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Polystyrene-Supported Triphenylarsine Reagents and Their Use in Suzuki Cross-Coupling Reactions

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Soluble and insoluble polystyrene-bound triphenylarsine reagents have been prepared from 4-styryldiphenylarsine. The utility of these reagents as ligands for palladium in Suzuki cross-coupling reactions is demonstrated. In these applications, the use of polymeric triphenylarsine simplifies the purification of the coupled product and allows for the ligand to be recycled. Furthermore, the soluble polymeric arsine reagent permits the palladium catalyst to be recovered and reused.

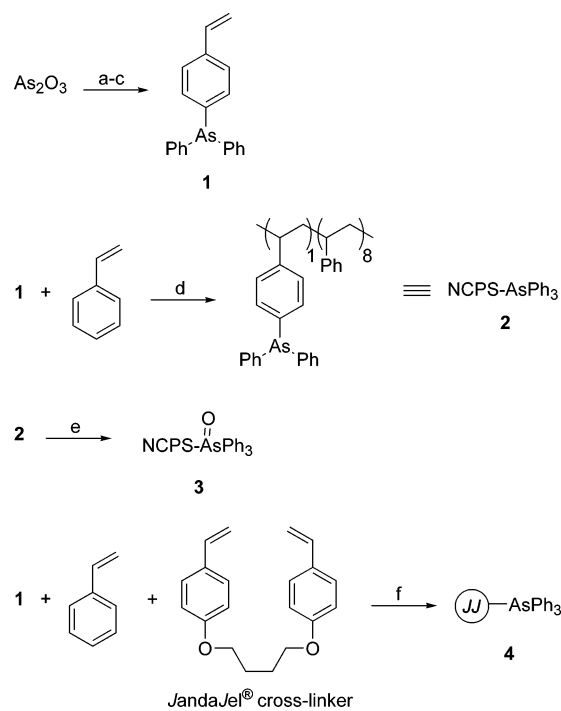
Polymer-supported reagents and catalysts have become common tools for organic synthesis in what is known as polymer-assisted synthesis, because they can simplify product purification and have the potential to be easily recycled.¹ A vast array of such reagents and catalysts have been reported that use both insoluble² and soluble³ polymers as their carriers. In this regard, we have long-standing interests in the development of new insoluble polymers that can be used as both synthesis and reagent supports⁴ and in the development of both soluble and insoluble amine,⁵ ketone,⁶ sulfide,⁷ and sulfoxide⁸ polymer-supported reagents. In addition, we have recently reported the preparation of non-cross-linked (soluble) and cross-linked (insoluble) polystyrene-supported triphenylphosphine reagents that were observed to be useful in Mitsunobu and alcohol bromination reactions, respectively.⁹ Because of the simplicity of the syntheses of these phosphine reagents, we sought to extend our methodology to the preparation of analogous triphenylarsine functionalized polymers.

Similar to triphenylphosphine, triphenylarsine¹⁰ is a versatile reagent for organic synthesis, and the replacement of phosphines by arsines has led to improved results in many synthetic reactions. Triphenylarsine has been determined to be particularly useful in the form of arsonium ylides¹¹ and as a ligand for palladium in various metal-catalyzed cross-coupling reactions.¹² Although there have been many applications of polymer-supported triphenylphosphine,¹³ reports regarding supported triphenylarsine are few^{14,15} and it has only been used synthetically in Heck reactions¹⁵ and in the oxide oxidation state for the preparation of carbodiimides.^{14a,16}

As in our previous syntheses of functionalized polymers,^{4,9} we chose to use a functional monomer,¹⁷ **1**, for incorporation of the triphenylarsine moieties into both soluble and insoluble polystyrene. Monomer **1** was synthesized via a two-step sequence using Grignard reagents in 61% yield from arsenic oxide, according to the literature procedure (Scheme 1).^{14b}

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Scheme 1^a



^a Reaction conditions: (a) PhMgBr , THF, 0 °C to room temperature; (b) HCl; (c) $p\text{-BrMg}-\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$, THF, 0 °C to room temperature; (d) AIBN, PhMe, 85 °C; (e) H_2O_2 , THF, room temperature; and (f) PhCl, H_2O , acacia gum, NaCl, AIBN, 85 °C.

