7330 *Macromolecules* **2008**, *41*, 7330−7338

Effect of Reaction Parameters on the Molecular Weights of Polymers Formed in a Suzuki Polycondensation

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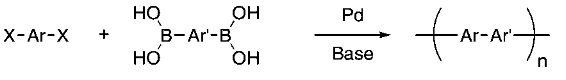
Received June 6, 2008; Revised Manuscript Received September 2, 2008

ABSTRACT: A comprehensive investigation was undertaken in order to determine the effect of different reaction parameters on the molecular weights of polymers formed in a Suzuki polycondensation. In particular, we studied how the choice of solvent, base, ligand cocatalyst, palladium source, and monomers could affect the molecular weights. For these particular polymerizations, the best solvent and base were found to be CH_2Cl_2 and aqueous 3 M K_3PO_4, respectively. More interestingly, we determined that tri(*o*-tolyl)phosphine far surpassed not only the traditional triphenylphospine ligand cocatalyst, but also the more-recently developed hindered, electron-rich ligands that have yielded impressive results in small-molecule Suzuki coupling reactions. Molecular weights were also found to depend upon the source of palladium, with bis[tri(*o*-tolyl)phosphine]palladium(0) providing the best overall catalyst system. Finally, contrary to earlier reports, we found no advantage to replacing the more readily accessible bromide monomers with the corresponding iodides, and that pinacol boronic esters were inferior to the more traditional 1,3-propanediol boronic ester monomers. In sum, the work performed here shows that under optimized conditions, molecular weights on the order of 10^5 g/mol can be readily achieved with a Suzuki polycondensation.

Introduction

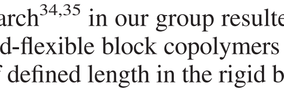
Conjugated polyarylenes such as derivatives of poly(*p*-phenylene)[1−4] and poly(fluorene)[5−8] have been the subject of increasing interest in recent years, due primarily to their light-emitting properties, which make them potentially useful candidates for emissive layers in light emitting diodes[9] and photovoltaic devices.[10] One of the most common means by which these polymers are formed is the Suzuki coupling polycondensation (eq 1).[11,12] This procedure, developed originally by Schlüter in 1989,[13] is based on the equally prolific small molecule Suzuki coupling reaction between an aryl or alkenyl halide and an aryl or alkenyl boronic acid.[14−16] Due largely to its increasing use in the synthesis of small molecule pharmaceuticals, there have been numerous developments in Suzuki coupling methodology in recent years that have led to remarkable improvements in catalytic efficiency, product yield, and ease of manipulation.[17,18] Despite this fact, most recent Suzuki coupling polycondensations, however, still utilize only slight modifications of Schlüter's original protocol, often resulting in molecular weights that are limited to the 10^3 to 10^4 g/mol regime.[19−21]



$$\text{X–Ar–X} + (HO)_2B\text{–Ar'–}B(OH)_2 \xrightarrow[\text{Base}]{\text{Pd}} \left(\text{Ar–Ar'}\right)_n \qquad (1)$$

The reasons for this oversight are obvious when one considers the involved monomer syntheses required for the generation of these well-engineered materials.[19] The focus of research has largely been on the optimization of the more technologically interesting properties of the polymers. As a result, investigators have been reluctant to spend precious monomer on polymerization optimization studies, relying instead on well-established protocols that yield characterizable polymer, albeit at nonoptimized molecular weights. However, *materials* properties are extremely sensitive to the size of the polymer chains. So, while the light-emitting properties of a given material may be quite impressive, a device made from this substance will ultimately fail if it softens, melts, or cracks under the conditions of device operation.

There are some notable exceptions to the above generalization that should be mentioned. Schlüter later showed that catalysts based on tri(*p*-tolyl)phosphine yielded polymers with higher molecular weights than the traditional triphenylphosphine-based systems,[22] and that iodide monomers produced better results than bromides.[23] About the same time, Wegner noted that catalysts using the chelating diphenylphosphinoferrocene (DPPF) ligand worked under less basic conditions, allowing for the synthesis of polymers containing base-sensitive functionalities.[24] Soon afterward, Novak disclosed that a prevalent side reaction, the exchange of phosphine-bound aryl groups with those bound to palladium (eq 2),[25,26] could be reduced significantly with the use of tri(*o*-tolyl)phosphine as a ligand.[27] More recently, Scherf and co-workers successfully applied microwave radiation to promote the synthesis of a polymer that had proved troublesome under the standard Suzuki coupling protocol.[28] In a very interesting recent development, Higashimura, Yokozawa, and co-workers disclosed a Suzuki coupling polymerization which proceeded via a chain-growth mechanism, although the highest reported molecular weight was still limited to 19 200 g/mol.[29] Finally, various groups have experimented with some more recent nontraditional catalyst systems,[28,30−33] though generally without large improvements in molecular weight. Despite these efforts, thorough optimization studies involving head-to-head comparisons of different coupling protocols have remained, for the most part, elusive.



$$\begin{matrix}\text{Ar–PAr}_2\\ \text{Ar'–Pd·X}\\ \text{PAr}_3\end{matrix} \rightleftharpoons \begin{matrix}\text{Ar'–PAr}_2\\ \text{Ar–Pd·X}\\ \text{PAr}_3\end{matrix} \qquad (2)$$

Recent research[34,35] in our group resulted in the synthesis of alternating rigid-flexible block copolymers containing oligophenylene units of defined length in the rigid blocks (eq 3).[35] These polymers are formed via a Suzuki coupling polycondensation

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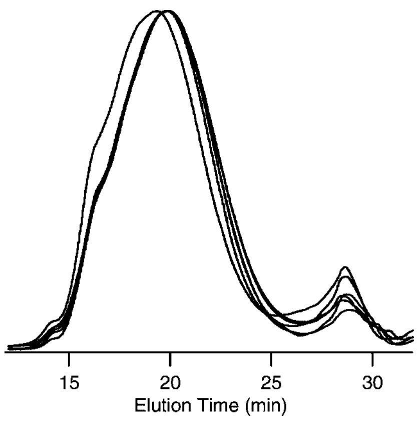
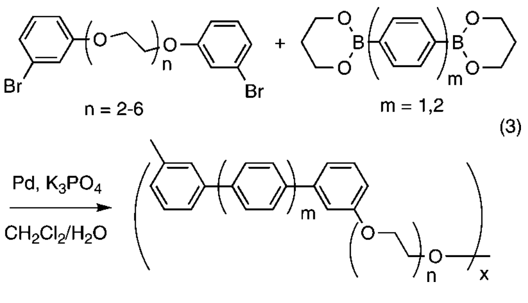


Figure 1. GPC chromatograms (normalized to maximum intensity) for six identical, simultaneous polymerizations (eq 4, CH_2Cl_2, 3 M K_3PO_4).

from monomers that can be synthesized on a multigram scale in a single step from readily available precursors. We have since been able to take advantage of this convenient monomer synthesis to perform a comprehensive investigation on the effect of various reaction parameters (solvent, base, palladium source, ligand cocatalyst) on the molecular weights of the polymers formed from this polymerization protocol. In this paper, we present the results of these studies.



