

# Recovery of *in Situ*-Generated Pd Nanoparticles with Linear Polystyrene

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## Abstract

Palladium nanoparticles generated *in situ* for Suzuki coupling reactions and aerobic alcohol oxidation in water were recovered completely using linear polystyrene. The resultant polystyrene-stabilized palladium nanoparticles were shown to be reusable without any loss of activity.

**Keywords:** Polystyrene, Pd Nanoparticles, Water, Suzuki Coupling, Alcohol Oxidation

## 1. Introduction

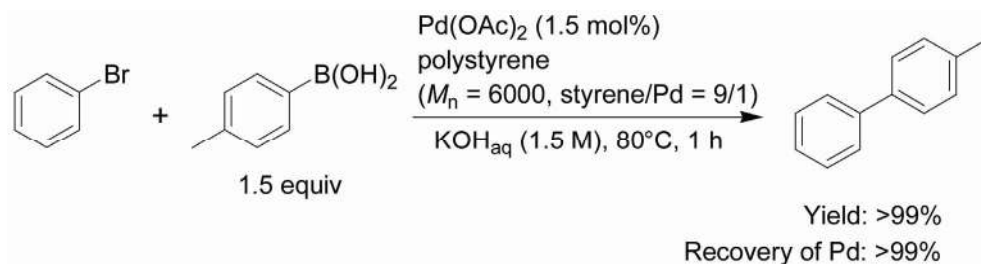
In view of the increasing demand for environmentally benign reaction processes, intensive efforts have been directed to reducing or eliminating the use of flammable, hazardous and nonrenewable organic solvents [1,2]. Palladium-catalyzed reactions such as carbon-carbon coupling and alcohol oxidation, which are some of the most common transition-metal-catalyzed processes, are more and more often being performed in aqueous media. Recovery of palladium catalysts is also important to enable reuse of these expensive reagents and to reduce palladium contamination of the isolated products. One reaction system employing a highly active immobilized catalyst shows good promise in incorporating these considerations [3]. However, the synthesis of heterogeneous catalysts typically requires several steps, such as preparation of the polymer support, introduction of ligand units into the polymer support, and immobilization of the metal complex. In contrast, palladium nanoparticles (PdNPs) generated *in situ* are easy-to-use catalysts and have high catalytic activities for coupling reactions in water in the presence of additives such as quaternary ammonium salts [4,5], cationic and anionic surfactants [6,7], and poly(ethylene glycol) [8]. Nevertheless, recovery of the palladium species can be difficult when the reaction is complete, as they are dispersed in water.

Recently, we found that PdO nanoparticles (PdONPs)

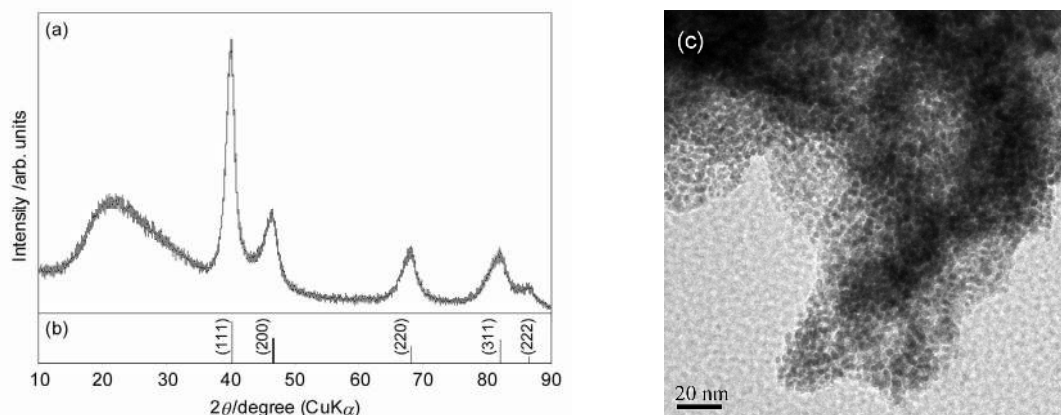
are readily stabilized on linear polystyrene, and the resultant polystyrene-stabilized PdONPs have high catalytic activities for Suzuki and copper-free Sonogashira coupling reactions in water [9,10]. Separately, polystyrene-stabilized PdNPs have been prepared using a phenylboronic acid as the reductant. Based on these successful results, we proposed that PdNPs generated *in situ* for Suzuki coupling reactions might also be stabilized and recovered by linear polystyrene. Herein we report that *in situ*-generated PdNP catalysts can be recovered completely with linear polystyrene without loss of their catalytic activity.

