

Palladium Nanoparticles on Thermoresponsive Hydrogels and their Application as Recyclable Suzuki–Miyaura Coupling Reaction Catalysts in Water

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Abstract: Palladium nanoparticles were immobilized on PNIPAM:4-VP hydrogels. The resultant palladium catalysts showed high activities for Suzuki–Miyaura coupling reactions in water. The recyclability of the catalysts was improved by using 4-VP as a co-monomer in the hydrogels due to reduced Pd leaching during the reactions.

Keywords: palladium nanoparticles; PNIPAM:4-VP co-polymers; reusable catalysts; Suzuki–Miyaura reactions; water

The Suzuki reaction is one of the most powerful synthetic pathways for constructing the aryl–aryl bond. It involves a palladium-catalyzed coupling reaction between an aryl halide and an areneboronic acid. The synthesis of biaryl compounds *via* Suzuki coupling is very attractive because this reaction can tolerate the presence of water. In addition, the reaction works with a wide range of functional groups, and the non-toxic by-products are easily separated from the desired compound.^[1] The Suzuki reaction is usually carried out with a homogeneous Pd catalyst, phosphorus derivatives as ligands, and an inorganic base (i.e., carbonate, bicarbonate, and hydroxide) in aqueous organic solvents.^[1c,2] However, in order to use the Suzuki reaction in a wide range of industrial applications, a heterogeneous Pd catalyst must be developed. This is necessary because homogeneous Pd catalysts are not reusable, and they need toxic and expensive ligands to stabilize the catalytically active Pd(0) species. Moreover, complicated purification steps are often required to remove the residual Pd and ligand

after reactions are completed. To overcome these problems, various methods have been investigated for developing heterogeneous Pd catalysts, including the immobilization or stabilization of Pd nanoparticles on ionic liquids,^[3] functionalized polymers,^[4] graphene oxide and its derivatives,^[5] and inorganic substrates such as silica, zeolites, etc.^[6] However, the catalytic activity of heterogeneous catalysts is still not as efficient as those of homogeneous Pd catalysts. In addition to the development of recyclable catalysts, the reaction conditions for large-scale Suzuki applications need to be more environmentally benign and economically attractive. For example, a lower reaction temperature could be used, and water could be used instead of organic solvents.^[7]

Poly(*N*-isopropylacrylamide) (PNIPAM) is a well known temperature-responsive polymer that demonstrates phase separation (i.e., the coil-to-globule transition) from an aqueous solution at the lower critical solution temperature (LCST), which is typically about 32 °C.^[8] The swelling of PNIPAM hydrogels is mainly due to changes in the hydrogen bonding of the PNIPAM network with water molecules.^[9] At a temperature above LCST, some of the hydrogen bonds are dissociated, and the hydrophobic interactions among the hydrophobic groups in the PNIPAM network are dominant. This causes the water molecules trapped in the network to be released, making the hydrogel collapse. By changing the solution temperature, PNIPAM can selectively provide hydrophilic or hydrophobic nanoenvironments. Hydrophobic molecules can be dissolved into the brushes of PNIPAM in water if the temperature of the medium is above its LCST. Therefore, the Suzuki reaction with hydrophobic substrates can likely be carried out in water without any surfactants or organic solvents. The LCST of

PNIPAM can also be controlled by forming a co-polymer with a co-monomer.^[10] For example, the LCST of PNIPAM-*N*-(acryloyloxy)succinimide (NASI) co-polymer is at about 8°C.^[10] On the other hand, the LCST of PNIPAM-sulfonic acid-containing copolymer is above 100°C.^[10] Furthermore, PNIPAM can easily be recovered from aqueous solution above its LCST by simple filtration. Because of these versatile properties, PNIPAM-grafted Pd nanoparticles have been investigated as recyclable heterogeneous Pd catalysts in water and aqueous organic solvents.^[10–11] However, due to Pd leaching during reactions, the recyclability of these catalysts still requires improvement. Milder reaction conditions, including a low reaction temperature, are also desirable.