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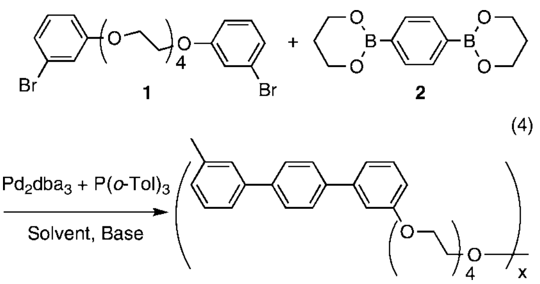
Results and Discussion

Initial feasibility experiments were performed by running six simultaneous polymerizations in sealed ampules with dibromide monomer **1** and diboronic ester monomer **2** (eq 4, CH_2Cl_2, 3 M K_3PO_4), and the results are presented in Figure 1. Since the method of termination can have an effect on molecular weight,[36] all of these polymerizations were terminated in the same manner (basic aqueous workup with cyanide—*vide infra*) after the same prolonged reaction time (3 days). The chromatograms shown are typical for the polymers formed from this system. The low molecular peaks are most likely due to a competing cyclic oligomerization, which is unfortunately facilitated by the *meta* regiochemistry of the monomers.[37] Since these oligomers are removed upon polymer purification,[35] they were not considered when determining the molecular weight averages of the polymer samples. The high molecular weight shoulders were present in the chromatograms from all reactions that gelled during polymerization. This could be due to a Trommsdorff-like effect in which the increased viscosity affects a molecular-weight limiting side reaction more than the desired polymerization. As can be seen from the chromatograms, the reproducibility is good. These samples yielded average values (determined by tandem GPC-Multi angle light scattering) for M_n and M_w of 105 000 and 355 000 g/mol, respectively, with standard deviations of 8300 and 21 500. From these values, we determined 95% confidence limits of ± 15.8% for M_n, and 12.1% for M_w.



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During the course of our investigations, we came across several factors that led to large deviations from expected values. The first, and most important of these was oxygen contamination. While there are examples in the literature of small molecule Suzuki coupling protocols that are stable to air,[38] this is absolutely not the case for these Suzuki polycondensations.[39] It may be true that some catalyst systems possess a fair amount of oxygen stability. However, the oxidative homocoupling of boronic acids, a competing side reaction that would disrupt the stoichiometric balance of monomers, is known to be facilitated by oxygen.[40,41] Furthermore, Slugovc recently provided evidence for hydroxyl end caps in polymers formed from Suzuki polycondensations performed in air, suggesting an additional molecular-weight limiting oxidation of boronic acid monomers.[31] For these reasons, oxygen needs to be rigorously excluded from Suzuki polycondensations in order for high molecular weights to be obtained. Fortunately, oxygen contamination caused a telltale orange-brown color to develop during our polymerizations, allowing us to discard the data obtained whenever this occurred.

A second, more subtle issue came to light when polymer samples were allowed to stand over a period of several weeks. At the end of the polymerizations, spent palladium catalyst aggregated in the form of microscopic clusters, which unfortunately were extremely proficient at scattering light. If the samples were analyzed via GPC−MALS immediately upon isolation, these clusters appeared in the light scattering chromatogram as a peak that eluted with the void volume of the GPC columns. At this point, they did not pose a significant problem since they were clearly resolved from the polymer peaks. However, upon standing, the clusters changed size (or possibly adhered to the macromolecules) to the point where they coeluted with the polymer, significantly inflating the molecular weight values obtained. We later discovered that these particles could be removed by extracting polymer solutions with 5% aqueous NaCN. Doing so allowed us to obtain molecular weight values close to those measured immediately upon polymer isolation. In order to eliminate this effect, all data presented here were from samples extracted with NaCN prior to analysis.

The third factor should not have been a surprise considering the well-known sensitivity of condensation polymerizations to monomer stoichiometry.[42] When the above polymerizations were performed with a different monomer stock solution (but under otherwise identical conditions), the molecular weights, while consistent with each other, were significantly lower (Table 1, entry 1) than those obtained previously (Figure 1). This indicated to us that polymerizations had to be performed with the same monomer stock solution (thereby ensuring consistent monomer stoichiometry) in order for the molecular weights to be truly comparable. Indeed, we believe the unusually high values obtained above were due to a particularly fortuitous stoichiometric match, (with that particular monomer stock solution) which we have unfortunately been unable to repeat in our subsequent studies.

The first parameter investigated was the effect of solvent on polymer molecular weights (eq 4, Table 1, Figures 2 and 3). As can be seen from these data, CH_2Cl_2 appears to be the best

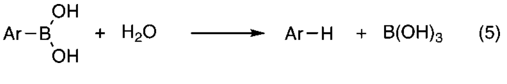
Table 1. Effect of Solvent and Base on Polymer Molecular Weight[a]

entry	solvent	base	M_n	M_w
1	CH_2Cl_2	3 M K_3PO_4	63 600	178 000
2	toluene	3 M K_3PO_4	39 600	92 300
3	DMF	3 M K_3PO_4	6290	9140
4	DME	3 M K_3PO_4	44 200	117 000
5	THF	3 M K_3PO_4	51 900	124 000
6	dioxane	3 M K_3PO_4	39 600	84 300
7	CH_2Cl_2	3 M KF	2520	3150
8	CH_2Cl_2	3 M $KHCO_3$	4400	6810
9	CH_2Cl_2	3 M K_2CO_3	52 600	108 000
10	CH_2Cl_2	3 M KOH	500	1085
11	CH_2Cl_2	2 M K_3PO_4	47 800	106 000
12	CH_2Cl_2	sat. K_3PO_4	50 300	128 000
13[b]	toluene	3 M K_3PO_4	20 800	30 600

[a] Polymerizations (eq 4) set up with 0.150 mL of organic solvent and 0.300 mL of base. Unless otherwise indicated, all polymerizations were performed with 0.5% Pd/Br $Pd_2(dba)_3$ and tri(*o*-tolyl)phosphine with a P/Pd ratio of 2. Values are the averages of at least two trials. [b] Set up with 0.5% Pd/Br tetrakis(triphenylphosphine)palladium(0).