## 2. Results and Discussion

To investigate the recovery of *in situ*-generated PdNPs, we examined the Suzuki coupling reaction of bromobenzene with 4-methylphenylboronic acid using Pd(OAc)<sub>2</sub> as the catalyst in 1.5 M aqueous KOH solution at 80°C for 1 h. Under these conditions, the coupling reaction proceeded efficiently to give 4-methylbiphenyl quantitatively, with no palladium species recovered. Simple filtration of the reaction mixture in the presence of linear polystyrene (**Scheme 1**,  $M_n = 6000$ , styrene/Pd = 9/1), however, led to recovery of the palladium species. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that the quantitative recovery of Pd was achieved. In contrast, 85% and 86% of Pd were recov-



**Scheme 1.** Recovery of *in situ*-generated PdNPs for Suzuki coupling reaction in water.



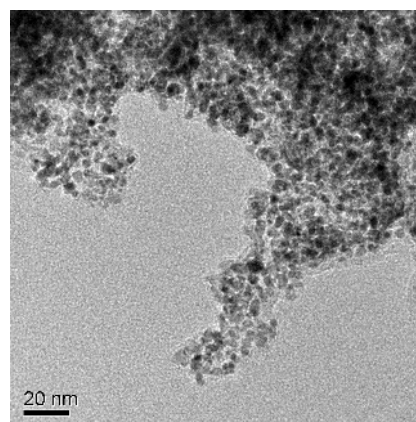
**Figure 1.** (a) XRD patterns of a recovered polystyrene-stabilized PdNPs. (b) JCPDS data (#46-1043) for Pd. (c) TEM image of a recovered polystyrene-stabilized PdNPs.

ered when the reduced amount of linear polystyrene (styrene/Pd = 1/1) and cross-linked polystyrene (2% DVB, styrene/Pd = 9/1) were used as stabilizer. An XRD pattern of the recovered palladium species is presented in **Figure 1(a)**. In addition to the broad diffraction with  $2\theta$  ranging from  $12^\circ$  to  $30^\circ$  ascribed to polystyrene, five other diffraction peaks assigned to the Pd nanoparticles (JCPDS #46-1043) are clearly observed. A transmission electron microscopy (TEM) image of recovered polystyrene-stabilized PdNPs is shown in **Figure 1(c)**, where a fairly uniform particle size of  $2.8 \text{ nm} \pm 0.4 \text{ nm}$  is evident. These results indicate that PdNPs generated *in situ* are stabilized onto the linear polystyrene and recovered completely, even in the presence of organic compounds.

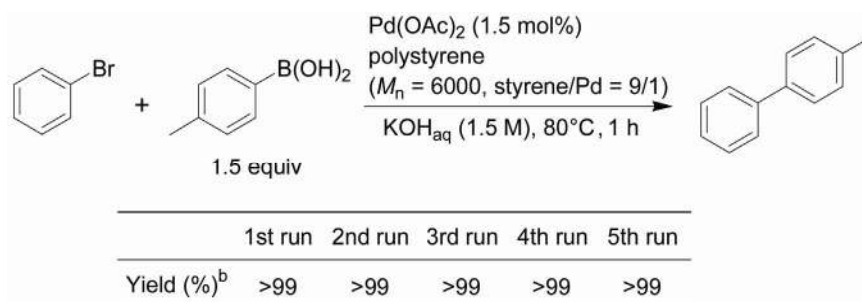
We next examined the reusability of the recovered polystyrene-stabilized PdNPs (**Table 1**). Similar yields were obtained even after the fifth use. It was confirmed by ICP-AES analysis that no leaching of the palladium into either the aqueous or organic solutions occurred. Furthermore, no change in particle size ( $2.8 \text{ nm} \pm 0.6 \text{ nm}$ ) was observed by TEM (**Figure 2**). It is noteworthy that a similar yield was obtained from the reaction of 4-chloroacetophenone with 4-methylphenylboronic acid at  $80^\circ\text{C}$  for 3 h (1st run, 32%; 2nd run, 30%; 3rd run, 32%), indicating that the catalytic activity of the *in situ*-generated PdNPs was retained after stabilization by

polystyrene.