In this study, temperature-responsive poly(*N*-isopropylacrylamide-co-4-vinylpyridine) (PNIPAM-co-4-VP) co-polymers^[12] were employed as supports for catalytic Pd nanoparticles (instead of PNIPAM). Pyridine is a well known ligand that forms complexes with transition metal ions.^[7e,13] It is expected to provide a stronger binding site for Pd nanoparticles within the co-polymer and to decrease Pd leaching during the Pd-catalyzed organic reactions. Thus, the recyclability of Pd nanoparticles can be improved with the PNIPAM-co-4-VP copolymer. Due to the PNIPAM moiety, the Suzuki reaction can be performed in water and with easy work-up after reaction completion. Due to these advantages, Pd nanoparticles were synthesized and embedded in a series of the PNIPAM-co-4-VP co-polymers. The catalytic activity and recyclability of the co-polymers were also investigated for use in the Suzuki reactions of arylboronic acids and aryl bromides with a wide range of functional groups in water and under mild reaction conditions ($\approx 60^\circ\text{C}$). In the present study, PNIPAM-co-4-VP co-polymers with various molar ratios of NIPAM:4-VP (9:1, 8:2, 7:3, 6:4, and 5:5) were synthesized and named M1, M2, M3, M4, and M5, respectively [Figure 1, (a)]. Differential scanning calorime-

try (DSC) experiments were performed to measure the LCST of the synthesized PNIPAM-co-4-VP copolymers (M1–M5) [Figure 2, (a)]. DSC curves showed noticeable endothermic peaks in the temperature range of 31 to 48°C. M1 showed the coil-to-globule transition at about 31°C, which is very close to the previously reported LCST of PNIPAM.^[8] As the ratio of 4-VP in PNIPAM-co-4-VP co-polymers increased from 8:2 (PNIPAM:4-VP) to 5:5, the LCST gradually increased from 43 to 48°C. The observed shifts in LCST with 4-VP can be attributed to the increased number of hydrogen bonds between the PNIPAM networks and water molecules trapped in the network. This is due to the increased amount of 4-VP, which contains electron-rich nitrogen.^[10] Therefore, higher enthalpy is likely needed to break the hydrogen bonds. The DSC measurements allowed the determination of a temperature range for the Suzuki coupling with Pd-grafted co-polymers as catalysts.

The Pd nanoparticles grafted on the PNIPAM-co-4-VP co-polymers (M1–M5) were synthesized by reducing aqueous Pd²⁺ on the copolymers with NaBH₄ [Figure 1, (b)]. The formation of Pd nanoparticles was visually observed with the mixture's change in color to black, and it was confirmed by TEM and energy dispersive X-ray analysis (EDAX) measurements [Figure 2, (b)–(d) and Supporting Information]. Figure 2, (b) shows a TEM image of the Pd nanoparticles on M5 as a representative sample, which has irregular morphologies with a diameter of about 0.6 μm. The Pd nanoparticles on M1, M2, M3, M4, and M5 were named C1, C2, C3, C4, and C5, respectively. TEM images of the other Pd catalysts are not shown here (see Figure S2 in the Supporting Information). C5 shows spherical morphology with diameters of less than 8 nm and narrow particle size distributions of about 2 nm [Figure 2, (b)–(d) and Figure S3 in the Supporting Information]. Multiple lattice fringes were observed in the high-resolution TEM