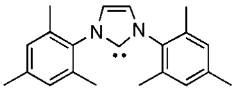
solvent for this polymerization, although good molecular weights were also obtained in toluene as well as the ethereal solvents THF, DME, and dioxane. While it is tempting to conclude that CH_2Cl_2 must therefore be the best solvent for all Suzuki polycondensations, we believe that these data show, instead, the impressive flexibility of the protocol, since polymerizations worked well in a variety of solvents. In DMF, polymer precipitated from solution almost immediately, while in CH_2Cl_2, the end result was a solvent-swollen gel. Thus, the best solvent to use for a given polymerization appears to be the one in which the polymer is the most soluble, which in this particular case, happens to be CH_2Cl_2. Table 1 also includes data (entry 13) from polymerizations performed under more commonly used conditions ($Pd(PPh_3)_4$, toluene, Aliquat 336). Thus, significant improvements in molecular weight can be obtained by simply modifying the solvent and catalyst of the polymerization system.

We next utilized the same monomer stock solution to investigate how the choice of base would affect polymer molecular weights (eq. 4, Table 1, Figures 2 and 3). The interesting trend here, is that molecular weights increase with base strength, up to a point.[43] When hydroxide was used as a base, only oligomeric material was recovered at the end. It is well established that the chief molecular-weight limiting side reaction in Suzuki polycondensations is the hydrolytic deboronation of boronic acid functionalities (eq 5).[44] Both the deboronation and the desired cross coupling are facilitated by stronger bases. However, it appears that the former has a stronger pH-dependence, and that the best compromise entails the use of phosphate, rather than the more commonly employed carbonate, as the base in this system. To explore this trend further, we then investigated the use of different concentrations of K_3PO_4. Interestingly, while increasing base concentration from 2 to 3 M provided a noticeable improvement in molecular weight, increasing the concentration further by utilizing a saturated solution caused a molecular weight decrease, presumably as the deboronation rate increased under the more basic conditions. In support of this, Reynolds and co-workers noticed a similar pH effect on the chain length of water soluble poly(*p*-phenylene)s formed in an aqueous Suzuki polycondensation.[45]



$$\mathrm{Ar{-}B(OH)_2} + \mathrm{H_2O} \longrightarrow \mathrm{Ar{-}H} + \mathrm{B(OH)_3} \qquad (5)$$

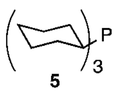
Arguably, the most significant improvements in small molecule Suzuki coupling reactions have been in the development of more active catalyst systems. In particular, the use of electron-rich ligands, such as *N*-heterocyclic carbenes (e.g., **3**),[46,47] sterically hindered trialkyl phosphines (in particular **4**,[48,49] **5**,[49] and **6**[50]), Hartwig's Q-phos system (**7**)[51] and Buchwald's biphenyl-based phosphine ligands (e.g., **8**),[52] has made possible the activation of sluggish aryl chloride substrates in Suzuki coupling reactions. Also nonphosphine systems such as Nolan's diazabutadiene (**9**)[53] and Bedford's phosphite (**10**)[54] have similarly provided for particularly active and efficient coupling reactions. Some of these new ligands have seen use in polymerizations,[28,33] with varying degrees of success.



3

$(t\text{-Bu})_3P$

4



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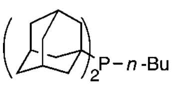

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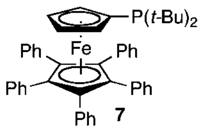

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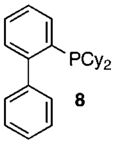

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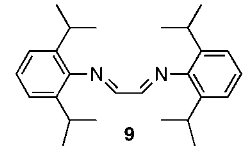

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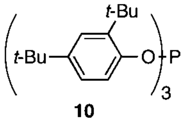

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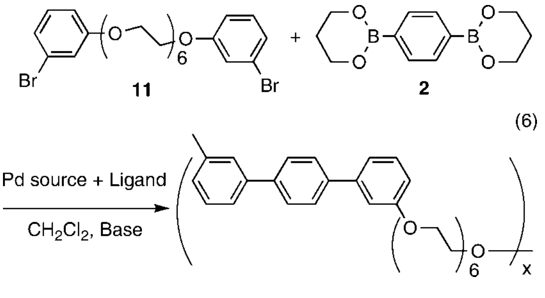
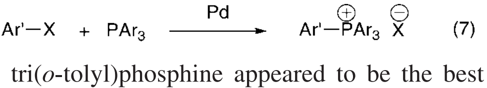
To eliminate concerns of decreased solubility with higher molecular weights, we switched to a more soluble polymerization utilizing monomer **11** (eq 6, $Pd_2(dba)_3$) to study the effects of incorporating these new ligands, as well as more traditional triarylphosphines that have seen use in Suzuki polycondensations (triphenylphosphine, tri(*o*-tolyl)phosphine, tri(*p*-tolyl)phosphine, and diphenylphosphinoferrocene—DPPF), in our polymerizations (Table 2, Figures 4 and 5). We were immediately surprised by the failure of triphenylphosphine, DPPF, and tri(*p*-tolyl)phosphine to yield reasonable molecular weights, considering the successful use of these ligands in other Suzuki polycondensations.[13,22,24,55] However, Novak[26] and Grushin[56] have both noted that halogenated solvents, such as CH_2Cl_2, facilitate a competing phosphonium salt formation (eq 7)[57,58] (a reaction intimately involved with the aforementioned aryl−aryl exchange (eq 2)[26]) to the point where quantitative conversion of aryl halide is not possible. Thus, halogenated solvents are not compatible when catalyst systems based upon these ligands are employed. However, since the steric hindrance provided by the tri(*o*-tolyl)phosphine ligand is known to inhibit both the aryl−aryl exchange[26] and the phosphonium salt formation,[57] polymerizations utilizing this phosphine proceeded without difficulty.[59] Electron-rich phosphines **4**−**8** all promoted successful polymerizations, although the molecular weights were not as high as those obtained with the standard tri(*o*-tolyl)phosphine system. The nonphosphine based cocatalysts (**3**, **9**, and **10**) all failed to produce molecular weights beyond the oligomeric regime.