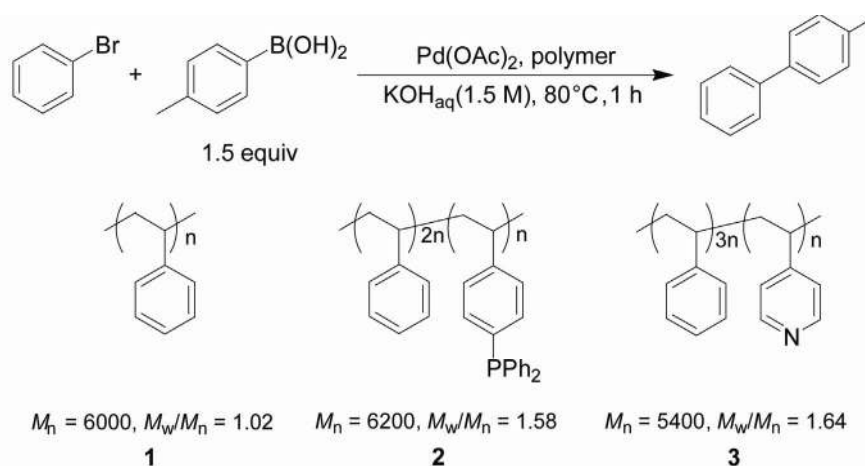
It is known that PdNPs are generally stabilized by functionalized polymers containing ligand units such as phosphine [11] and pyridine [12,13]. Encouraged by these reports, we investigated the recovery of *in situ*-generated PdNPs by poly(4-diphenylphosphinostyrene-*co*-styrene) (**2**) and poly(4-vinylpyridine-*co*-styrene) (**3**) (**Table 2**). In both cases, the catalytic activities of the recovered PdNPs were decreased. These results can be explained by the strong binding capability of phosphine



**Figure 2.** TEM image of a polystyrene-stabilized PdNPs after the recycling experiment.

**Table 1. Recycling of the linear polystyrene-stabilized PdNPs<sup>a</sup>.**

<sup>a</sup>Reaction conditions: bromobenzene (0.5 mmol), 4-methylphenylboronic acid (0.75 mmol, 1.5 equiv), Pd(OAc)<sub>2</sub> (1.5 mol% of Pd), polystyrene (styrene/Pd = 9/1), 1.5 M KOH<sub>aq</sub> (1 mL). <sup>b</sup>Isolated yield.

**Table 2. Recovery of Pd with other polymers<sup>a</sup>.**

Entry	Polymer	Yield (%) <sup>b</sup>	Recovery of Pd (%) <sup>c</sup>	Size of Pd /nm <sup>d</sup>
1	<b>1</b>	>99	>99	2.8 ± 0.4
2	<b>2</b>	80	43	2.8 ± 0.5
3	<b>3</b>	74	82	3.0 ± 0.9

<sup>a</sup>Reaction conditions: bromobenzene (0.5 mmol), 4-methylphenylboronic acid (0.75 mmol, 1.5 equiv), Pd(OAc)<sub>2</sub> (1.5 mol% of Pd), polymer (monomer/Pd = 9/1), 1.5 M KOH<sub>aq</sub> (1 mL). Isolated yield. <sup>c</sup>Determined by ICP-AES. <sup>d</sup>Determined by TEM.

and pyridine, which hinders the growth of the nanoparticles [14]. Interestingly, the recovery of Pd was decreased for both of these systems, although similar sizes of Pd were observed by TEM (**Figure 3**). The reason for this differing behavior compared to polystyrene remains unclear. Given these results, we determined that polystyrene is the best stabilizer for recovery of *in situ*-generated PdNPs.

The effect of substituents on the polystyrene was then evaluated. When the Suzuki coupling reaction of bromobenzene with 4-methylphenylboronic acid was performed in the presence of substituted polystyrene (monomer/Pd = 1/1), the recovery of Pd increased with

an increase in the electron density on the benzene ring (**Table 3**). These results suggest that the PdNPs are immobilized on the polymer through interactions between  $\pi$  electrons of the benzene rings of the polystyrene and the vacant orbitals of the metal [15]. Unfortunately, however, we could not confirm any obvious differences between polystyrene and polystyrene-stabilized PdNPs in the FT-IR spectra [16]. In addition, similar sizes of Pd were observed by TEM in these cases, too (**Figure 4**).

Lastly, we investigated the recovery and reuse of *in situ*-generated PdNPs for aerobic alcohol oxidation in water (**Scheme 2**). The moderate catalytic activity was observed, probably due to the formation of Pd aggregates