For the preparation of the soluble, non-cross-linked polystyrene-supported (NCPS) reagent, **1** was copolymerized with styrene under free radical conditions in a molar ratio of 1:8.3 (**1**:styrene) to afford **2** (non-cross-linked polystyrene-AsPh₃ or NCPS-AsPh₃) in 48% yield (Scheme 1). The ratio of incorporation of **1** to styrene in **2** was determined by the oxidation of **2** to **3** with H_2O_2 , using the method for arsine oxidation reported by Sheldon et al.¹⁸ and analyzing its ¹H NMR spectra. In **3**, all of the aromatic proton signals associated with the triarylsarsine oxide moieties (14 in total) are shifted downfield from the polystyrene aromatic proton signals, allowing for integration and thus quantification.

Table 1. Synthesis and Loading Levels of Reagents **2** and **4**

	Reagent Preparation		Arsenic Content (%)		Loading (mmol/g)	
	1 (mmol) ^a	styrene (mmol) ^a	theoretical	observed	theoretical	observed
2	53.9	445.1	6.29	7.45 ^b	0.83	0.79 ^c
4	15.5	46.5	11.61	10.83 ^b	1.55	1.44 ^b

^a Amount of monomer used for reagent preparation. ^b Determined by elemental analysis. ^c Determined by ¹H NMR analysis of **3**.

Using this method, a ratio of incorporation of 1:8 was found for **3** and, thus, **2**. This corresponds to a loading level of 0.79 mmol AsPh₃/g **2** (Table 1), which is close to the theoretical value of 0.83 mmol AsPh₃/g. However, elemental analysis indicated a loading level of 0.99 mmol AsPh₃/g. The origin of this discrepancy is unclear; however, the lower loading determined by the analysis of **3** was probably not due to incomplete oxidation of the arsine moieties in **2**, because a control reaction in which triphenylarsine was oxidized to triphenylarsine oxide, using the same conditions, was complete in a matter of minutes. The different obtained loading values could be due to errors in elemental analysis determination or in the recording and analysis of the NMR spectra, or a combination of these factors. Regardless, the lower loading level obtained from ¹H NMR analysis was used in reactions with **2**, because this represents a minimum value.

To prepare the insoluble, cross-linked polystyrene triphenylarsine reagent, **1** was suspension-copolymerized¹⁹ with styrene and the flexible *Janda/Jel* cross-linker^{4,20} to afford **4** (*Janda/Jel*-AsPh₃) in 82% yield (Scheme 1). We decided to prepare **4** with less than the maximum possible loading level, because of our previous observation that heavily loaded *Janda/Jel*-PPh₃ shows very little swelling in organic solvents.⁹ Therefore, using the appropriate amount of styrene to dilute **1**, we attempted to prepare **4** with a loading level of ca. 1.55 mmol AsPh₃/g (see Table 1). Only elemental analysis was used to determine the actual loading level of **4** (1.44 mmol AsPh₃/g), because its insolubility and hydrophobicity made it seem unlikely that its oxidation would go to completion, especially because most of the arsine moieties are buried deep within the interior of the beads. The fact that the observed loading level of **4** is slightly lower than the theoretical value gives us confidence in the NMR-determined loading level of **2**. Both of these lower-than-expected values are in agreement with the notion that **1** and styrene are incorporated into the polymers at approximately the same rate under the two different radical polymerization procedures used, as one might expect. Furthermore, it is significant that the observed loading levels of **2** and **4** are similar to their theoretical values, because it should therefore be facile to prepare such polymeric reagents with any theoretically possible loading level that is desired, as we have done previously with triphenylphosphine reagents.⁹

To assess the synthetic utility of polymeric reagents **2** and **4**, we chose to examine them as ligands for palladium in Suzuki cross-coupling reactions^{21,22} of arylboronic acids with 2-iodo-2-cyclohexen-1-one, iodobenzene, and 2-bromomesitylene. Both polymers were used in these reactions, and comparisons were made with AsPh₃. Polymer **2** was removed at the end of each reaction by precipitation from methanol, followed by filtration, and polymer **4** was removed directly