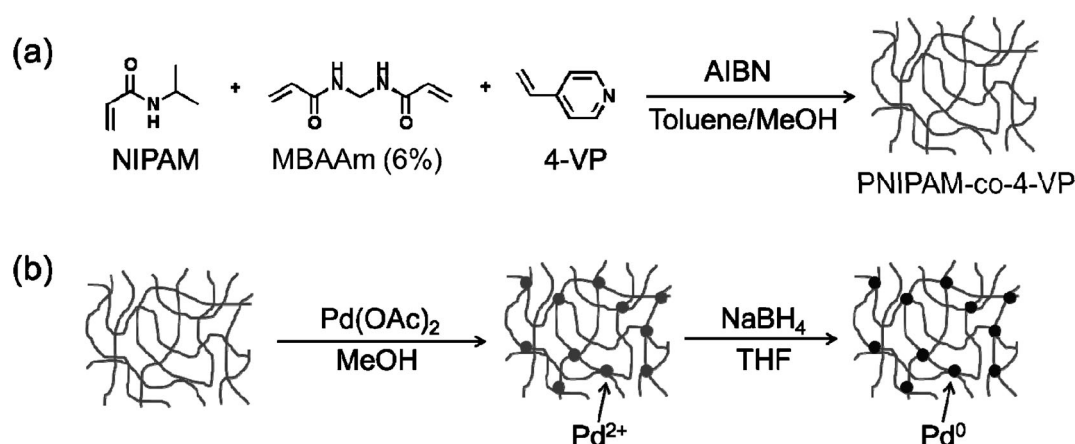


Figure 1. (a) Preparation of the PNIPAM-co-4-VP (M1–M5) co-polymers and (b) preparation of Pd nanoparticles on them.