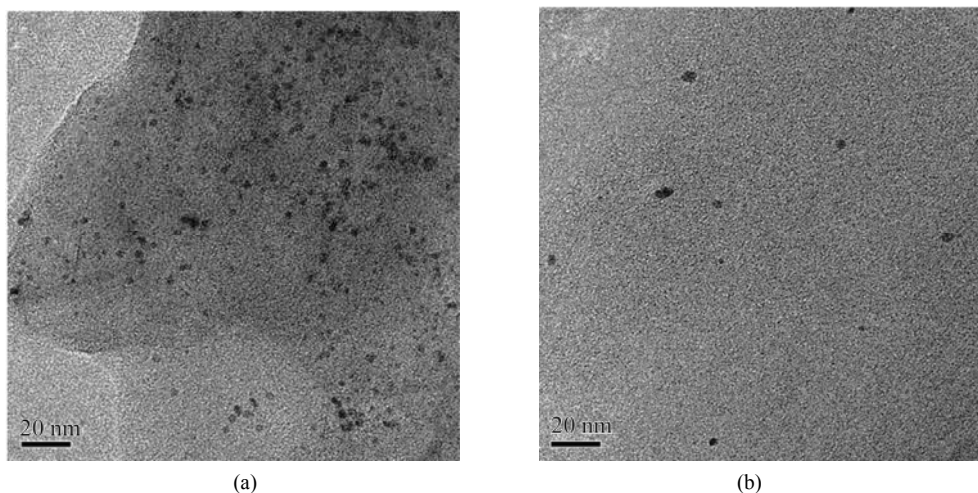
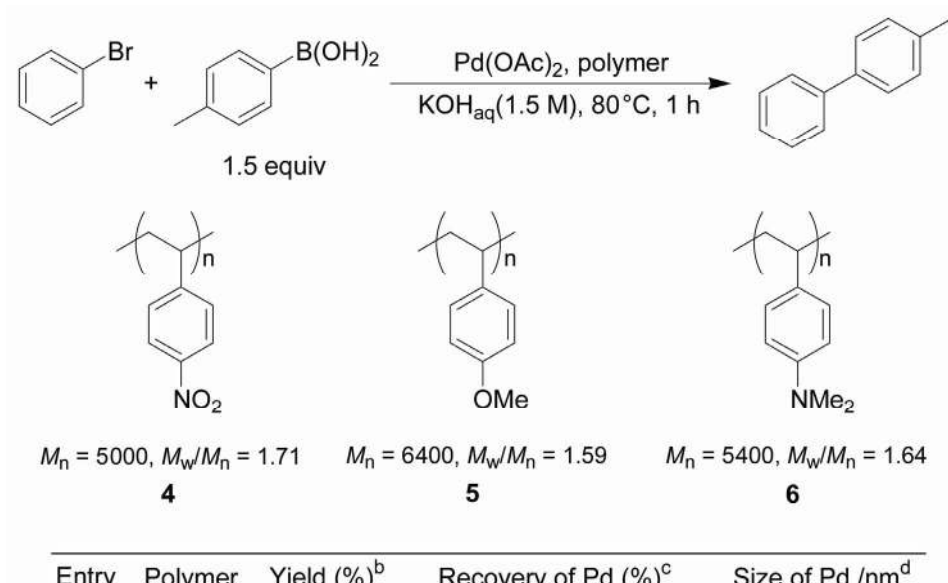


Figure 3. TEM images of recovered PdNPs by polymer 2 (a) and polymer 3 (b).

Table 3. Effect of the substituent on the recovery of Pd.



<sup>a</sup>Reaction conditions: bromobenzene (0.5 mmol), 4-methylphenylboronic acid (0.75 mmol, 1.5 equiv), Pd(OAc)<sub>2</sub> (1.5 mol% of Pd), polymer (monomer/Pd = 1/1), 1.5 M KOH<sub>aq</sub> (1 mL). <sup>b</sup>Isolated yield. <sup>c</sup>Determined by ICP-AES. <sup>d</sup>Determined by TEM.

(Figure 5). The quantitative recovery of Pd was achieved, and the recovered polystyrene-stabilized PdNPs was re-used two times without any loss of catalytic activity. Furthermore, it was confirmed by ICP-AES analysis that no leaching of the palladium into either the aqueous or organic solutions occurred.

### 3. Conclusions

In summary, *in situ*-generated PdNPs were recovered completely by linear polystyrene. The scope and applicability of this methodology for aqueous Suzuki coupling and aerobic oxidation reactions was investigated. The

