

# Synthesis of efficient and reusable palladium catalyst supported on pH-responsive colloid and its application to Suzuki and Heck reactions in water

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## Abstract

An efficient and reusable pH-responsive colloid supported palladium catalyst was synthesized by loading 3-nm Pd nanoparticles into the pH-responsive colloid of core–shell microspheres of poly[styrene-*co*-2-(acetoacetoxy)ethyl methacrylate-*co*-methyl acrylic acid] (PS-*co*-PAEMA-*co*-PMAA). The colloidal scaffold of the core–shell microspheres, which contained a pH-responsive shell of PMAA segment and a coordinative core of PAEMA and PS segments, was synthesized by one-stage soap-free emulsion polymerization in water. The pH-responsive colloid supported palladium catalyst was dispersed in basic aqueous medium like a homogeneous catalyst, and also could be simply separated and recovered like a heterogeneous one just by adjusting pH of the aqueous medium. The pH-responsive colloid-supported palladium catalyst proved to be efficient and reusable for the Suzuki and Heck reactions performed in water.

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**Keywords:** Colloid; Heck reaction; Palladium catalyst; pH-responsive; Suzuki reaction

## 1. Introduction

From the standpoint of environmentally benign organic synthesis, the development of highly active and easily reusable immobilized catalysts and the use of water instead of organic compounds as solvent are of great interest to chemists [1–3]. Ideally, the catalytic synthesis is efficiently performed in water, and the catalyst can be easily separated from the reaction mixture by simple filtration. Cross-linked silica gels and polystyrene resins have been widely used as insoluble supports for the immobilization of catalysts [3–5]. To date, numerous polymer-supported catalysts have been reported, including the assembled titanium and palladium catalysts bounded to non-cross-linked amphiphilic polymers [6,7], an Rh-based catalyst immobilized in the polymeric matrix of polyvinyl alcohol [8], and an oxime carbapalladacycle catalyst anchored on a soluble polyethyleneglycol scaffold [9]. Abrol et al. [10] even successfully immobilized the lipase catalyst in polymeric mem-

brane. All of these accomplishments suggest that the polymer-supported catalyst is a promising alternative. However, compared with its homogeneous counterparts, the catalyst immobilized in insoluble polymeric scaffold often shows lower activity, due in part to the heterogeneous polymeric scaffold and in part to leaching of catalyst from the polymeric scaffold.

The Suzuki reaction (the Pd-catalyzed cross-coupling of aryl boronic acids with aryl halides) is recognized as the most promising and versatile method for construction of noble biaryls, which are widely used in the synthesis of fine chemicals, agrochemicals, and active pharmaceutical intermediates [11–15]. The Heck reaction is a well-established method for the coupling of aryl halides with olefins [16–18]. The general conditions for performing both the Suzuki and Heck reactions include a catalyst of palladium nanoparticles (usually generated in situ from the corresponding palladium salt [19–22]) and a base such as K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, or triethylamine. In this work, we used the pH-responsive colloid of core–shell microspheres containing a core-forming segment of poly[2-(acetoacetoxy)ethyl methacrylate] (PAEMA) and a shell-forming segment of poly(methyl acrylic acid)

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(PMAA) as a scaffold to immobilize the palladium catalyst, and then studied the Suzuki and Heck reactions via the resultant pH-responsive colloid-supported palladium catalyst. We chose the core-shell microspheres of poly[styrene-*co*-2-(acetoacetoxy)ethyl methacrylate-*co*-methyl acrylic acid] (PS-*co*-PAEMA-*co*-PMAA) as the scaffold for three reasons. First, because PAEMA is a typical coordination polymer containing tethered ligands, the present colloid is able to coordinate with the ions of Pd<sup>2+</sup>, and thus no additional ligand is needed [23–25]. Second, the pH-responsive colloid and the colloid-supported palladium catalyst can be dispersed in basic aqueous solution. This suggests that the present palladium catalyst has a potential to bridge the gap between the easy recoverable heterogeneous catalyst and the highly efficient homogeneous one. Third, the pH-responsive colloid-supported palladium catalyst can be easily separated from the reaction mixture and recovered by first acidifying and then filtrating the dispersion of the catalyst due to the pH-responsive PMAA segment. Furthermore, the PS segment with a relatively high glass transition temperature (~103 °C) is also introduced into the core of the core-shell microspheres to increase the thermal stability of the colloids, because the glass transition temperature of the core-forming segment of PAEMA is as low as 3 °C [24].