Table 2. Suzuki Cross-Coupling Reactions of Arylboronic Acids with 2-Iodo-2-cyclohexen-1-one

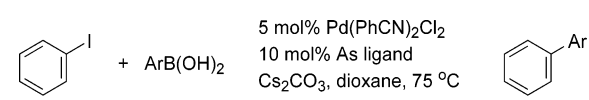
entry	ligand	X	Ar	temp (°C)	time	yield (%) ^a
1	AsPh ₃	I	Ph-	rt ^b	2 h	79
2	2	I	Ph-	rt ^b	2 h	85
3	2	I	4-MeO-C ₆ H ₄ -	rt ^b	2 h	85
4	2	I	3-MeO-C ₆ H ₄ -	rt ^b	2 h	92
5	2	Br	Ph-	66	2 d	26
6	4	I	Ph-	rt ^b	4 d	75 ^c
7	4	I	Ph-	66	18 h	86
8	<i>JJ</i> -PPh ₃	I	Ph-	66	18 h	48
9	4	I	4-MeO-C ₆ H ₄ -	66	18 h	82
10	4	I	3-MeO-C ₆ H ₄ -	66	18 h	93
11	4	I	3,4-(MeO) ₂ -C ₆ H ₃ -	66	18 h	85

^a Isolated yield of product after silica gel chromatography. See Supporting Information for product characterization details. ^b Room temperature. ^c A composition of 45 mol % of **4** and 20 mol % of Pd(PhCN)₂Cl₂ was used.

by simple filtration. Note that **2** can also be precipitated from diethyl ether or hexanes, should methanol prove to be an inappropriate solvent for the desired product.

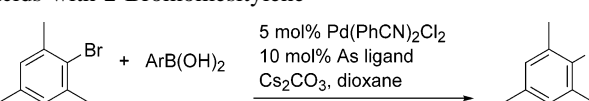
For the Suzuki coupling reactions of 2-iodo-2-cyclohexen-1-one, the procedure of Johnson et al. was used, in which Ag₂O is the base and the solvent is tetrahydrofuran (THF) (Table 2).²³ Both electron-rich and unsubstituted arylboronic acids were studied. It was found that reactions involving the soluble polymer **2** proceeded at approximately the same rate and in comparably good yields (see entries 2–4 in Table 2) as the control reaction using AsPh₃ (see entry 1 in Table 2). An additional control reaction was performed in which the polymeric arsine ligand was omitted, and no desired product was observed. Furthermore, when 2-bromo-2-cyclohexen-1-one was used, the reaction was very sluggish and only 26% of the desired product was formed after refluxing for 2 days (see entry 5 in Table 2). When insoluble polymer **4** was used, the reactions were sluggish at room temperature. This was most likely due to the heterogeneity of the reaction. Even when the amount of catalyst and ligand were increased 4-fold, the reaction required 4 days for completion (see entry 6 in Table 2). However, when heated to reflux, the reactions occurred more efficiently (see entries 7 and 9–11 in Table 2). Despite the need to heat these reactions and their extended reaction times, good yields of coupled products were obtained. Importantly, **4** afforded a significantly higher product yield than the analogous and readily available insoluble triphenylphosphine resin, *Janda/Jel*-PPh₃,⁹ in a side-by-side competition (see entry 8 in Table 2).

For the Suzuki coupling reactions of iodobenzene, Cs₂CO₃ served as the base in 1,4-dioxane at 75 °C (Table

Table 3. Suzuki Cross-Coupling Reactions of Arylboronic Acids with Iodobenzene


entry	As ligand	boronic acid	time	yield (%) ^a
1	AsPh ₃	4-MeO-C ₆ H ₄ -	2 h	84
2	2	Ph-	2 h	76
3	2	4-MeO-C ₆ H ₄ -	2 h	85
4	2	3-MeO-C ₆ H ₄ -	2 h	78
5	4	Ph-	18 h	86
6	4	4-MeO-C ₆ H ₄ -	18 h	85
7	4	3,4-(MeO) ₂ -C ₆ H ₃ -	18 h	81

^a Isolated yield of product after silica gel chromatography. See Supporting Information for product characterization details.