(6)



$$\mathrm{Ar'{-}X} + \mathrm{PAr_3} \xrightarrow{\mathrm{Pd}} \mathrm{Ar'{-}\overset{\oplus}{P}Ar_3}\ \overset{\ominus}{\mathrm{X}} \qquad (7)$$

Since tri(*o*-tolyl)phosphine appeared to be the best ligand cocatalyst to use in our polymerizations,[59] we next screened different palladium catalyst precursors that either contained this

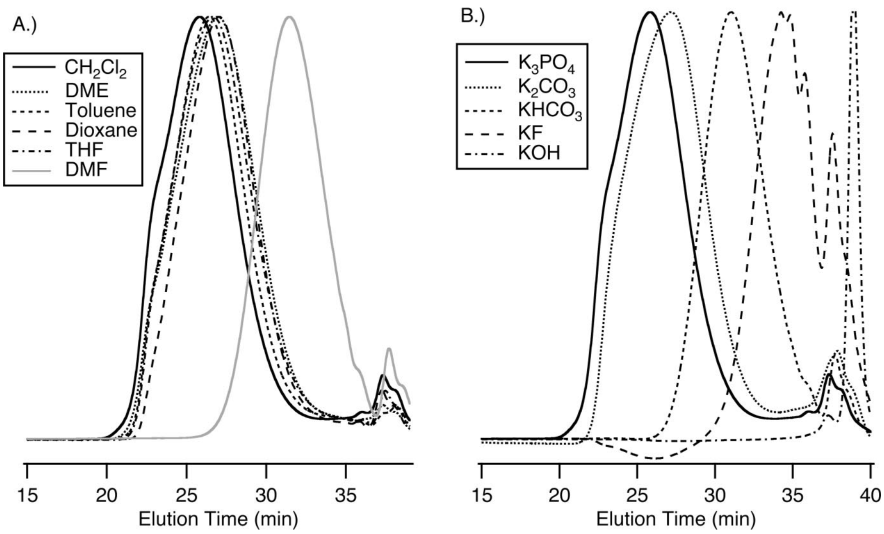


Figure 2. GPC chromatograms (normalized to maximum intensity) for polymerizations run with (A) different solvents and (B) different bases (all 3 M in water).

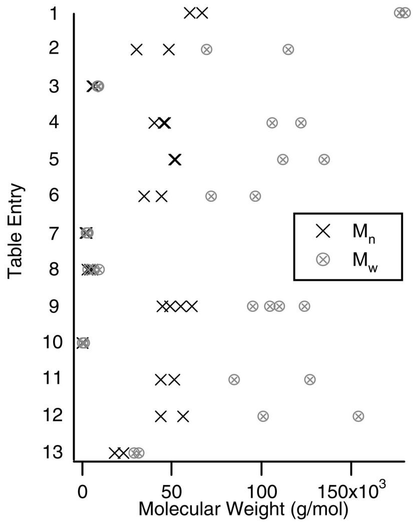


Figure 3. Molecular weights for individual polymerizations run with different solvent/base combinations (Table 1).

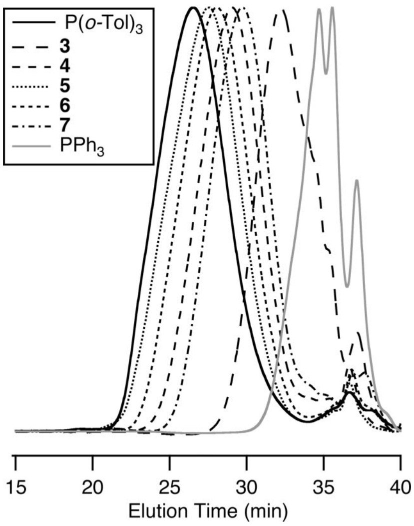


Figure 4. GPC chromatograms (normalized to maximum intensity) for polymerizations run with different ligand cocatalysts (eq 6, Table 2).

Table 2. Effect of Ligand Cocatalyst on Polymer Molecular Weight[a]

entry	ligand	M_n	M_w
1	P(*o*-Tol)$_3$	52 800	98 800
2	PPh$_3$	1370	1830
3	P(*p*-Tol)$_3$	1680	2380
4	DPPF[b]	2750	5870
5	**3**	4040	5630
6	**4**	14 800	26 700
7	**5**	35 400[c]	62 100[c]
8	**6**	25 200	43 800
9	**7**	11 400	17 600
10	**8**	11 000	18 200
11	**9**	1450	2180
12	**10**	1740	2720

[a] Polymerizations (eq 6) set up with 0.150 mL of organic solvent (CH_2Cl_2) and 0.300 mL of base (3 M K_3PO_4). All polymerizations were performed with 0.5% Pd/Br $Pd_2(dba)_3$ and ligand cocatalyst with a ligating atom to Pd ratio of 2:1. Unless otherwise indicated, values are the averages of at least two trials. [b] 1,1′-Bis(diphenylphosphino)ferrocene. [c] Median values, due to a low molecular weight outlier.

ligand or could react with it to enter the catalytic cycle (eq 6, Table 3, Figures 6 and 7). In particular, Herrmann's palladacycle, **12**, has been shown to provide extremely high turnover frequencies in small molecule Suzuki coupling reactions.[60] However, in the polymerizations presented here, this complex produced only oligomeric material. Others have similarly had difficulty obtaining good results with **12** in Suzuki coupling reactions.[61] This palladacycle could enter the catalytic cycle either through reaction with the transmetallating agent (thus disrupting the stoichiometric match of monomer functional groups) to form **13** (as was shown[61] to be the case for Stille coupling reactions), or, as hypothesized by Beller for Heck reactions,[62] through an unspecified reduction to form **13**, (thus providing for a nonproductive induction period). Either method of entry could explain the poor results observed here. On the other hand, the frequently used palladium acetate and tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) both yielded good molecular weights that were basically equivalent. However, $Pd(PPh_3)_4$, the most commonly used catalyst system, gave poor results, which can be explained by the halogenated solvent facilitated phosphonium salt formation described above.

The highest molecular weights obtained from this monomer stock solution were produced with palladium(0) complex **13** (entry 5). Initially, this was a bit of a surprise to us, since $Pd(OAc)_2$, $Pd_2(dba)_3$, and **13** should all yield the same catalytically active palladium species. One possible explanation is that

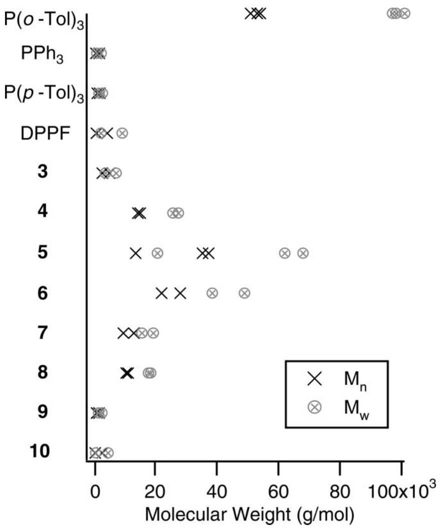


Figure 5. Molecular weights for individual polymerizations run with different ligand cocatalysts (Table 2).