Compared with heterogeneous palladium catalysts immobilized in cross-linked silica gels or insoluble polystyrene resins, the present pH-responsive colloid-supported palladium catalyst has four merits. First, it has the obvious advantage of high degree of dispersion, and thus its high efficiency is expected. Second, it can be easily separated from the reaction mixture and recovered simply by adjusting pH of the aqueous medium. Third, it can work efficiently in water. Finally, its preparation is simple. The pH-responsive colloid of core-shell microspheres can be synthesized by one-stage, soap-free emulsion polymerization in water.

## 2. Experimental

### 2.1. Materials

Styrene (St, >98%), methylacrylic acid (MAA, >99%) and methyl acrylate (MA, >99%) were purchased from Tianjin Chemical Company and distilled under vacuum before being used. The monomer of 2-(acetoacetoxy)ethyl methacrylate (AEMA, >95%; Aldrich) and the reagents such as benzenboronic acid (>99%; Beijing Wisdom Chemicals Company), *p*-chloroacetophenone (>99%, Merck-Schuchardt), *p*-bromophenol (>99%, Tianjin Guangfu Fine Chemical Research Institute), *p*-bromoacetophenone (>99%, Alfa Aesar), iodobenzene (>98%, Alfa Aesar), *p*-bromobenzoic acid (>99%, Beijing Henye Fine Chemical Company), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99.5%, Tianjin Chemical Company), PdCl<sub>2</sub>·2H<sub>2</sub>O (>99.99%, Tianjin Chemical Company), NaBH<sub>4</sub> (>98.9%, Tianjin Chemical Company), *p*-bromoanisole (>99%, Tianjin Chemical Company) and *p*-chlorophenol (>99.5%, Tianjin Chemical Company) were used as received.

### 2.2. Synthesis of PS-*co*-PAEMA-*co*-PMAA core-shell microspheres

To a 500-mL flask were added 3.0 g of MAA, 3.6 g of styrene, and 5.5 g of AEMA (at a molar ratio of 4:4:3). Subsequently, 390 mL of double-distilled water was added. The mixture was vigorously stirred for 30 min at room temperature. Then 0.47 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added, and the mixture was degassed under nitrogen purge. Finally, polymerization was performed at 80 °C for 24 h under vigorously stirring. The resultant core-shell microspheres of PS-*co*-PAEMA-*co*-PMAA were first precipitated in 0.1 mol/L HCl aqueous solution, filtrated, washed with water, and finally dried under vacuum.

### 2.3. Synthesis of pH-responsive colloid-supported palladium catalyst (pH-responsive catalyst)

First, a given amount of the core-shell microspheres of PS-*co*-PAEMA-*co*-PMAA was dispersed in aqueous solution at pH 8.0 to form 1.50 mg/mL of pH-responsive colloidal dispersion. Subsequently, a given volume of 10.0 mmol/L PdCl<sub>2</sub> aqueous solution was added to keep the molar ratio of AEMA to Pd<sup>2+</sup> equal to 4:1. The mixture was kept overnight at room temperature, after which a 20-fold excess of 0.40 mol/L NaBH<sub>4</sub> aqueous solution was added under vigorous stirring. The mixture immediately turned a deep-brown color and was maintained at room temperature under vigorous stirring for 4 h. The resultant pH-responsive colloidal dispersion was dialyzed against water at room temperature for 4 days.

### 2.4. Typical procedures for Suzuki reaction

To a screw-capped vial with a side tube 2.0 mmol of aryl halide, 6.0 mmol of K<sub>2</sub>CO<sub>3</sub>, 3.0 mmol of benzenboronic acid (50% excess), and 5.0 mL of dispersion of the pH-responsive catalyst were added. The mixture was degassed under nitrogen purge for 10 min at room temperature, after which the vial was put in a preheated oil bath at a given temperature and magnetically stirred under nitrogen. After the reaction was completed, the mixture was cooled to room temperature instantly, and then acidified with 0.1 mol/L HCl aqueous solution. The pH-responsive catalyst precipitated and was separated by simple filtration. Subsequently, a 4-fold excess volume of CH<sub>2</sub>Cl<sub>2</sub> was added into the filtrate to extract organic compounds for 3 times. The organic phase was collected and washed with 10 mL of water 3 times. Subsequently, the organic phase was concentrated and the resultant product was dried under vacuum at 40 °C, weighted, and analyzed by <sup>1</sup>H NMR.