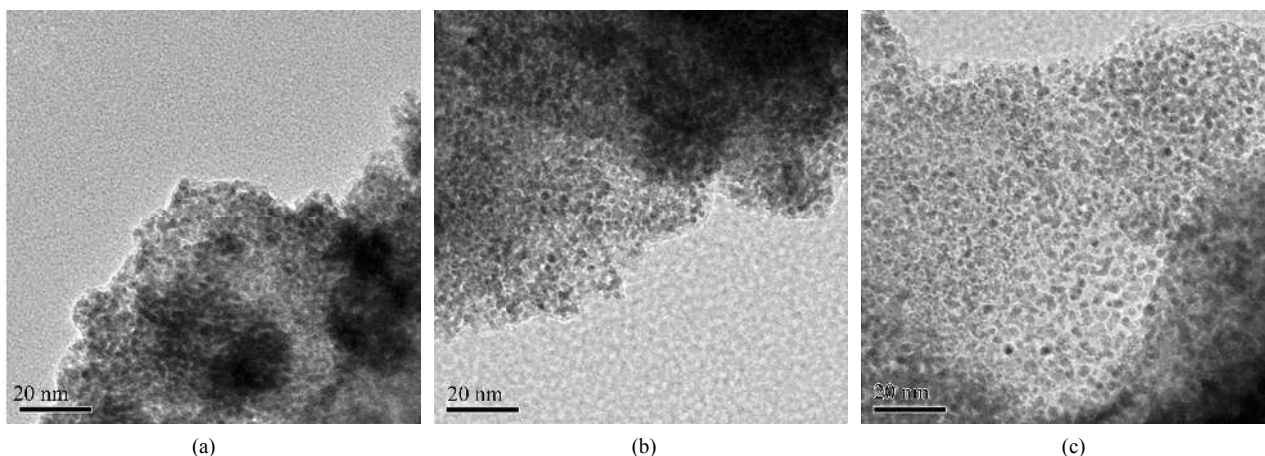
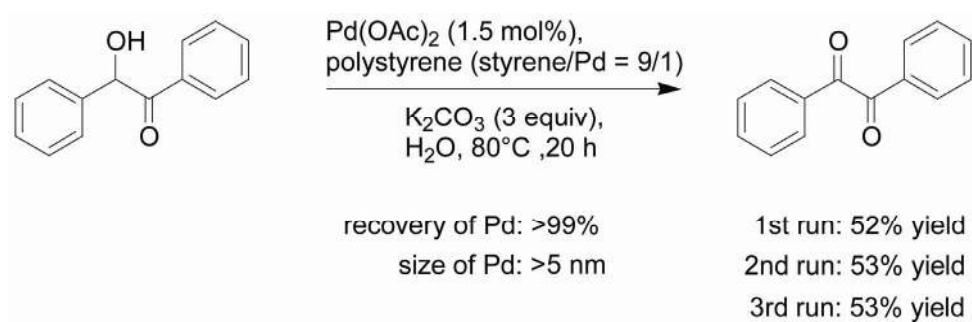


Figure 4. TEM images of recovered PdNPs by polymer 4 (a), polymer 5 (b), and polymer 6 (c).



Scheme 2. Recovery and reuse of *in situ*-generated PdNPs for aerobic alcohol oxidation.

recovered PdNPs were recycled without significant loss of activity.

## 4. Experimental

### 4.1. General Comments

$^1\text{H-NMR}$  spectra in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  were recorded with a 300 MHz NMR spectrometer (UNITY 300, Varian, Palo Alto, CA) using tetramethylsilane ( $\delta = 0$ ) as an internal standard. Gel permeation chromatographic (GPC) analysis in DMF was carried out with a HPLC-8020 instrument (Tosoh Co., Tokyo, Japan) (column: Tosoh TSKgel  $\alpha$ -3000 and  $\alpha$ -5000). The columns were calibrated with polystyrene of narrow molecular weight distribution standards. Lyophilization was carried out with a freeze dryer (FDU-830, Tokyo Rikakikai Co., Ltd., Tokyo, Japan). Powder X-ray diffractions were recorded on a Rigaku RINT 2500 diffractometer (Cu  $\text{K}\alpha$  radiation) equipped with a monochromator. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed using ICPS-8100 (Shimadzu Co., Kyoto, Japan). Pd nanoparticles were investigated by transmission electron microscopy (TEM) on a JEM 2100F transmission electron microscope (JEOL

Ltd., Tokyo, Japan). The samples were prepared by placing a drop of the solution on carbon coated copper grids and allowed to dry in air. Polystyrene of narrow molecular weight distribution standards was purchased from Tosoh Co., Ltd. (Tokyo, Japan).  $\text{Pd(OAc)}_2$  was obtained from Sigma-Aldrich Co. (Missouri, USA).