Table 4. Suzuki Cross-Coupling Reactions of Arylboronic Acids with 2-Bromomesitylene


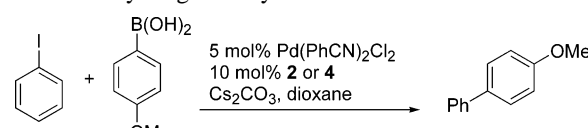
entry	As ligand	boronic acid	temp (°C)	time	yield (%) ^a
1	2	4-MeO-C ₆ H ₄ -	75	2 d	38
2	2	4-MeO-C ₆ H ₄ -	101	18 h	49
3	2	2-Me-C ₆ H ₄ -	101	2 d	n.d. ^b
4	2	2,6-Me ₂ -C ₆ H ₃ -	101	3 d	0

^a Isolated yield of product after silica gel chromatography. See Supporting Information for product characterization details. ^b Not determined.

3).²⁴ Again, a control reaction was performed in which the polymeric arsine ligand was omitted, and no desired product was observed. As in the previous set of reactions, the soluble reagent **2** allowed the reactions to proceed similarly (see entries 2–4 in Table 3) as with AsPh₃ (see entry 1 in Table 3), whereas reactions with insoluble **4** required extended reaction times (see entries 5–7 in Table 3).

Having established the utility of **2** in the Suzuki coupling reactions of reactive iodobenzene, we then performed an examination to determine if it is useful with less-reactive and more sterically hindered 2-bromomesitylene. As might be expected, reactions with this aryl halide were, by comparison, quite sluggish and only low yields of the desired products were obtained after extended reaction times in refluxing solvent (Table 4). The coupling reaction with 2-methylphenylboronic acid afforded only ~40% yield (by mass) of an inseparable mixture of what appeared to be the desired product and the homo-coupling product 2,2'-dimethylbiphenyl (see entry 3 in Table 4), whereas the attempted synthesis of a biphenyl *ortho*-methyl substituent failed to produce any detectable desired product, even after 3 days (see entry 4 in Table 4).

Finally, the possibility for the recycling of **2** and **4** was examined to determine if these polymers are more environmentally friendly alternatives to AsPh₃. For this study, we used the reactions of entries 3 and 6 in Table 3 and performed four cycles, using the same polymer sample that was recovered at the end of each reaction. When **4** was used in refluxing 1,4-dioxane, isolated yields of the product were essentially identical through three reuses of the same polymer

Table 5. Recycling of Polymers **2** and **4**


entry	As ligand	Cycle (% Yield) ^a			
		1	2	3	4
1	4 ^b	85	84	86	81
2	2 ^c	88	87	84	85
3	2 ^b	78	83	79	75

^a Isolated yield of product after silica gel chromatography. The polymer was washed and dried between cycles. ^b Reactions were performed at reflux, with an additional palladium catalyst being added for each cycle. ^c Reaction were performed at 75 °C, with no additional palladium catalyst being added for each cycle.

sample (see entry 1 in Table 5). However, these reactions seemed to be accompanied by the precipitation of palladium black, and the recovered polymer was contaminated with this material and it was necessary to add additional palladium catalyst to each subsequent reaction. In an attempt to minimize or eliminate palladium precipitation and allow the metal catalyst to also be reused, reactions with **2** were conducted at 75 °C. Gratifyingly, at this temperature, the reactions were still complete within 2 h and no palladium black precipitation was observed. In this manner, the mixture of **2** and palladium could be recovered and reused directly for the next cycle without the need for additional catalyst, and the yields of isolated product remained consistently high for all reactions (see entry 2 in Table 5). The ability to recover and reuse the mixture of **2** with palladium in this manner may be related to the process of microencapsulation, as reported by Kobayashi and others, in which the metal is physically enveloped by the polymer.²⁵ Note that, during each cycle, ~5–10% of **2** was lost, because of the difficulties in handling such small quantities of polymer, and the scale of the subsequent reaction was scaled accordingly. With refluxing 1,4-dioxane, **2** afforded slightly lower yields and, as done previously, it was necessary to add additional palladium for each cycle (see entry 3 in Table 5). The final test that was performed regarding the recyclability of the mixture of **2** and palladium was to first use it in the reaction represented by entry 3 in Table 3, recover it, and then use it in the reaction represented by entry 4 in Table 3. In this experiment, we found no evidence of contamination of the second product by the first product. This indicates that product microencapsulation is not a significant process and that only the palladium participates in this type of entrapment.