### 2.5. Typical procedures for Heck reaction

To a screw-capped vial with a side tube containing 2.0 mmol of aryl halide, 6.0 mmol of K<sub>2</sub>CO<sub>3</sub>, 3.0 mmol of methyl acrylate (50% excess), and 5.0 mL of dispersion of the pH-responsive catalyst were added. The mixture was degassed under nitrogen purge for 10 min at room temperature, after which the vial was

immersed in a preheated oil bath and magnetically stirred under nitrogen. After the reaction was completed, the mixture was cooled to room temperature instantly and then acidified with 0.1 mol/L HCl aqueous solution. Subsequently, a 4-fold excess volume of diethyl ether was added into the filtrate to extract the organic compounds. The collected organic phase was washed with water and then concentrated. Finally, the resultant product was dried under vacuum at 40 °C, weighted, and analyzed by  $^1\text{H}$  NMR.

### 2.6. Recovery of the palladium catalyst

Two kinds of catalyst recycling were performed. Following the first recycling method, the reaction mixture was first acidified with 0.1 mol/L HCl aqueous solution and then the precipitate of the pH-responsive catalyst was collected. The collected catalyst was reused in another run of Suzuki reaction of *p*-bromoacetophenone, with the proportional amounts of reactants and solvent being added to keep the same solvent-to-catalyst ratios and the same concentrations described above. Following the second method, the pH-responsive catalyst was not acidified and separated from the reaction mixture. The aqueous layer containing the catalyst was extracted with 4-fold excess volume of  $\text{CH}_2\text{Cl}_2$ , after which the substrates of *p*-bromoacetophenone (2.0 mmol), benzenboronic acid (3.0 mmol), and  $\text{K}_2\text{CO}_3$  (3.0 mmol) were directly charged into the screw-capped vial to perform the Suzuki reaction in another cycle. As explained previously, the organic extracts were concentrated, dried, and analyzed by  $^1\text{H}$  NMR.

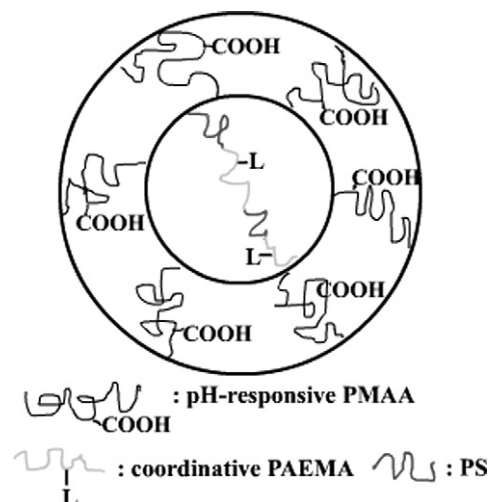
### 2.7. Characterization

Transmission electron microscopy (TEM) measurements were performed using a Philips T20ST electron microscope at an acceleration of 200 kV, whereby a small drop of the colloidal dispersion was deposited onto a piece of copper grid and then dried at room temperature under vacuum. The FTIR measurement was performed on a Bio-Rad FTS-6000 IR spectrometer. For FTIR measurement, the mixture of the purified powder of the core-shell microspheres and KBr was first pressed to form a pellet, after which the spectra were recorded. The powder X-ray diffraction (XRD) measurement was performed on a Rigaku D/max 2500 X-ray diffractometer. The XRD patterns were recorded by using  $\text{CuK}\alpha$  irradiation ( $\lambda = 1.54178 \text{ \AA}$ ). The  $^1\text{H}$  NMR measurement was carried out on a Varian UNITY PLUS-400 NMR spectrometer.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the pH-responsive colloid of core-shell microspheres

The core-shell microspheres of PS-*co*-PAEMA-*co*-PMAA were synthesized by one-stage soap-free emulsion polymerization in water. The synthesis of the PS-*co*-PAEMA-*co*-PMAA core-shell microspheres is very similar to those of the PS-*co*-PMAA core-shell microspheres as described elsewhere [26]



Scheme 1. Schematic structure of the core-shell microspheres of PS-*co*-PAEMA-*co*-PMAA.

