 \times 50$  mL of 5% aqueous NaCN to remove residual catalyst, washed with  $3 \times 100$  mL of water and  $1 \times 50$  mL brine, and dried over  $\text{MgSO}_4$ . Frequently, persistent emulsions formed during these extractions, and a centrifuge was required to break them. The solution was then concentrated to about 5 mL with a rotary evaporator and precipitated into 40 mL of methanol. The resulting polymer plug was placed in a Soxhlet extraction thimble and extracted with hexanes for 24 h to remove residual grease. The polymer was then extracted into chloroform (4 h), and the solvent was removed with a rotary evaporator, leaving behind a white, opalescent film. This was dissolved in 5–10 mL of benzene and freeze-dried to yield 159.1 mg (0.1630 mmol repeat unit) of poly(**VI**) as a spongy white solid:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J$  = 6.7 Hz, 3H), 1.2 (br s, 26H), 1.73 (br m, 2H), 3.85 (br m, 2H), 7.26 (br, 1H), 7.32 (br, 1H), 7.44 (br, 1H), 7.85 (br, 1H), 8.06 (br, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 26.0, 29.4, 29.7, 31.9, 68.8, 111.0, 119.0, 122.2, 124.0, 125.8, 127.8, 129.2, 132.2, 136.1, 139.7, 141.4, 157.2, other resonances not resolved;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$   $-57.8$ ; Anal. Calcd for  $\text{C}_{42}\text{H}_{46}\text{F}_6\text{O}_8$ : C, 75.62; H, 8.53. Found: C, 75.33; H, 8.29. Refractive index increment (THF, 25.0 °C, 688 nm) 0.142 mL/g.

**Polymerization of IV with V.** In a typical procedure, a sealable 20 mL ampule was charged with 3.30 mL (0.283 mmol) of a THF stock solution that was 0.085 78 M in both **IV** and **V**, 0.280 g (1.69 mmol) of potassium carbonate sesquihydrate, 2.5 mL of THF, 3.2 mL of water (HPLC grade), and a stir bar. The mixture was degassed via several freeze–pump–thaw cycles, after which 0.660 mL (2.83  $\mu\text{mol}$ ) of a 0.0043 M stock solution of bis[tri(*o*-tolyl)phosphine]palladium-(0) in THF was added via syringe. The ampule was degassed once more and sealed under vacuum, and the polymerization was stirred in a 65 °C oil bath for 1 week, during which time the solution gelled. Workup identical to that described for poly(**VI**) was applied to yield 165.4 mg (0.209 mmol repeat unit, 73.7% recovery) of poly(**VII**) as a white sponge-like solid. For specific conditions and molecular weight characterization, see Tables 1 and 2.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.19 (t,  $J$  = 7.0 Hz, 3H), 3.50 (q,  $J$  = 7.0 Hz, 2H), 3.58 (br, 8H), 3.82 (br, 2H), 4.27 (br, 2H), 7.08 (br, 1H), 7.31 (br, 1H), 7.57 (br, 1H), 7.94 (br, 1H), 8.07 (br, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  15.1, 66.6, 68.7, 69.8, 70.7, 70.9, 111.5, 119.5, 122.3, 124.6, 125.7, 127.7, 129.2, 130.6, 131.0, 131.4, 132.4, 136.2, 137.3, 139.8, 141.2, 156.9, other resonances not resolved;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$   $-57.8$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{46}\text{F}_6\text{O}_8$ : C, 63.63; H, 5.85. Found: C, 63.37; H, 5.66. Refractive index increment: (THF, 25.0 °C, 688 nm) 0.135 mL/g; ( $\text{CHCl}_3$ , 25.0 °C, 688 nm) 0.103 mL/g.

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**Supporting Information Available:** Supporting Information The  $^{31}\text{P}$  NMR spectra for poly(**VI**) samples prepared using TPP- and TOTP-based catalysts (1 page). This material can be ordered from the ACS and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

## References and Notes

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