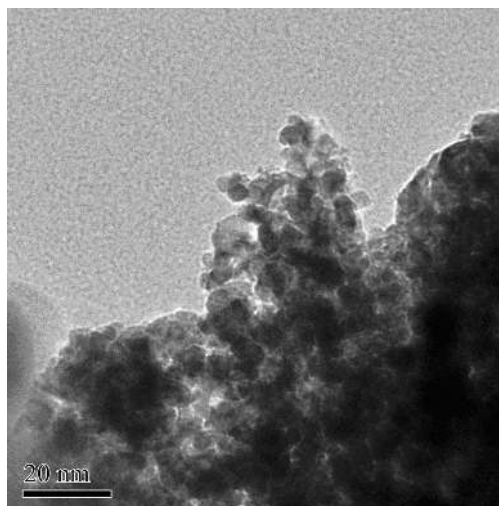


Figure 5. TEM image of a recovered PdNPs for aerobic alcohol oxidation.

## 4.2. Typical Procedures for Suzuki Coupling Reaction

To a screw-capped vial with a stirring bar were added bromobenzene (78 mg, 0.5 mmol), 4-methylphenylboronic acid (102 mg, 0.75 mmol), Pd(OAc)<sub>2</sub> (1.7 mg, 7.5 μmol), polystyrene (7.0 mg, 0.068 mmol of styrene unit), and 1.5 M aqueous KOH solution (1 mL). After stirring at 80°C for 1 h, the reaction mixture was cooled to room temperature. Subsequently, the aqueous phases were removed, and recovered catalyst was washed with water (5 × 1.5 mL) and diethyl ether (5 × 1.5 mL), which were then added to the aqueous phase. The aqueous phase was extracted five times with diethyl ether. The combined organic extracts were dried over MgSO<sub>4</sub>, concentrated under reduced pressure, and purified by flash column chromatography on silica gel. The resulting product was analyzed by <sup>1</sup>H-NMR. The recovered catalyst was dried *in vacuo* and reused. Furthermore, the amount of Pd metal in the recovered catalyst determined by ICP-AES analysis was 15.8 ppm.

## 4.3. Typical Procedures for Aerobic Alcohol Oxidation

To a screw-capped vial with a stirring bar were added benzoin (106 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (1.7 mg, 7.5 μmol), polystyrene (7.0 mg, 0.068 mmol of styrene unit), and 1.5 M aqueous K<sub>2</sub>CO<sub>3</sub> solution (1 mL). After stirring at 80°C for 20 h, the reaction mixture was cooled to room temperature. Subsequently, the aqueous phases were removed, and recovered catalyst was washed with water (5 × 1.5 mL) and diethyl ether (5 × 1.5 mL), which were then added to the aqueous phase. The aqueous phase was extracted five times with diethyl ether. The combined organic extracts were dried over MgSO<sub>4</sub>, concentrated under reduced pressure, and purified by flash column chromatography on silica gel. The resulting product was analyzed by <sup>1</sup>H-NMR. The recovered catalyst was dried *in vacuo* and reused. Furthermore, the amount of Pd metal in the recovered catalyst determined by ICP-AES analysis was 16.1 ppm.

## 4.4. Preparation of Poly(4-Diphenylphosphinostyrene-co-Styrene)

Into a two-necked reaction vessel were added 4-diphenylphosphinostyrene (0.29 g, 1.0 × 10<sup>-3</sup> mol), styrene (0.31 g, 3.0 × 10<sup>-3</sup> mol), AIBN (16 mg, 1.0 × 10<sup>-4</sup> mol), and THF (5 mL). After stirring at 70°C for 20 h under N<sub>2</sub> atmosphere, the solvent was removed *in vacuo* to give a crude product. Reprecipitation was carried out at least three times in a THF-MeOH system. The last precipitate

was dried under reduced pressure and lyophilized with a freeze dryer to give **2** (0.17 g, 29% yield) as a white powder. The number-average molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) determined by GPC analysis were ca. 6.2 × 10<sup>3</sup> and 1.5, respectively. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.61 - 7.10 (br, 14 H), 6.98 - 6.25 (br, 10 H), 2.15 - 1.05 (br, 9 H). <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 121 MHz): δ - 6.22.

## 4.5. Preparation of Poly(4-Vinylpyridine-co-Styrene)

Into a two-necked reaction vessel were added 4-vinylpyridine (0.11 g, 1.0 × 10<sup>-3</sup> mol), styrene (0.26 g, 2.5 × 10<sup>-3</sup> mol), AIBN (16 mg, 1.0 × 10<sup>-4</sup> mol), and DMF (5 mL). After stirring at 70°C for 20 h under N<sub>2</sub> atmosphere, the solvent was removed *in vacuo* to give a crude product. Reprecipitation was carried out at least three times in a DMF-Et<sub>2</sub>O system. The last precipitate was dried under reduced pressure and lyophilized with a freeze dryer to give **3** (0.11 g, 29% yield) as a white powder. The number-average molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) determined by GPC analysis were ca. 5.4 × 10<sup>3</sup> and 1.6, respectively. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 8.26 (br, 2 H), 7.11 (br, 11 H), 6.58 (br, 6 H), 2.18 - 0.83 (br, 12 H).