and the total conversion of the three monomers is >96%. The monomer of MAA is hydrophilic, and the monomers of styrene and AEMA are hydrophobic in water; therefore, the resultant microspheres are expected to contain a shell rich in PMAA segment and a complex core rich in PS and PAEMA segments, as shown in Scheme 1. Fig. 1A shows the TEM image of the core-shell microspheres. The core-shell structure of the microspheres can be clearly distinguished. The average diameter, the core thickness, and the shell thickness of the core-shell microspheres are about 208, 70, and 34 nm, respectively. Fig. 1B shows the FTIR spectra of the core-shell microspheres of PS-*co*-PAEMA-*co*-PMAA. Along with the characteristic absorptions at 1600, 1493, 1452, 757, and 697  $\text{cm}^{-1}$  ascribed to the PS segment, a broad absorption at 1660–1780  $\text{cm}^{-1}$  ascribed to the two kinds of carbonyl groups in the PAEMA segment and the carboxyl group in the PMAA segment and an absorption at 1160  $\text{cm}^{-1}$  attributed to the vibration of the C–O in the PAEMA segment also can be observed, confirming the component of the PS-*co*-PAEMA-*co*-PMAA core-shell microspheres.

As demonstrated above, because the core-shell microspheres of PS-*co*-PAEMA-*co*-PMAA contain an acidic shell-forming segment of PMAA, the core-shell microspheres can be dispersed in aqueous solution at  $\text{pH} > 8$  to form a colloidal dispersion with a copolymer concentration as high as 30 mg/mL. At  $\text{pH} < 3$ , the colloid becomes unstable, and precipitation occurs. The precipitate can be redispersed when the pH value of the aqueous solution is further adjusted to >8.

### 3.2. Synthesis and characterization of the pH-responsive catalyst

The pH-responsive colloid of the PS-*co*-PAEMA-*co*-PMAA core-shell microspheres is used as a scaffold to load palladium nanoparticles because the PAEMA segment is a coordinative polymer able to dissolve metal compounds due to coordination [23–25]. In the present study, the ions of  $\text{Pd}^{2+}$  first coordinate with the chelating groups in the PAEMA segment and then are reduced by  $\text{NaBH}_4$  to form discrete Pd nanoparticles in situ.

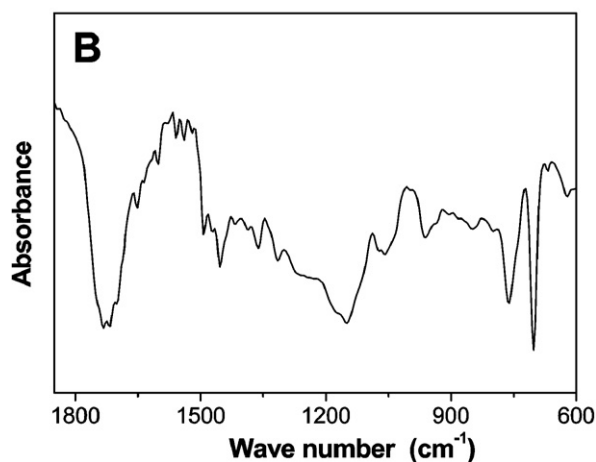
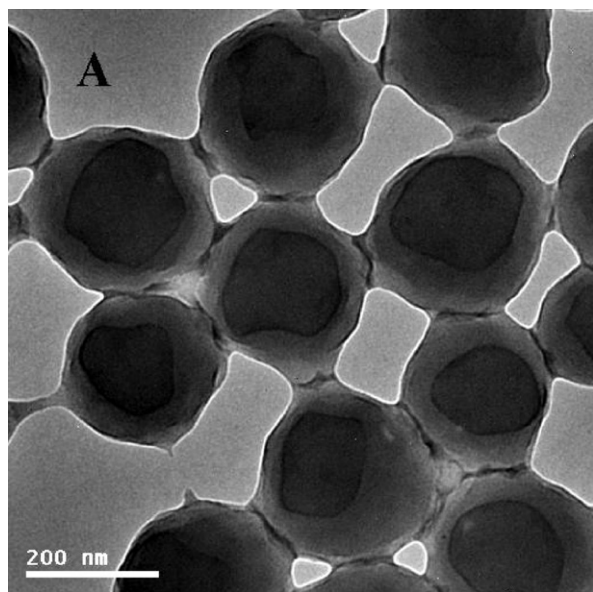


Fig. 1. The TEM image (A) and FTIR spectra (B) of the core-shell microspheres of PS-co-PAEMA-co-PMAA.