Table 3. Effect of Palladium Source on Polymer Molecular Weight[a]

entry	catalyst system	M_n	M_w
1	$Pd_2(dba)_3$ + 2 P(*o*-Tol)$_3$	52 800	98 800
2	$Pd(OAc)_2$ + 2 P(*o*-Tol)$_3$	55 300	103 000
3	**12**	4720	7860
4	$Pd(PPh_3)_4$	1860	2640
5	**13**	69 100	142 000
6	$Pd_2(dba)_3$ + P(*o*-Tol)$_3$	51 500	100 000

[a] Polymerizations (eq 6) set up with 0.150 mL of organic solvent (CH_2Cl_2) and 0.300 mL of base (3 M K_3PO_4). Unless otherwise indicated, polymerizations were performed with 0.5% Pd/Br and tri(o-tolyl)phosphine with a P/Pd ratio of 2. Values are the averages of at least two trials.

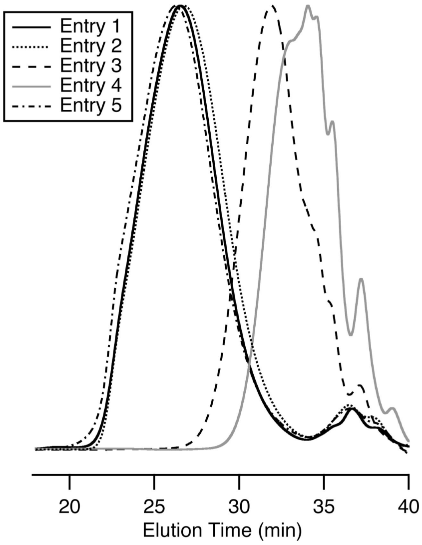
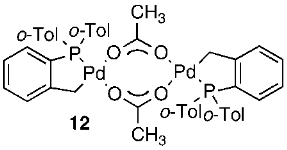


Figure 6. GPC chromatograms (normalized to maximum intensity) for polymerizations run with different catalyst systems (eq 6, Table 3).



12

$(o\text{-Tol})_3P\text{-}Pd\text{-}P(o\text{-Tol})_3$

13

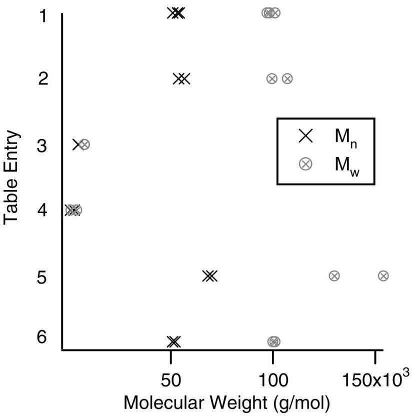
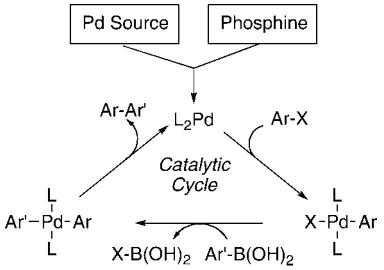


Figure 7. Molecular weights for individual polymerizations run with different catalyst systems (Table 3).

Scheme 1. Entry of Palladium into the Catalytic Cycle



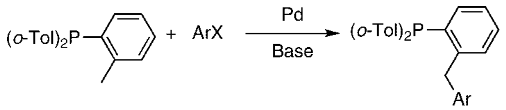
while **13** is already part of the catalytic cycle, $Pd(OAc)_2$, and $Pd_2(dba)_3$, both have to undergo some sort of activation external to the cycle in order to become catalytically active (Scheme 1). Any prolonged induction period for this process would allow noncatalyzed side reactions, such as hydrolytic deboronation, to gain a head start. This explanation makes sense for $Pd(OAc)_2$, since this precursor needs to be reduced to enter the catalytic cycle. However, reactions between $Pd_2(dba)_3$, phosphines and aryl halides are known to occur at room temperature,[63,64] while the catalysis requires heating in order to proceed at a reasonable rate. Thus, the activation of this complex should be rapid relative to the polymerization, and any induction period here should be insignificant. A better explanation lies in the fact that Amatore and Jutand have shown that the dba ligand remains involved with the catalytic cycle when $Pd_2(dba)_3$ is used as a palladium source in cross-coupling reactions,[64] a supposition bolstered by Fairlamb's recent observation that rates and yields in Suzuki coupling reactions could be improved by varying the substituents on the dba ligands.[65,66] Thus, for this palladium source, the actual catalytic species is some complex of dba and tri(*o*-tolyl)phosphine, which appears to be slightly less active than **13**. Others have noted that when a strict 1:1 Pd to phosphine ratio is employed in cross coupling reactions, more active catalyst systems can be achieved.[67] However, when we changed the molar ratio of tri(*o*-tolyl)phosphine to $Pd_2(dba)_3$ from 2:1 to 1:1 in our polymerization (entry 6), identical molecular weights were obtained, providing further evidence that the active species was the same in both cases, likely Pd(dba)P(*o*-Tol)$_3$.[68]

Upon reviewing these data, it is apparent that none of the newly designed catalyst systems, which have yielded remarkable activities in small molecule Suzuki coupling reactions, matches the performance, in terms of higher molecular weights, of the more traditional tri(*o*-tolyl)phosphine-based catalysts. Recently, Scherf and co-workers similarly observed that tri(*tert*-butyl)phosphine, a highly touted ligand for various small molecule cross coupling reactions,[49,67] failed to produce high molecular weights for their Suzuki polycondensations.[28] On the other hand, Cao and co-workers obtained very good molecular weights (M_w as high as 101 000 g/mol) when using tricylohexylphosphine as a ligand.[33] While these and the other hindered alkylphosphines did yield viable molecular weights for the polymerizations presented here, the values were not as high as those obtained with tri(*o*-tolyl)phosphine.