## 4.6. Preparation of Poly(4-Nitrostyrene)

Into a two-necked reaction vessel were added 4-nitrostyrene (1.2 g, 8.0 × 10<sup>-3</sup> mol), AIBN (33 mg, 2.0 × 10<sup>-4</sup> mol), and THF (5 mL). After stirring at 70°C for 24 h under N<sub>2</sub> atmosphere, the solvent was removed *in vacuo* to give a crude product. Reprecipitation was carried out at least three times in a THF-MeOH system. The last precipitate was dried under reduced pressure and lyophilized with a freeze dryer to give **4** (0.29 g, 24% yield) as a white powder. The number-average molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) determined by GPC analysis were ca. 5.0 × 10<sup>3</sup> and 1.7, respectively. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.20 - 7.58 (br, 2 H), 7.42 - 6.60 (br, 2 H), 2.15 - 1.05 (br, 3 H).

## 4.7. Preparation of Poly(4-Methoxystyrene)

Into a two-necked reaction vessel were added 4-methoxystyrene (0.54 g, 4.0 × 10<sup>-3</sup> mol), AIBN (16 mg, 1.0 × 10<sup>-4</sup> mol), and THF (5 mL). After stirring at 70°C for 20 h under N<sub>2</sub> atmosphere, the solvent was removed *in vacuo* to give a crude product. Reprecipitation was carried out at least three times in a THF-MeOH system. The last precipitate was dried under reduced pressure and lyophilized with a freeze dryer to give **5** (95 mg, 18%

yield) as a white powder. The number-average molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) determined by GPC analysis were ca.  $6.4 \times 10^3$  and 1.6, respectively.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.80 - 6.25 (br, 4 H), 3.74 (br, 3 H), 1.95 - 1.20 (br, 3 H).

#### 4.8. Preparation of Poly(4-Dimethylaminostyrene)

Into a two-necked reaction vessel were added 4-dimethylaminostyrene (0.88 g,  $6.0 \times 10^{-3}$  mol), AIBN (98 mg,  $6.0 \times 10^{-4}$  mol), and THF (4 mL). After stirring at 70°C for 20 h under  $\text{N}_2$  atmosphere, the solvent was removed *in vacuo* to give a crude product. Reprecipitation was carried out at least three times in a THF-MeOH system. The last precipitate was dried under reduced pressure and lyophilized with a freeze dryer to give **6** (0.28 g, 32% yield) as a white powder. The number-average molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) determined by GPC analysis were ca.  $5.4 \times 10^3$  and 1.6, respectively.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.95 - 6.22 (br, 4 H), 2.87 (br, 6 H), 2.15 - 1.05 (br, 3 H).