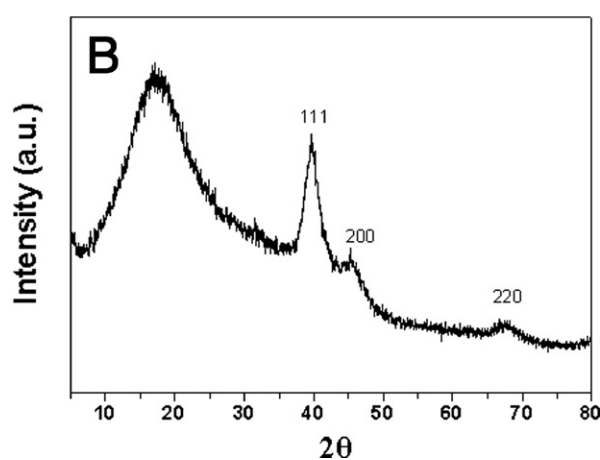
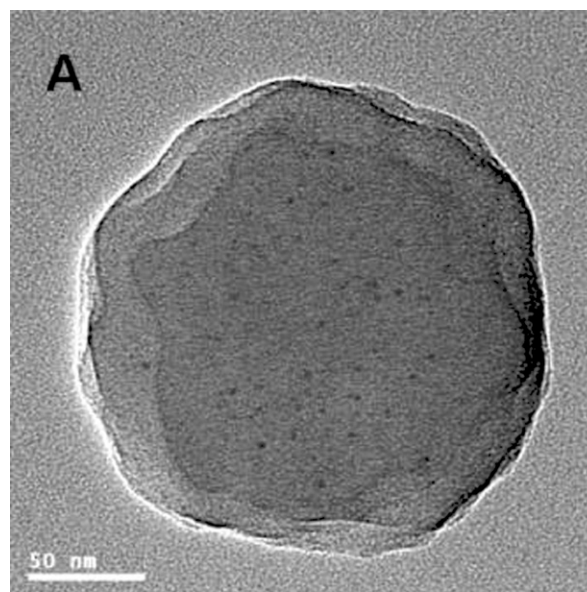


Fig. 2. The TEM image (A) and XRD pattern (B) of the pH-responsive colloid-supported palladium catalyst.

Fig. 2A shows a TEM image of the resultant Pd nanoparticles supported on the core-shell microspheres. Clearly, the size of the core-shell microspheres is as same as that shown in Fig. 1A, and the resultant Pd nanoparticles (about 3 nm in size) are immobilized uniformly in the core of the core-shell microspheres. The XRD pattern of the colloid-supported palladium catalyst, shown in Fig. 2B, displays three diffraction peaks at  $2\theta$  of  $39.6^\circ$ ,  $45.1^\circ$ , and  $67.5^\circ$ , corresponding to the diffraction of the (111), (200), and (220) lattice planes of the face-centered cubic crystalline structure of the Pd nanoparticles. Furthermore, the broad diffraction with  $2\theta$  ranging from 8 to  $35^\circ$  ascribed to the scaffold of the core-shell microspheres also can be observed clearly. In terms of Scherrer's equation [27], using the diffraction peak of (111) lattice plane of the Pd nanoparticles, the average size of the Pd nanoparticles is calculated as 2.3 nm, consistent with that observed on TEM.

Similar to the colloid of the PS-co-PAEMA-co-PMAA core-shell microspheres, the colloid-supported palladium catalyst also is pH-responsive (see supplementary information). At pH  $>8$ , the pH-responsive catalyst is dispersed in water; thus, the

pH-responsive catalyst has an obvious advantage of high dispersion and consequently is expected to be more active than those immobilized in insoluble cross-linked silica gels and polystyrene resins. When the pH value decreases to 3, precipitation occurs. The precipitate of the pH-responsive catalyst can be recovered when the pH value is further adjusted to  $>8$ . This suggests that the present catalyst can be easily separated by simple filtration and further recovered by adjusting the pH value of the aqueous medium.