At first we were concerned that the molecular weight discrepancy (between polymers formed with tri(*o*-tolyl)phosphine versus those with the alkylphosphines) might be due to a side reaction incorporating phosphorus (and thus trifunctional branch points) into the polymer backbone, as was the case with the molecular weight enhancements caused by aryl−aryl exchange (eq 2) observed by Novak in his water soluble poly(*p*-phenylene) derivatives.[69,70] Since the equilibrium for the analogous alkyl-aryl exchange far favors the placement of the alkyl group on the phosphine,[71] this branch point creating side reaction would not be a concern with the alkylphosphine ligands. However, Novak later showed that tri(*o*-tolyl)phosphine, when used with CH_2Cl_2 solvent, produced polymers with no phosphine incorporation (and thereby no trifunctional branch points) observable by ^{31}P NMR.[27] While Janssen later showed that aryl-aryl exchange was still occurring with this ligand, his mass spectrometry results indicated that it had been slowed down to the point where it resulted in end caps,[72] rather than phosphorus branch points. Thus, under the conditions of the polymerizations presented here, any aryl−aryl exchange should result in a molecular weight reduction, rather than a molecular weight enhancement.

Another concern was the possibility of phosphine incorporation through C−H activation of the *ortho* methyl groups in the tri(*o*-tolyl)phosphine ligands (eq. 8). This side reaction was noted by Hartwig in the synthesis of his poly(*N*-aryl)aniline derivatives.[37] However, the amination polymerizations discussed in this paper require a much stronger base (*tert*-butoxide) than the Suzuki polycondensations. The C−H activation was likely not an issue with the standard carbonate basic conditions, since Novak[27] and Janssen[72] saw no evidence for its occurrence in their NMR and MS studies. However, since the data in Tables 2 and 3 were obtained with a stronger phosphate base, we were concerned that this side reaction might be behind the surprising results we observed here.

To test for phosphine incorporation via either route, we subjected a purified polymer obtained with the $Pd_2(dba)_3$ and tri(*o*-tolyl)phosphine catalyst system to analysis by ^{31}P NMR. After a long data acquisition (25 000 scans) we observed three weak signals (δ 37.9, 35.2, 35.1) in the phosphine oxide region of the spectrum, indicating that some phosphine is making its way onto the polymer chains. Whether this is due to aryl−aryl exchange or to C−H activation is not presently certain. However, the weakness of the signal indicates that only a small percentage of the phosphine is incorporated into the polymer, and that this uptake is slow relative to polymerization. Under these conditions, the phosphines should serve as end caps rather than as branch points, in agreement with the mass spectrometry observations of Jannsen (*vide supra*). From this we can, in turn, conclude that the higher molecular weights obtained with tri(*o*-tolyl)phosphine are indeed due to its being a better ligand to use in Suzuki polycondensations.[59] However, the fact that this molecular-weight-limiting reaction is still occurring, suggests that there is yet more room for improvement. Efforts toward this end are currently underway.



(8)

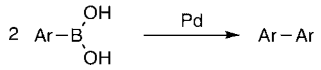
Various investigators[30,45,73,74] have successfully eliminated phosphine incorporation issues in their polymerizations by utilizing a "ligandless"[75−77] palladium acetate catalyst system without added phosphine. However, literature precedent[78] suggests that this type of catalyst would not promote quantitative monomer conversion in the nonpolar CH_2Cl_2 solvent system found to be best for our polymerizations. Thus, the ligandless methodologies were not screened in the experiments presented here.

Table 4. Effect of Monomers and Polymerization Additives on Polymer Molecular Weights[a]

entry	monomers	additives	M_n	M_w
1	**11** + **2**	none	52 800	98 800
2	**14** + **2**	none	43 800	66 600
3	**14** + **15**	none	13 000	20 800
4	**11** + **2**	Aliquat 336[b]	61 700	101 200

[a] Polymerizations (eq 10) set up with 0.150 mL of organic solvent (CH_2Cl_2), 0.300 mL of base (3 M K_3PO_4), and 0.5% Pd/Br $Pd_2(dba)_3$ plus tri(o-tolyl)phosphine with a P/Pd ratio of 2. Values are the averages of at least two trials. [b] Methyltrioctylammonium chloride.

The results of our studies suggest that it is not the activity of the catalyst that is of paramount importance (since the improved kinetic activities of the new systems are well documented), but rather its selectivity. Protodeboronation (eq 5), which has been shown to be the most significant molecular-weight-limiting side reaction,[72] can be catalyzed by salts of heavy metals such as silver and cadmium.[79] While catalysis by palladium has not been investigated, it has to be considered as a distinct likelihood. Furthermore, the competing homocoupling of boronic acids (eq 9) is known to be catalyzed by palladium.[40] (However, more recent studies[41] indicate that this side reaction does not occur under the strictly anaerobic conditions of our polymerizations.) It is conceivable that the above-mentioned failure of these newly designed catalyst systems is due to their activating these side reactions more than the desired cross coupling. (This factor could be easily overlooked in the studies of small molecule reactions, as these are generally performed with an excess of boronic acid reagent.) Further efforts to explore this possibility are currently underway.

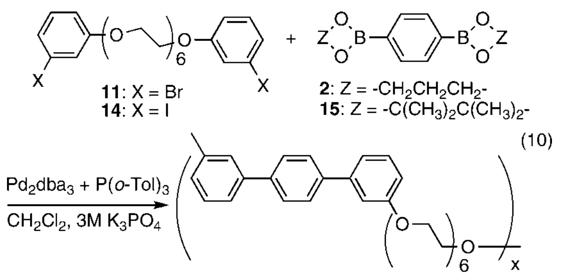


$$2\ \mathrm{Ar{-}B(OH)_2} \xrightarrow{\mathrm{Pd}} \mathrm{Ar{-}Ar} \qquad (9)$$

Finally, we also investigated the effect of utilizing different monomers and polymerization additives on polymer molecular weights (eq 10, Table 4). In contrast to the observations of Schlüter,[23] we found no advantage in replacing the dibromide monomer **11** with the corresponding to diiodide **14** (although, of necessity, different monomer stock solutions were employed in the two sets of polymerizations). Since the dibromide **11** is more volatile (and thereby easier to purify) and more stable, it remains the monomer of choice for this particular system. Urawa has suggested that another possible side reaction, reductive dehalogenation of the aryl halide substrate, can be eliminated by removing all sources of primary alcohols (such as 1,3-propanediol) from the reaction mixture.[80] This could be achieved here by replacing the diboronic ester **2** with the corresponding bis(pinacol) ester **15**. Indeed, Jannsen and co-workers found that higher molecular weights could be obtained in their Suzuki polycondensations when propanediol boronic ester monomers were replaced with the analogous pinacol esters.[30] However, as the data in Table 4 indicate, this substitution resulted in a significant molecular weight reduction in our polymerization system. Finally, while the addition of the surfactant Aliquat 336[81] to the polymerization appeared to result in only a marginal molecular weight improvement (entry 4), it did serve to quash the formation of emulsions during the cyanide extractions, significantly simplifying the workup of the polymer samples.