In summary, we have prepared non-cross-linked and cross-linked polystyrene-supported triphenylarsine reagents **2** and **4**, using a functional monomer that allows for the direct incorporation of the arsine groups during the polymerization process. These polymeric reagents have been demonstrated to be useful in Suzuki cross-coupling reactions as a ligand for palladium, where they facilitate product purification. Reactions involving **2** proceed in a manner similar to reactions using triphenylarsine, whereas reactions with **4** require elevated temperatures and prolonged reaction times. Finally, these polymers can readily be recovered and reused

with no decrease in effectiveness and the use of soluble polymer **2** even allows for the recovery and recycling of the palladium catalyst. We are currently examining the application of these reagents in arsonium ylide chemistry.

Experimental Section

4-Styrylidiphenylarsine (1). Arsenic oxide (8.9 g, 44.9 mmol) was added into a solution of the Grignard reagent prepared from bromobenzene (28.0 g, 180 mmol) and magnesium (4.4 g, 180 mmol) in dry THF (200 mL) at 0 °C under N₂. The mixture was stirred at room temperature for 4 h. At this time, the reaction mixture was acidified with 1 N HCl and then extracted with diethyl ether (3 × 150 mL). The organic layers were combined and washed sequentially with saturated aqueous NaHCO₃ (3 × 100 mL) and brine (3 × 100 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography to afford a pale yellow solid (10.5 g). This reaction was performed twice, and the combined products were used for the next step.

The solid (21.0 g) was dissolved in THF (70 mL) and added slowly at 0 °C to a solution of the Grignard reagent prepared from 4-bromostyrene (10.0 g, 54.6 mmol) and magnesium (1.57 g, 65.4 mmol) in dry THF (150 mL). The mixture was stirred at room temperature for 3 h. At this time, the reaction mixture was diluted with diethyl ether (400 mL) and then washed sequentially with water (3 × 100 mL), 10% aqueous HCl (3 × 100 mL), saturated aqueous NaHCO₃ (3 × 100 mL), and brine (3 × 100 mL). The organic layer was dried over MgSO₄, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (100% hexane) to afford **1** as a light yellow liquid (10.9 g, 33.1 mmol, 61% based on 4-bromostyrene). ¹H NMR (400 MHz, CDCl₃): δ 5.25 (dd, 1H, *J* = 10.9, 0.9), 5.76 (dd, 1H, *J* = 17.6, 0.9), 6.66–6.70 (m, 1H), 7.28–7.37 (m, 14H). ¹³C NMR (75 MHz, CDCl₃): δ 114.4, 126.4 (2C), 128.5 (2C), 128.7 (4C), 133.7 (4C), 134.0 (2C), 136.5 (2C), 137.7, 139.3, 139.6. IR (cm⁻¹): 3069–2861, 1973, 1958, 1900, 1881, 1824, 1627, 1579, 1550, 1492, 1481, 1433, 1391, 1302, 1184, 1074, 1023, 999, 989, 910, 831, 736, 695, 591. HR EI-MS Anal. Calcd for C₂₀H₁₇As: 332.0546. Found: 332.0543.