### 3.3. Suzuki reaction in DMF-water

The Suzuki reaction is usually performed in the DMF-water solvent mixture, which aids solvation of the organic substrates and the inorganic base [11–15]. In this work, the Suzuki reaction was first performed in the DMF-water mixture (1:1 by volume) via the pH-responsive catalyst using  $K_2CO_3$  as a base. It was found that the pH-responsive catalyst can be dispersed in the reaction solution similar to a homogeneous one. To cover a wide range of substrates, the Suzuki coupling reac-

Table 1  
Suzuki coupling reaction of aryl halide and benzenboronic acid via the pH-responsive colloid supported palladium catalyst in the mixture of DMF/water and the sole solvent of water<sup>a</sup>

Entry	R-X	Solvent	R-X + Ph-B(OH) <sub>2</sub> $\xrightarrow[\text{K}_2\text{CO}_3, \text{ solvent}]{0.20 \text{ mol\% catalyst}}$ Ph-R		Product	Yield <sup>d</sup> (%)
			T <sup>c</sup> (°C)	Time (h)		
1		D/W <sup>b</sup>	80	6		98
2		D/W <sup>b</sup>	120	6		99 (100)
3		D/W <sup>b</sup>	120	6		99
4		D/W <sup>b</sup>	120	10		97
5		D/W <sup>b</sup>	120	8		98
6		D/W <sup>b</sup>	150	10		(3)
7		D/W <sup>b</sup>	150	10		51
8		H <sub>2</sub> O	80	6		83
			90	6		99
9		H <sub>2</sub> O	80	6		(100)
			50	1		63
10		H <sub>2</sub> O	90	10		57
11		H <sub>2</sub> O	90	1		99
			50	2		99
12		H <sub>2</sub> O	80	0.5		99
			50	1		93
13		H <sub>2</sub> O	90	10		3
14		H <sub>2</sub> O	90	10		(-) <sup>e</sup>

<sup>a</sup> Reaction conditions: aryl halide (2.0 mmol) and benzenboronic acid (3.0 mmol, 1.5 eq.), K<sub>2</sub>CO<sub>3</sub> (6.0 mmol, 3 eq.), 5.0 mL of colloidal dispersion containing 0.20 mol% palladium catalyst.

<sup>b</sup> D/W represented the mixture of DMF and H<sub>2</sub>O (1:1 by volume).

<sup>c</sup> Oil bath temperature.

<sup>d</sup> Isolated yield and the purity of isolated product was confirmed by <sup>1</sup>H NMR. The conversion of aryl halide shown in parentheses was determined <sup>1</sup>H NMR.

<sup>e</sup> No *p*-hydroxybiphenyl was detected by <sup>1</sup>H NMR.

tions of benzenboronic acid with iodobenzene and brominated and chlorinated aromatic compounds were tested; the catalysis results are summarized in Table 1. When iodobenzene was used as the substrate, the coupling reaction was almost completed (entry 1). The coupling reactions of the two electron-deficient (and thus reactive) aryl bromides of *p*-bromoacetophenone and *p*-bromobenzoic acid with benzenboronic acid were almost quantitative (entries 2 and 3). For the electron-rich acryl bromides of *p*-bromoanisole and *p*-bromophenol, the pH-responsive catalyst afforded a reasonable yield of 4-methoxybiphenyl (entry 4) and *p*-hydroxybiphenyl (entry 5). For the electron-rich aryl chloride of *p*-chlorophenol, the pH-responsive catalyst was inefficient, and the conversion of *p*-chlorophenol was as low as 3% (entry 6). The coupling was unsatisfactory even for the

electron-deficient acryl chloride of *p*-chloroacetophenone (entry 7). These results demonstrate that the present pH-responsive catalyst is suitable for the Suzuki coupling of iodobenzene or aryl bromides with benzenboronic acid in the DMF–water solvent mixture.

### 3.4. Suzuki reaction in water

Concerning that one of our aims is to synthesize an environmentally benign catalyst, we further studied the Suzuki coupling reactions of aryl halides with benzenboronic acid performed in water via the pH-responsive catalyst. We performed the Suzuki reactions at a lower temperature due to the limit of the lower boiling temperature of water. Similar to that in