Conclusions

In the work presented in this paper, we have shown that through the optimization of the solvent, base, and catalyst



system, molecular weights of polymers formed in Suzuki coupling polycondensations can be improved significantly. In particular, for our polymerizations, dichloromethane appears to be the solvent of choice, 3 M K_3PO_4 is the best base, and bis[tri(*o*-tolyl)phosphine]palladium(0) (**13**) is the optimal catalyst. While the base and catalyst effects may well be general for all Suzuki polycondensations, the solvent trends are most likely due to the fact that our polymers are simply more soluble in this solvent than in the others that we investigated. Consequently, the choice of solvent is a parameter that should be screened for a given polymerization system.

While **13** did yield the best results in head-to-head comparisons with other catalyst systems, there are a few disadvantages that may make the use of this complex less appealing. In particular, it is not presently commercially available; it is air, heat, and light sensitive; and it is only sparingly soluble in common organic solvents. As a result a catalyst system utilizing $Pd(OAc)_2$ or $Pd_2(dba)_3$, (which are both commercially available, air stable, and relatively soluble) in combination with tri(*o*-tolyl)phosphine (the performance of which far surpassed that for both traditional triphenylphosphine and the newly investigated hindered electron-rich ligands), may provide a more convenient catalyst system that still yields acceptable results.

Finally, it should be emphasized that like other condensation polymerizations, the single most important factor that affects molecular weight is the stoichiometric match of the monomers. In fact, the highest molecular weights that we observed (M_w = 355 000) were (rather frustratingly) obtained with the very first polymerizations that we performed in this study (due most likely to a serendipitous well-balanced stoichiometry with that particular monomer stock solution). Nevertheless, these results do show that under optimized conditions with an improved catalyst system, molecular weights in the 10^5 g/mol regime are readily achievable with Suzuki polycondensation reactions.

Experimental Section

General Data. Hexaethylene glycol di(*p*-toluene)sulfonate;[82] monomers **1**,[35] **2**,[34] **11**,[35] and **15**;[83] and palladium complex **13**[84] were synthesized via literature procedures. Palladium acetate, tris(dibenzylideneacetone)dipalladium(0), palladium complex **12**, and all ligands (obtained air-free from commercial suppliers) were stored and weighed out in an argon-filled drybox. Tetrakis(triphenylphosphine)palladium(0) (obtained similarly) was stored under argon at −30 °C and weighed out in an argon-filled drybox. Polymerization solvents were obtained air-free and anhydrous from Aldrich, and were similarly stored and dispensed in the drybox. All other chemicals were used as received from commercial suppliers. The water content for commercial $K_3PO_4{\bullet}xH_2O$ varies from sample to sample, and that for the particular sample we used was determined to be 19% from TGA and titration experiments. Nuclear magnetic resonance spectra were obtained at 300 MHz (proton) and 75 MHz (carbon) using a General Electric QE 300 NMR spectrometer. The long acquisition ^{31}P NMR spectrum was obtained on a polymer synthesized previously,[35] at 162 MHz using a Bruker Avance III 400 MHz NMR spectrometer. Molecular weights were measured in chloroform solution with a tandem GPC-LS apparatus that consisted of an Agilent Technologies Series 1100 HPLC pump equipped with Waters Styrogel GPC columns (HR5E, HR4, HR4E connected in series) in line with a Wyatt Technologies DAWN-EOS light scattering photometer and a Wyatt Optilab DSP interferometic refractometer. Measurements were made at 25.0 °C and a wavelength of 690 nm. Analytical data were obtained by Robertson Microlit Laboratories, Inc. Characterization data for the polymers are presented elsewhere.[35]

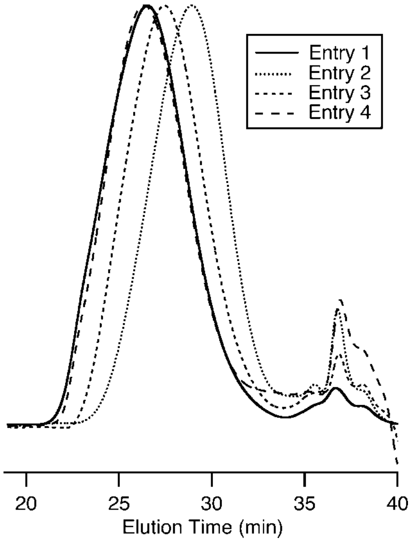


Figure 8. GPC chromatograms (normalized to maximum intensity) for polymerizations run with different monomers and additives (eq 10, Table 4).

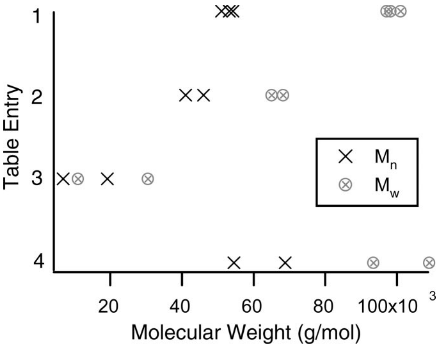


Figure 9. Molecular weights for individual polymerizations run with different monomers and additives (Table 4).

Hexaethylene Glycol Di(3-iodophenyl) Ether (14). A 250 mL round-bottomed flask was charged with 5.41 g (9.41 mmol) of hexaethylene glycol di(*p*-toluenesulfonate), 5.96 g (27.1 mmol) of 3-iodophenol, 12.8 g of K_2CO_3 (92.6 mmol), and 50 mL of DMF. The flask was then placed in a heated oil bath at 60 °C overnight, after which the solvent was removed via vacuum distillation. The residue was then suspended in $CHCl_3$ and filtered to remove excess carbonate and salt byproducts. Upon removal of the solvent via rotary evaporator, unreacted 3-iodophenol was distilled away from the product by heating the mixture to 100 °C under a dynamic (1 mtorr) vacuum in a bulb-to-bulb apparatus. The material left in the pot was then chromatographed on silica with an eluent of ethyl acetate and hexanes, adjusted to give an R_f of 0.25. Hexaethylene glycol di(3-iodophenyl) ether (**14**) (2.69 g, 3.92 mmol, 42% yield), was then isolated as a pale yellow oil after distillation at 200 °C (<1 mtorr): ^1H NMR (300 MHz, $CDCl_3$) δ 7.25−7.26 (multiple resonances, 4H), 6.97 (t, J = 8.4 Hz, 2H), 6.84 (dm, J_d = 8.1 Hz, 2H), 4.06 (t, J = 4.8 Hz, 4H), 3.81 (t, J = 4.5 Hz, 4H), 3.64−3.74 (multiple resonances, 8H), 3.66 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 130.5, 129.7, 123.5, 114.0, 94.1, 70.6, 70.3, 70.3, 69.3, 67.4, (one signal not resolved). Anal. Calcd for $C_{24}H_{32}I_2O_7$: C, 42.00; H, 4.70; Found: C, 41.74; H, 4.52.