#### 5. Acknowledgements

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#### 6. References

- [1] P. A. Grieco, "Organic Synthesis in Water," Blackie Academic & Professional, London, 1998.
- [2] C. J. Li, "Organic Reactions in Aqueous Media with a Focus on Carbon-Carbon Bond Formations: A Decade Update," *Chemical Reviews*, Vol. 105, No. 8, 2005, pp. 3095-3165. [doi:10.1021/cr030009u](https://doi.org/10.1021/cr030009u)
- [3] M. Lamblin, L. Nassar-Hardy, J. C. Hierso, E. Fouquet and F. X. Felpin, "Recyclable Heterogeneous Palladium Catalysts in Pure Water: Sustainable Developments in Suzuki, Heck, Sonogashira and Tsuji-Trost Reactions," *Advanced Synthesis & Catalysis*, Vol. 352, No. 1, 2010, pp. 33-79. [doi:10.1002/adsc.200900765](https://doi.org/10.1002/adsc.200900765)
- [4] D. Badone, M. Baroni, R. Cardamone, A. Ielmini and U. Guzzi, "Highly Efficient Palladium-Catalyzed Boronic Acid Coupling Reactions in Water: Scope and Limitations," *The Journal of Organic Chemistry*, Vol. 62, No. 21, 1997, pp. 7170-7173. [doi:10.1021/jo970439i](https://doi.org/10.1021/jo970439i)
- [5] T. Jeffery, "Heck-Type Reactions in Water," *Tetrahedron Letters*, Vol. 35, No. 19, 1994, pp. 3051-3054. [doi:10.1016/S0040-4039\(00\)76825-0](https://doi.org/10.1016/S0040-4039(00)76825-0)
- [6] S. Bhattacharya, A. Srivastava and S. Sengupta, "Remarkably Facile Heck and Suzuki Reactions in Water using a Simple Cationic Surfactant and Ligand-Free Palladium Catalysts," *Tetrahedron Letters*, Vol. 46, No. 20, 2005, pp. 3557-3560. [doi:10.1016/j.tetlet.2005.03.118](https://doi.org/10.1016/j.tetlet.2005.03.118)
- [7] D. Saha, K. Chattopadhyay and B. C. Ranu, "Aerobic Ligand-Free Suzuki Coupling Catalyzed by *in Situ*-Generated Palladium Nanoparticles in Water," *Tetrahedron Letters*, Vol. 50, No. 9, 2009, pp. 1003-1006. [doi:10.1016/j.tetlet.2008.12.063](https://doi.org/10.1016/j.tetlet.2008.12.063)
- [8] L. Liu, Y. Zhang and Y. Wang, "Phosphine-Free Palladium Acetate Catalyzed Suzuki Reaction in Water," *The Journal of Organic Chemistry*, Vol. 70, No. 15, 2005, pp. 6122-6125. [doi:10.1021/jo050724z](https://doi.org/10.1021/jo050724z)
- [9] A. Ohtaka, T. Teratani, R. Fujii, K. Ikeshita, O. Shimomura and R. Nomura, "Facile Preparation of Linear Polystyrene-Stabilized Pd Nanoparticles in Water," *Chemical Communications*, No. 46, 2009, pp. 7188-7190. [doi:10.1039/b915039k](https://doi.org/10.1039/b915039k)
- [10] T. Teratani, A. Ohtaka, K. Kawashima, O. Shimomura and R. Nomura, "Copper-Free Sonogashira Coupling in Water with Linear Polystyrene-Stabilized PdO Nanoparticles," *Synlett*, No. 15, 2010, pp. 2271-2274. [doi:10.1055/s-0030-1258018](https://doi.org/10.1055/s-0030-1258018)
- [11] L. Wu, B. L. Li, Y. Y. Huang, H. F. Zhou, Y. M. He and Q. H. Fan, "Phosphine Dendrimer-Stabilized Palladium Nanoparticles, a Highly Active and Recyclable Catalyst for the Suzuki-Miyaura Reaction and Hydrogenation," *Organic Letters*, Vol. 8, No. 16, 2006, pp. 3605-3608. [doi:10.1021/ol0614424](https://doi.org/10.1021/ol0614424)
- [12] X. Jiang, G. Wei, X. Zhang, W. Zhang, P. Zheng, F. Wen and L. Shi, "A Strategy to Facilitate Reuse of Palladium Catalyst Stabilized by Block Copolymer Micells," *Journal of Molecular Catalysis A: Chemical*, Vol. 277, No. 1-2, 2007, pp. 102-106. [doi:10.1016/j.molcata.2007.07.021](https://doi.org/10.1016/j.molcata.2007.07.021)
- [13] F. Wen, W. Zhang, G. Wei, Y. Wang, J. Zhang, M. Zhang and L. Shi, "Synthesis of Nobel Metal Nanoparticles Embedded in the Shell Layer of Core-Shell Poly(styrene-co-4-vinylpyridine) Microspheres and Their Application in Catalysis," *Chemistry of Materials*, Vol. 20, No. 6, 2008, pp. 2144-2150. [doi:10.1021/cm703378c](https://doi.org/10.1021/cm703378c)
- [14] S. U. Son, Y. Jang, K. Y. Yoon, E. Kang and T. Hyeon, "Facile Synthesis of Various Phosphine-Stabilized Monodisperse Palladium Nanoparticles through the Understanding of Coordination Chemistry of the Nanoparticles," *Nano Letters*, Vol. 4, No. 6, 2004, pp. 1147-1151. [doi:10.1021/nl049519+](https://doi.org/10.1021/nl049519+)
- [15] S. Kobayashi and R. Akiyama, "Renaissance of Immobilized Catalysts. New Types of Polymer-Supported Catalyst, 'Microencapsulated Catalysts', Which Enable Environmentally Benign and Powerful High-Throughput Organic Synthesis," *Chemical Communications*, No. 4, 2003, pp. 449-460. [doi:10.1039/B207445A](https://doi.org/10.1039/B207445A)
- [16] Z. Bai, L. Yang, L. Li, J. Lv, K. Wang and J. Zhang, "A Facile Preparation of Hollow Palladium Nanosphere Catalysts for Direct Formic Acid Fuel Cell," *The Journal of Physical Chemistry C*, Vol. 113, No. 24, 2009, pp. 10568-10573. [doi:10.1021/jp902713k](https://doi.org/10.1021/jp902713k)