the DMF–water solvent mixture, the pH-responsive catalyst was dispersed in the basic aqueous solution. The catalysis results are also summarized in Table 1. For the active substrate such as iodobenzene (entry 8) and the electron-deficient aryl bromide of *p*-bromoacetophenone (entry 9), catalysis in water was almost as efficient as that in the DMF–water solvent mixture, and the yields of the corresponding biaryls in water were satisfactory. In contrast, for the electron-rich aryl bromide of *p*-bromoanisole, the yield of 4-methoxybiphenyl was much lower (entry 10). Interestingly, the hydrophilic electron-rich aryl bromide of *p*-bromophenol was extremely active, and its coupling with benzenboronic acid in water was much more efficient than in the DMF–water solvent mixture even at much lower temperature (entry 11). This possibly suggests that the pH-responsive colloid acts beyond a scaffold of the palladium catalyst as well as a reactor or capsule, which affects partitioning of the reactants between the solvent and colloid and thus affects the chemical equilibrium in the Suzuki coupling reaction. To confirm this hypothesis, we tested two substrates of the hydrophilic *p*-bromobenzoic acid and the hydrophobic *p*-bromoacetophenone, both of which are electron-deficient aryl bromides with similar activity in the Suzuki coupling reactions with benzenboronic acid in the DMF–water mixture. Just as expected, the hydrophilic *p*-bromobenzoic acid was much more active than the hydrophobic *p*-bromoacetophenone whether the Suzuki reactions were performed in water as the sole solvent at high temperature (80 °C) or at low temperature (50 °C) (entries 9 and 12). For the hydrophilic aryl chloride of *p*-chlorophenol or the hydrophobic *p*-chloroacetophenone, the Suzuki coupling reaction with benzenboronic acid is very inefficient, and almost no biaryl is synthesized (entries 13 and 14). These results demonstrate that the present pH-responsive catalyst is a suitable catalyst for the substrate of iodobenzene or aryl bromides, especially for the hydrophilic aryl bromides when the Suzuki reaction is performed in water, and that the catalysis is almost as efficient as or more efficient than those in the DMF–water solvent mixture.

### 3.5. Recovery and reuse of the pH-responsive catalyst

The reuse of the pH-responsive catalyst was tested in the Suzuki coupling reaction of *p*-bromoacetophenone with benzenboronic acid in the sole solvent of water and in the mixture of DMF–water (1:1 by volume), respectively. As discussed above, the pH-responsive catalyst could be easily recovered first by adjusting the pH to <3, and then separating the resultant precipitate by simple filtration. As shown in Table 2, the conversion of *p*-bromoacetophenone was satisfactory in the first two cycles when the DMF–water mixture was used as the solvent, but dropped to 13% in the third cycle, possibly due to the relatively rapid breakage of the colloidal scaffold and leaching of the palladium catalyst in the DMF–water solvent mixture (because DMF is a good solvent for the PS, PAEMA, and PMAA segments). TEM measurements confirmed the hypothesis. It was found that the polymeric scaffold of the core–shell microspheres was broken and the Pd nanoparticles conglomerated (see supplementary information). We suppose that shell-cross-

Table 2

Recycling of pH-responsive colloid supported palladium catalyst in the Suzuki coupling of *p*-bromoacetophenone with benzenboronic acid in DMF/water and water, respectively<sup>a</sup>

$$\text{Br-Ph-COCH}_3 + \text{Ph-B(OH)}_2 \xrightarrow[\text{K}_2\text{CO}_3, \text{ solvent}]{0.20 \text{ mol\% catalyst}} \text{Ph-Ph-COCH}_3$$

Run	Conversion <sup>b</sup> (%)	Conversion <sup>c</sup> (%)
Fresh use	100	100
1st reuse	89	87 (99)
2nd reuse	13	76 (100)
3rd reuse	8	79 (97)

<sup>a</sup> Reaction conditions in the first cycle: *p*-bromoacetophenone (2.0 mmol) and benzenboronic acid (3.0 mmol, 1.5 eq.), K<sub>2</sub>CO<sub>3</sub> (6.0 mmol, 3 eq.), 5.0 mL of colloidal dispersion containing 0.20 mol% palladium catalyst.

<sup>b</sup> DMF/water (1:1 by volume) was used as solvent and the conversion to biphenyl was determined by <sup>1</sup>H NMR.

<sup>c</sup> Water was used as solvent and the conversion to biphenyl was determined by <sup>1</sup>H NMR. The numbers in parentheses represent the conversion of *p*-bromoacetophenone following the second catalyst recycling, where the pH-responsive catalyst was not separated and was directly used.