General Procedure for Microscale Polymerization Screening Experiments. To each of several 10 mL ampules was added 0.500 mL of a CH_2Cl_2 stock solution 0.3 M in dibromide and diboronic ester monomers. Solvent was removed *in vacuo* after which the ampules were back-filled with nitrogen, capped, wax-sealed, and stored at −10 °C in the dark until ready for use. Polymerizations were set up 6−12 at a time by charging the ampules with stir bars along with the appropriate base, catalyst, and ligand solutions so that each tube contained 0.150 mL of organic solvent, 0.0015 mmol of palladium, and 0.300 mL of aqueous solution. The vessels were degassed via three freeze−pump−thaw cycles, sealed under vacuum, and placed in a thermostatted 50 °C water bath over an efficient magnetic stirrer for three days. The resulting materials were taken up in a minimal amount of $CHCl_3$ spiked with Aliquat 336 (2 drops per 100 mL), transferred to centrifuge tubes, extracted with 5% aqueous NaCN (1 mL) and washed 6 times with 1 mL of HPLC-grade water. The organic phases were transferred to separate scintillation vials (no drying agent was used), after which the solvent was removed with a rotary evaporator. The resulting films were then dried at 100 °C under a 1 mtorr vacuum for 20 min, and analyzed via GPC−LS without further purification.

Reproducibility Screening. The above general procedure was followed by charging each of six ampules with 0.500 mL of a CH_2Cl_2 stock solution containing 1.5122 g (2.9991 mmol) of **1** and 0.7374 g (2.999 mmol) of **2** in 10.0 mL of CH_2Cl_2. After removal of the solvent, each was charged with 0.300 mL of 3 M aqueous K_3PO_4 (previously degassed via three freeze−pump−thaw cycles). A stock solution (75 μL, 0.0030 mmol) containing tri(*o*-tolyl)phosphine (12.2 mg, 0.040 mmol in 1.00 mL of degassed CH_2Cl_2) was then added via syringe, followed by 75 μL (0.0015 mmol Pd) of a $Pd_2(dba)_3$ stock solution (9.2 mg, 0.020 mmol Pd in 1.00 mL of degassed CH_2Cl_2). The ampules were then degassed, sealed, and allowed to react as described above.

Solvent Screening. Ampules prepared with monomers **1** and **2** as described above were each charged with 75 μL (0.0030 mmol) of a stock solution containing tri(*o*-tolyl)phosphine (12.2 mg, 0.040 mmol in 1.00 mL of degassed CH_2Cl_2) and 75 μL (0.0015 mmol Pd) of a $Pd_2(dba)_3$ stock solution (9.2 mg, 0.020 mmol Pd in 1.00 mL of degassed CH_2Cl_2). The solvent was then removed *in vacuo*, after which 0.300 mL of degassed 3 M aqueous K_3PO_4 and 0.150 of the appropriate air-free organic solvent were added via syringe. The ampules were then degassed, sealed, and allowed to react as described above.

Base Screening. Ampules prepared with monomers **1** and **2** as described above were each charged with 0.300 mL of the appropriate degassed aqueous base solution, 75 μL (0.0030 mmol) of a stock solution containing tri(*o*-tolyl)phosphine (12.2 mg, 0.040 mmol in 1.00 mL of degassed CH_2Cl_2), and 75 μL (0.0015 mmol Pd) of a $Pd_2(dba)_3$ stock solution (9.2 mg, 0.020 mmol Pd in 1.00 mL of degassed CH_2Cl_2). The ampules were then degassed, sealed, and allowed to react as described above.

Ligand Screening. Ampules prepared with monomers **2** and **11** as described above were each charged with 0.300 mL of degassed 3 M aqueous K_3PO_4, 75 μL (0.0030 mmol, or 0.0015 mmol for bidentate ligands) of a stock solution containing the appropriate ligand (0.040 mmol ligating atom in 1.00 mL of degassed CH_2Cl_2), and 75 μL (0.0015 mmol Pd) of a $Pd_2(dba)_3$ stock solution (9.2 mg, 0.020 mmol Pd in 1.00 mL of degassed CH_2Cl_2). (The solution of carbene **3** was generated in situ by treating (in a drybox) 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (13.7 mg, 0.040 mmol) with sodium *tert*-butoxide (3.8 mg, 0.040 mmol) in 5 mL dry THF, filtering the resulting suspension, removing the solvent *in vacuo*, and taking up the residue in 1 mL of air-free CH_2Cl_2.) The ampules were then degassed, sealed, and allowed to react as described above.

Catalyst Screening. For polymerizations run with the insoluble palladium complex (**13**), 0.0015 mmol of the complex were weighed directly into an ampule (preloaded with **2** and **11**) in a drybox, prior to charging with 0.300 mL of degassed 3 M aqueous K_3PO_4 and 0.150 mL of degassed CH_2Cl_2 on a vacuum line. The other polymerizations were set up with catalyst and ligand stock solutions in the usual manner. For polymerizations run with less or no additional ligand, enough CH_2Cl_2 was added to bring the total volume of organic solvent to 0.150 mL. The ampules were degassed, sealed, and allowed to react as described above.

Monomer Screening. The above general procedure was applied using ampules preloaded with the appropriate monomers, 0.300 mL of degassed 3 M aqueous K_3PO_4, 75 μL (0.0030 mmol) of a stock solution containing tri(*o*-tolyl)phosphine (12.2 mg, 0.040 mmol in 1.00 mL of degassed CH_2Cl_2), and 75 μL (0.0015 mmol Pd) of a $Pd_2(dba)_3$ stock solution (9.2 mg, 0.020 mmol Pd in 1.00 mL of degassed CH_2Cl_2). The ampules were degassed, sealed, and allowed to react as described above.

Acknowledgment. The authors gratefully acknowledge support for this work by grants from the Camille and Henry Dreyfus Foundation (Startup Award for Faculty at Undergraduate Institutions) and the Petroleum Research Fund administered by the ACS (Type GB). Light scattering and NMR instrumentation were purchased with grants from the National Science Foundation (CRIF and MRI programs, respectively).

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MA801275Y