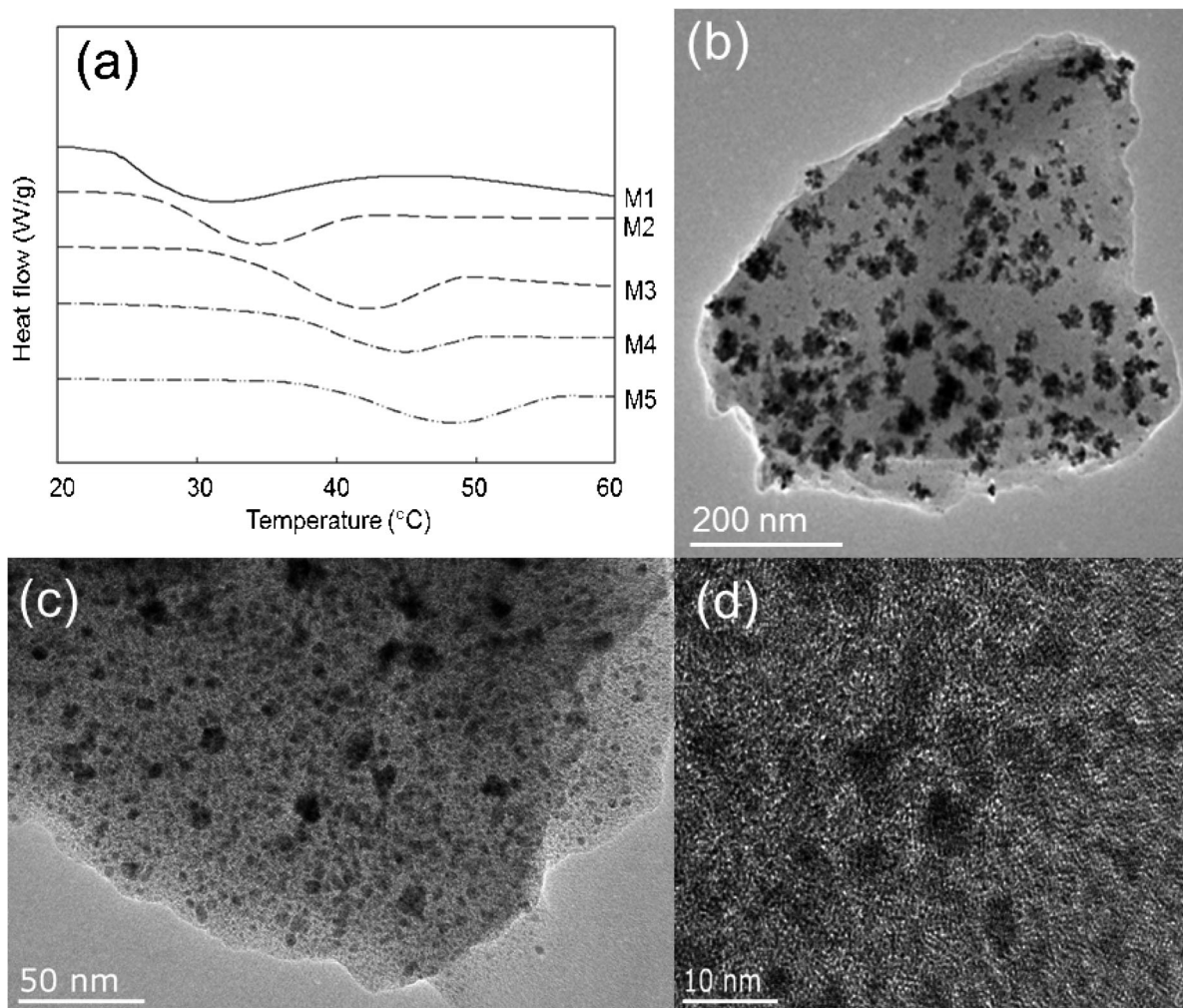


Figure 2. (a) Differential scanning calorimetry (DSC) curves for M1–M5 at pH 10 and (b)–(d) transmission electron microscopic (TEM) images of Pd nanoparticles grafted on the PNIPAM-co-4-VP copolymer [PNIPAM:4-VP = 5:5 (M5)].

image [Figure 2, (d)], confirming the crystalline structure of the Pd nanoparticles.

To estimate the catalytic activities of the Pd catalysts (C1–C5), coupling reactions between bromobenzene **1a** and 4-methylbenzeneboronic acid **2b** were carried out with 1 mmol% Pd catalysts and K_2CO_3 (3 equiv.) as a base at 60 °C in water (Table 1). The highest catalytic activity was observed with C5, which allowed quantitative conversion of the substrates within 30 min. The other catalysts afforded 65–89% yields of 4-methylbiphenyl **3e**. These results indicate that C5 is the most suitable catalyst for the Suzuki reaction in water. It is worthy of note that when we used commercially available 10% Pd/C (1 mmol% Pd, Aldrich) to compare the catalytic activity with that of C5, it showed only a 70% yield of **3e** under the same reaction conditions, which represents a lower catalytic activity than that of C5.

The optimal reaction temperature using C5 was also investigated by performing coupling reactions of

4-bromoacetophenone **1j** with benzenboronic acid **2a** as a function of temperature from room temperature

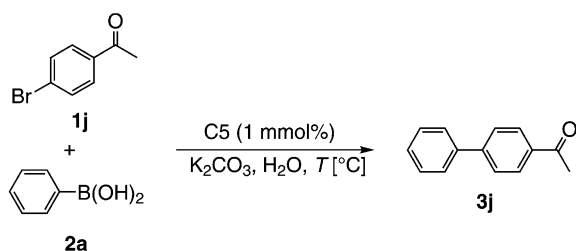
Table 1. Suzuki coupling reactions of bromobenzene **1a** and 4-methylbenzeneboronic acid **2b** with Pd nanoparticles on the PNIPAM-co-4-VP co-polymers (C1–C5).^[a]

<chem>c1ccccc1Br</chem> (1a) + <chem>Cc1ccc(B(O)O)cc1</chem> (2b)		$\xrightarrow[60\text{ }^\circ\text{C}]{1\text{ mmol\% Pd catalyst, } K_2CO_3, H_2O}$		<chem>Cc1ccc(cc1)-c2ccccc2</chem> (3e)	
Catalyst	9:1 (C1)	8:2 (C2)	7:3 (C3)	6:4 (C4)	5:5 (C5)
Yield [%] ^[b]	83	65	65	89	Quant.

^[a] Reaction conditions: bromobenzene (**1a**, 1 mmol), 4-methylbenzeneboronic acid (**2b**, 1.5 mmol, 1.5 equiv.), K_2CO_3 (3 mmol, 3 equiv.), H_2O (2 mL), 1 mmol% Pd catalyst, and a reaction time of 30 min.

^[b] Isolated yield (the purity of the isolated product was confirmed by 1H NMR).

Table 2. Suzuki coupling reactions of 4-bromoacetophenone **1j** and benzenboronic acid **2a** with C5 as a function of temperature.^[a]



Entry	Time [h]	Temp. [°C]	Yield [%] ^[b]
1	24	r.t.	NR ^[c]
2	1.3	50	93.8
3	0.6	60	97
4	0.6	80	94.4

^[a] Reaction conditions: 4-bromoacetophenone (**1j**, 1 mmol), benzenboronic acid (**2a**, 1.5 mmol, 1.5 equiv.), K₂CO₃ (3 mmol, 3 equiv.), H₂O (2 mL), and 1 mmol% Pd catalyst (C5).

^[b] Isolated yield (the purity of the isolated product was confirmed by ¹H NMR).