Non-cross-linked Polystyrene-Bound Triphenylarsine (2). AIBN (0.7 g, 4.1 mmol) was added to a solution of styrene (46.4 g, 445.1 mmol) and **1** (17.9 g, 53.9 mmol) in toluene (300 mL). The mixture was purged at room temperature with N₂ for 30 min and then stirred at a temperature of 85 °C for 24 h. The solution was then concentrated in vacuo and the resulting residue was dissolved in 45 mL of THF. This solution was added slowly to vigorously stirred cold methanol (0 °C, 1 L). The resulting suspension was heated at 50 °C for 4 h and then cooled to room temperature and filtered to afford **2** as a white powder (30.7 g, 48%). ¹H NMR (400 MHz, CDCl₃): δ 1.42–1.83 (bm, 28H) and 6.45–7.38 (bm, 54H). The ratio of monomer **1** to styrene in **2** was determined to be 1:8, by integration of the ¹H NMR of the oxidized polymer **3**. This corresponds to a loading level of 0.79 mmol AsPh₃/g for **2**. Elemental analysis indicated that **2** contained 7.45% arsenic. This corresponds

to a loading level of 0.99 mmol AsPh₃/g for **2**. IR (KBr, cm⁻¹): 3059, 3026, 2922, 2849, 1951, 1877, 1808, 1601, 1582, 1493, 1452, 1434, 1370, 1185, 1074, 1025, 907, 823, 757, 738, 697, 541.

Non-cross-linked Polystyrene-Bound Triphenylarsine Oxide (3). A solution of **2** (0.5 g, 0.4 mmol) in THF (4 mL) was added to H₂O₂ (0.5 mL, 50 wt %, 8.6 mmol) and stirred at room temperature for 4 h. The solution was then concentrated in vacuo, and the resulting residue was dissolved in 2 mL of THF. This solution was added slowly to vigorously stirred cold hexane (60 mL). The resulting suspension was filtered, and the precipitate was dried in vacuo to afford **3** (0.55 g). ¹H NMR (400 MHz, CDCl₃): δ 1.43–1.84 (bm, 28H), 6.57–7.05 (bm, 39H), 7.51–7.66 (bm, 14H). IR (KBr, cm⁻¹): 3414, 3152, 2828, 2178, 1991, 1917, 1682, 1578, 1483, 1439, 1315, 1184, 1162, 1087, 1026, 998, 932, 874, 759, 743, 691.

Poly(styrene-co-4-styrylidiphenylarsine-co-1,4-bis(4-vinylphenoxy)butane) (JandaJel-AsPh₃, 4). A solution of acacia gum (6.0 g) and NaCl (3.8 g) in warm deionized water (45 °C, 150 mL) was placed in a 150-mL flanged reaction vessel that was equipped with a mechanical stirrer and deoxygenated by purging with N₂ for 2 h.²⁶ A solution of **1** (5.15 g, 15.5 mmol), styrene (4.84 g, 46.5 mmol), 1,4-bis(4-vinylphenoxy)butane (0.37 g, 1.2 mmol), and AIBN (0.2 g) in chlorobenzene (10 mL) was injected into the rapidly stirred aqueous solution. The resulting suspension was heated at 85 °C for 20 h. The crude polymer was collected and washed with hot water (3 × 100 mL) and then placed in a Soxhlet extractor and washed with THF for 24 h. The beads were then washed sequentially with methanol, diethyl ether, and hexanes, and dried in vacuo to afford **4** (8.2 g, 82%). Elemental analysis indicated that **4** contained 10.83% arsenic. This corresponds to a loading level of 1.44 mmol AsPh₃/g for **4**. IR (KBr, cm⁻¹): 3069, 3027, 2904, 2853, 1948, 1877, 1809, 1601, 1581, 1510, 1452, 1403, 1238, 1184, 1156, 1074, 999, 905, 821, 759, 736, 695, 538.