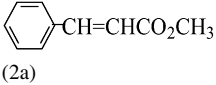
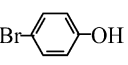
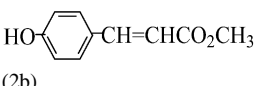
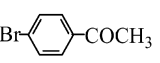
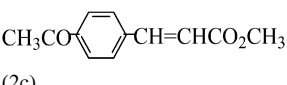
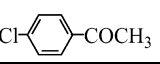
linking in the core–shell colloid could enhance the durability of the colloidal scaffold and thus increase the reusability of the pH-responsive catalyst in the mixture of DMF–water mixture; we will study this further in future work. The pH-responsive catalyst was more durable and had much higher conversion in the fourth cycle in water than in the DMF–water mixture. Furthermore, it should be pointed out that even through great care was taken, a little of the pH-responsive catalyst was lost during filtration of the catalyst precipitate. Thus the decreased conversion in water can be ascribed mainly to the loss of catalyst during filtration. To further study the reuse of the pH-responsive catalyst, we performed another catalyst recycling procedure similar to the method adopted by SanMartin and co-workers [28]; that is, after extracting the organic products with CH<sub>2</sub>Cl<sub>2</sub>, we used the resulting aqueous layer containing the palladium catalyst without further treatment in successive runs, just addition of the substrates and base. Clearly, this catalyst recycling eliminated the loss of Pd catalyst during filtration. We repeated the Suzuki reaction in water up to 4 times with no obvious loss of catalytic activity, as demonstrated by yields >97%. These results suggest that the leaching of the pH-responsive catalyst in water can be ignored.

### 3.6. Heck reaction in water

We further studied the activity of the pH-responsive catalyst in the Heck coupling of aryl halides with methyl acrylate in water. The catalysis results are listed in Table 3. For the highly reactive iodobenzene, the yield of 2a reached 76% after 6 h at 80 °C, and increasing temperature or time led to even higher yields (entry 1). For the hydrophilic electron-rich aryl bromide of *p*-bromophenol, a satisfactory yield of 2b was achieved (entry 2). For the hydrophobic electron-deficient *p*-bromoacetophenone and *p*-chloroacetophenone (entries 3 and 4), the yields of 2c were as low as 16% and 1%, respectively. As demonstrated in the Suzuki coupling of aryl halides and benzenboronic acid in water, the hydrophilic *p*-bromophenol was extremely active; however, the hydrophilic

Table 3  
Heck coupling reaction of aryl halide with methyl acrylate in water via the pH-responsive colloid supported palladium catalyst<sup>a</sup>

$$\text{R-X} + \text{CH}_2=\text{CHCO}_2\text{CH}_3 \xrightarrow[\text{K}_2\text{CO}_3, \text{H}_2\text{O}]{0.20 \text{ mol\% catalyst}} \text{RCH}=\text{CHCO}_2\text{CH}_3$$

Entry	R-X	T (°C)	Time (h)	Product	Yield <sup>b</sup> (%)
		80	6		76
1		90	12	 (2a)	89
		90	16		93
2		90	24	 (2b)	62
3		90	16	 (2c)	16
4		90	24	(2c)	1

<sup>a</sup> Reaction conditions: aryl halide (2.0 mmol) and methyl acrylate (3.0 mmol, 1.5 eq.), potassium carbonate (4.0 mmol, 3 eq.), 5.0 mL of colloidal dispersion in water containing 0.20 mol% palladium catalyst.

<sup>b</sup> Isolated yield and the purity of the product was confirmed by <sup>1</sup>H NMR.

*p*-bromophenol was not as active as iodobenzene in the Heck coupling with methyl acrylate. This may be due to the great difference in hydrophilicity between hydrophilic *p*-bromophenol and hydrophobic methyl acrylate, which weakens the acceleration of the hydrophilic aryl bromide.

#### 4. Conclusion

In conclusion, pH-responsive core-shell microspheres of PS-co-PAEMA-co-PMAA, in which the pH-responsive PMAA segment forms the shell and the PS and the coordinative PAEMA segments form the core, were synthesized by one-stage, soap-free emulsion polymerization in water. The pH-responsive core-shell microspheres were used as scaffolds to load 3-nm palladium nanoparticles synthesized in situ to form a pH-responsive colloid-supported palladium catalyst. In this work, the pH-responsive catalyst was dispersed in basic aqueous medium like a homogeneous catalyst; it also can be simply separated and recovered like a heterogeneous catalyst by simply adjusting the pH of the aqueous medium. The pH-responsive catalyst was demonstrated to be a good alternative for the Suzuki and Heck reactions in view of two advantages: (i) It is dispersed in the reaction mixture, and the reactions proceed efficiently in both water and the DMF-water solvent mixture, and (ii) the pH-responsive catalyst can be easily separated from the reaction mixture and readily recovered.

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#### Supplementary material

The online version of this article contains additional supplementary material.

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