^[c] No biaryl was detected by ¹H NMR.

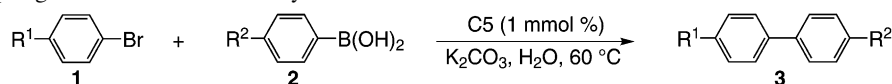
to 80 °C (Table 2). At room temperature, no conversion reaction was observed, even with a reaction time of 24 h. When the reaction temperature was increased to 50, 60, and 80 °C, much higher yields of 93.8, 97, and 94.4% were achieved within a shorter reaction time (<1.5 h). These experimental data demonstrate that the Suzuki reaction can be efficiently performed at 50 °C. These results are well matched with our DSC data, which showed the LCST of C5 at about 48 °C. As mentioned above, hydrophobic substrates can be solubilized into the brushes of the PNIPAM-co-4-VP co-polymer above the LCST in water. The excellent yields observed above 50 °C can be ascribed to the increased local concentration of hydrophobic substrates around Pd nanoparticles in the hydrophobic nanoenvironment of the co-polymer in water.^[11e] From these data, 60 °C was confirmed as the optimal reaction temperature for the Suzuki coupling reaction with C5 in water.

The scope of the Suzuki coupling reaction was thoroughly investigated under the established reaction conditions of 1 mmol% C5 and 60 °C in water (Table 3). High conversions (above 93%) were observed in the coupling reactions of benzenboronic acid **2a** with a wide range of aryl bromides **1** containing electron-donating groups (entries 1–5) and electron-withdrawing groups (entries 6–12). Due to the very low solubility of 1-bromo-4-nitrobenzene **1f** and 4-bromobenzonitrile **1g** in H₂O, the reactions were performed in a solvent mixture of H₂O and dioxane (v/v=1:1) (entries 6 and 7). The reactions showed

complete conversion in 30 min. The coupling reactions of bromobenzene **1a** with various areneboronic acids (entries 13–15 and 17) also showed excellent yields above 93%. However, the coupling reaction with 4-nitrobenzenboronic acid **2f** afforded a modest conversion of about 50%, even in a solvent mixture of H₂O and THF (v/v=1:1) and with a longer reaction time of 10 h (entry 16).

Finally, the recyclability of C5 was estimated by repeatedly carrying out Suzuki coupling reactions at 60 °C in water with two model reactions. The coupling reaction of 4-bromoacetophenone **1j** with benzenboronic acid **2a** was performed for the first five runs (Table 4) and then the reaction between bromobenzene **1a** and 4-methylbenzenboronic acid **2b** was performed for the next five runs (Table 5). As shown in Table 4, the catalyst showed excellent activity for the first five runs, resulting in high yields above 90–95% in 40 min. The high catalytic activity was preserved for the following five runs of the model reactions, resulting in 93–96% conversion (Table 5). After each run, the amount of Pd leaching from C5 was estimated by performing ICP (inductively coupled plasma) measurements on the supernatant solutions. The solutions were collected by filtering the catalyst from the reaction mixture after the reactions were complete. No significant Pd leaching (<0.5 ppm) was observed. In addition, there was no significant agglomeration of Pd nanoparticles on the TEM images prepared after the recycling experiments (Figure S4 in the Supporting Information). This suggests that the excellent recyclability is attributed to the 4-VP moiety, the comonomer introduced to PNIPAM to increase the binding strength of the co-polymer with Pd nanoparticles.

In conclusion, Pd nanoparticles were successfully immobilized on PNIPAM-co-4-VP co-polymers. The Pd catalysts were applied to Suzuki coupling reactions and demonstrated high catalytic activity. The reactions formed various biaryl compounds at a relatively low reaction temperature of 60 °C, even in water. The catalysts were successfully reused with constant catalytic activity in the repeated recycling studies. Through this research, we have developed a highly active heterogeneous Pd catalyst. This Pd catalyst will be industrially and environmentally valuable because of its mild reaction conditions, which include a low reaction temperature and water as a sole solvent. We believe that these Pd catalysts can be applied to a variety of Pd-catalyzed reactions such as Heck, Stille, Sonogashira, Hiyama, Negishi, and oxidation/reduction reactions.