Pd(PhCN)₂Cl₂-Catalyzed Cross-Coupling Reactions of 2-Iodo-2-cyclohexen-1-one with Arylboronic Acids Using 2. A 10-mL round-bottomed flask that was equipped with a magnetic stirring bar was charged with 2-iodo-2-cyclohexen-1-one (0.200 g, 0.903 mmol), arylboronic acid (1.406 mmol), Ag₂O (0.334 g, 1.443 mmol), **2** (0.106 g, 0.090 mmol), Pd(PhCN)₂Cl₂ (0.017 g, 0.045 mmol), THF (4 mL), and water (0.5 mL). The reaction mixture was stirred for 2 h under argon and then filtered through a pad of Celite and concentrated under reduced pressure. A minimum amount of boiling THF (<1.5 mL) was used to redissolve the residue, and this solution was added slowly to methanol (35 mL). The precipitated polymer was separated from the reaction mixture by suction filtration. The filtrate was concentrated, and the residue was purified by silica gel column chromatography (20–30% ethyl acetate in hexane) and characterized.

Pd(PhCN)₂Cl₂-Catalyzed Cross-Coupling Reactions of 2-Iodo-2-cyclohexen-1-one with Arylboronic Acids Using 4. A 10-mL round-bottomed flask that was equipped with a magnetic stirring bar was charged with 2-iodo-2-cyclohexen-1-one (0.200 g, 0.903 mmol), arylboronic acid (1.406 mmol),

Ag₂O (0.334 g, 1.443 mmol), **4** (0.060 g, 0.090 mmol), Pd(PhCN)₂Cl₂ (0.017 g, 0.045 mmol), THF (4 mL), and water (0.5 mL). The reaction mixture was refluxed for 18 h under argon and then allowed to cool to room temperature. The polymer was separated from the reaction mixture by suction filtration. The filtrate was concentrated, and the resulting crude product was purified by silica gel column chromatography (20–30% ethyl acetate in hexane) and characterized.

Pd(PhCN)₂Cl₂-Catalyzed Cross-Coupling Reactions of Iodobenzene and 2-Bromomesitylene with Arylboronic Acids Using **2.** A 10-mL round-bottomed flask that was equipped with a magnetic stirring bar was charged with arylboronic acid (1.406 mmol), Cs₂CO₃ (0.530 g, 1.625 mmol), **2** (0.106 g, 0.090 mmol), Pd(PhCN)₂Cl₂ (0.017 g, 0.045 mmol), iodobenzene or 2-bromomesitylene (0.90 mmol), and 1,4-dioxane (4 mL). The reaction mixture was heated at 75 °C for the indicated period of time under argon and then allowed to cool to room temperature, filtered through a pad of Celite, and concentrated under reduced pressure. A minimum amount of boiling THF (<1.5 mL) was used to redissolve the residue, and this solution was added slowly to methanol (35 mL). The precipitated polymer was separated from the reaction mixture by suction filtration. The filtrate was concentrated and the resulting crude product was purified by silica gel column chromatography (4% ethyl acetate in hexane) and characterized. For the recycling experiments, the separated polymer was washed with water (2 × 15 mL) and methanol (2 × 15 mL) and dried before reuse. The second set of recycling experiments was performed at reflux and required additional palladium catalyst for each cycle.

Pd(PhCN)₂Cl₂-Catalyzed Cross-Coupling Reactions of Iodobenzene with Arylboronic Acids Using **4.** A 10-mL round-bottomed flask that was equipped with a magnetic stirring bar was charged with arylboronic acid (1.406 mmol), Cs₂CO₃ (0.530 g, 1.625 mmol), **4** (0.060 g, 0.090 mmol), Pd(PhCN)₂Cl₂ (0.017 g, 0.045 mmol), 1,4-dioxane (4 mL), and iodobenzene (0.10 mL, 0.91 mmol). The reaction mixture was refluxed for 18 h under argon and then allowed to cool to room temperature. The polymer was separated from the reaction mixture by suction filtration. The filtrate was concentrated, and the resulting crude product was purified by silica gel column chromatography (4% ethyl acetate in hexane) and characterized. For the recycling experiments, the separated polymer was washed with water (2 × 15 mL) and methanol (2 × 15 mL) and dried before reuse.

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Supporting Information Available. Characterization data including ¹H and ¹³C NMR spectra of monomer **1**, polymers **2** and **3**, and the coupling products (PDF). This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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