Table 3. Suzuki coupling reactions of various aryl bromides **1** and benzenboronic acids **2** with C5 at 60 °C in water.^[a]

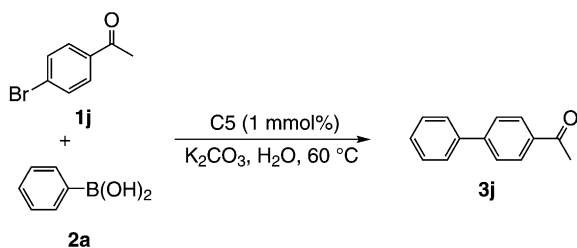
Entry	1 (R ¹)	2 (R ²)	Product 3	Time [h]	Yield [%] ^[b]
1	1a (H)	2a (H)	3a	1	95
2	1b (NH ₂)	2a	3b	4	95
3	1c (OH)	2a	3c	1.5	98
4	1d (OCH ₃)	2a	3d	2	94
5	1e (CH ₃)	2a	3e	5	95
6	1f (NO ₂)	2a	3f	0.5	quant. ^[c]
7	1g (CN)	2a	3g	0.5	quant. ^[c]
8	1h (CO ₂ CH ₃)	2a	3h	4	98
9	1i (COOH)	2a	3i	5	93
10	1j (COCH ₃)	2a	3j	1	95
11	1k (CHO)	2a	3k	5	quant.
12	1l (CF ₃)	2a	3l	3	quant.
13	1a	2b (CH ₃)	3e	0.5	quant.
14	1a	2c (OCH ₃)	3d	2	96
15	1a	2d (Cl)	3m	4	93
16	1a	2f (NO ₂)	3f	10	50 ^[d]
17	1a	2g (CO ₂ CH ₃)	3h	4	quant.

^[a] Reaction conditions: bromobenzene (**1**, 1 mmol), phenylboronic acid (**2**, 1.5 mmol, 1.5 equiv.), K₂CO₃ (3 mmol, 3 equiv.), H₂O (2 mL), and 1 mmol% Pd catalyst (C5).

^[b] Isolated yield (the purity of the isolated product was confirmed by ¹H NMR).

^[c] Solvent mixture: H₂O:dioxane = 1:1 by volume.

^[d] Solvent mixture: H₂O:THF = 1:1 by volume.

Table 4. Recycling experiments (runs 1–5) of C5 in Suzuki coupling reactions at 60 °C in water.^[a]

Entry	1st	2nd	3rd	4th	5th
Yield [%] ^[b]	95	94	97	94	90

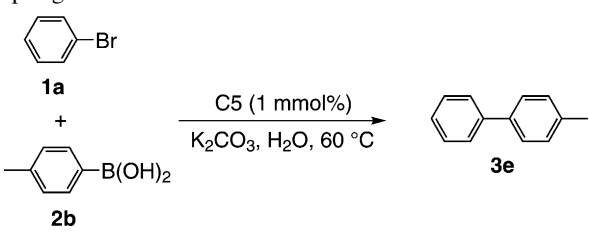
^[a] Reaction conditions: 4-bromoacetophenone (**1j**, 1 mmol), benzenboronic acid (**2a**, 1.5 mmol, 1.5 equiv.), K₂CO₃ (3 mmol, 3 equiv.), H₂O (2 mL), 1 mmol% Pd catalyst (C5), and a reaction time of 40 min.

^[b] Isolated yield (the purity of the isolated product was confirmed by ¹H NMR).

Experimental Section

Poly(*N*-isopropylacrylamide-co-4-vinylpyridine) Co-Polymers

Poly(NIPAM-co-4-VP) co-polymer hydrogels were prepared by free radical solution polymerization according to the standard procedure.^[12d] The molar ratio of NIPAM:4-VP varied from 9:1, 8:2, 7:3, 6:4, and 5:5, with 6 mol% MBAAm. In a typical run for the synthesis of a 6 mol% cross-linked 5:5 poly(NIPAM-co-4-VP) co-polymer hydrogel, 1.173 g of NIPAM (10.1 mmol, 47 mol%) dissolved in 2 mL of methanol, 0.2 g of MBAAm (1.28 mmol, 2 mol%) dissolved in 2 mL of methanol, and 1.06 g 4-VP (10.1 mmol, 47 mol%) dissolved in 16 mL of toluene were placed in a 100-mL flask. The polymerization was initiated by adding 2 mol% AIBN and then the reaction mixture was heated at 80 °C for 4 h. The white solid polymer was filtered off, washed with methanol and diethyl ether, and dried under vacuum at 50 °C for 24 h.

Table 5. Recycling experiments (runs 6–10) of C5 in Suzuki coupling reactions at 60 °C in water.^[a]


Entry	6th	7th	8th	9th	10th
Yield [%] ^[b]	96	95	93	95	96

^[a] Reaction conditions: bromobenzene (**1a**, 1 mmol), 4-methylphenylboronic acid (**2b**, 1.5 mmol, 1.5 equiv.), K₂CO₃ (3 mmol, 3 equiv.), H₂O (2 mL), 1 mmol% Pd catalyst (C5), and a reaction time of 30 min.

^[b] Isolated yield (the purity of the isolated product was confirmed by ¹H NMR).

Pd(0) Nanoparticles Grafted on the Co-Polymer

As-synthesized poly-NIPAM-co-4-VP co-polymer (100 mg) was dispersed in MeOH (20 mL) under mechanical shaking. Palladium acetate [Pd(OAc)₂] (10 mg, 0.0445 mmol) was then gradually added to the suspension, followed by sonication for 1 min to thoroughly dissolve the Pd source. The Pd mixture was shaken for 12 h. As the hydrogel reacted with Pd(OAc)₂, the hydrogel color changed to yellow. The mixture was filtered using a 0.20 μm Millipore nylon membrane filter and washed three times with 20 mL MeOH. The filtered Pd²⁺ adsorbed copolymer was then dried in air for 12 h. Black Pd(0) nanoparticles were generated by adding 10 mg (0.264 mmol) NaBH₄ as a reducing reagent into a suspension of the dried copolymers in THF (20 mL) under mechanical shaking for 12 h. 10 mL MeOH were added to remove the residual NaBH₄ and then the Pd(0)-grafted copolymer was separated by filtration. The filtered co-polymer was thoroughly washed with 20 mL MeOH and 20 mL THF and then dried in air for 12 h. A series of Pd-grafted copolymers (C1–C5) was prepared with M1–M5 by the same method. ICP measurements estimate the amount of Pd(0) nanoparticles in C1–C5 as 0.69, 0.95, 1.63, 0.94, and 0.65 mmol Pd/g, respectively.

General Procedure for the Suzuki Reaction

A 10-mL round-bottom flask was charged with 4-bromoacetophenone (**1j**, 1 mmol, 1 equiv.), benzeneboronic acid (**2a**, 1.5 mmol, 1.5 equiv.), K₂CO₃ (414 mg, 3 mmol, 3 equiv.), H₂O (2 mL), and Pd catalyst (1 mmol%). The content of flask was stirred at 60 °C in air. The reaction was monitored by thin layer chromatography (TLC). After the reaction was complete, the reaction mixture was cooled to room temperature and then filtered to recover the catalyst. It was then washed with 10 mL of H₂O and ethyl acetate (EtOAc). The organic phase was separated from the aqueous phase, which was extracted three times with 30 mL EtOAc. The organic phases were collected together, dried over MgSO₄, and filtered. The solvent was then evaporated under reduced pressure. The pure product was obtained *via* silica gel column

chromatography with an eluent of EtOAc and hexane. The resulting product was analyzed by ¹H NMR spectroscopy.

Recycling the Pd Catalyst

Two kinds of Suzuki reactions were performed. The first five runs were with bromoacetophenone **1j** and benzeneboronic acid **2a**, and the second five runs were with bromobenzene **1a** and 4-methylphenylboronic acid **2b**. The Suzuki reactions were carried out as described above. After the first reaction was complete, C5 was recovered by filtration and air-dried. The collected catalyst was reused in the next run of the coupling reaction under the same reaction conditions (e.g., concentration of reactants) as the first run. The filtrate (H₂O) was analyzed with ICP (inductively coupled plasma) measurements to estimate the amount of Pd leaching after each run.

Acknowledgements

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