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# Palladium–Poly(3-aminoquinoline) Hollow-Sphere **Composite: Application in Sonogashira Coupling Reactions**

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We report on the use of palladium acetate for the synthesis of a palladium-based polymer composite material as a catalyst for Sonogashira cross-coupling reactions for aryl and heteroaryl of iodides and bromides.

## Introduction

In situ polymerization and composite formation (IPCF) types of reactions  $^{\left[ 1-5\right] }$  for the synthesis of metal–polymer composite material have potential advantages in the field of 'synthetic material science' because these reactions produce both the polymer and the nanoparticles simultaneously and thus facilitates an intimate contact between the particles and the polymer through functionalization. Such a composite material with a higher degree of nanolevel interaction could be expected to demonstrate improved properties. The incorporation of metal nanoparticles into functional polymers provides enhanced catalytic performance for both the 'host' and the 'guest'.<sup>[6]</sup> Polymer-encapsulated palladium nanoparticles show a remarkable catalytic efficiency for the gas phase hydrogenation reaction. Polymer-palladium composite materials synthesized by using the IPCF approach have been reported to demonstrate excellent catalytic activity for both Heck and Suzuki types of carboncarbon coupling reactions.<sup>[7,8]</sup>

Palladium-based catalysts, particularly palladium nanoparticles, have drawn enormous attention because of their versatile role in organic synthesis.<sup>[9,10]</sup> The use of palladium nanoparticles in catalysis is not only industrially important<sup>[11,12]</sup> but also scientifically interesting in terms of the sensitive relationship between catalytic activity, nanoparticle size and shape, and the nature of the surrounding media.<sup>[13]</sup>

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Since the discovery of the Sonogashira reaction, several modifications have been reported, such as the variation of ligands, palladium sources, solvents and bases, to improve the coupling reactions. In the original protocol for the Sonogashira reaction, Cu<sup>+</sup> was recommended as a co-catalyst to facilitate the coupling reaction efficiently. However, it can also induce a Glaser-type oxidative homocoupling<sup>[23]</sup> of the terminal acetylene as a byproduct. To avoid the formation of this undesired byproduct, several Cu-free methods of the palladium-catalyzed Sonogashira coupling have been developed.<sup>[24-28]</sup>

We report here on the synthesis of a palladium-polymer supramolecular system by using the IPCF approach. We paid special attention to characterize the polymer product by using optical techniques. The subsequent spectral data confirmed the formation of the polymer, which is also supported by the microscopic characterization. The supramolecular material was used as a catalyst for the Sonogashira coupling reaction producing a high turnover frequency (TOF) value under Cu-free and ligand-free conditions.

## **Results and Discussion**

The SEM image in Figure 1 a reveals that the product was composed of microspheres. A higher-magnification SEM image in Figure 1b shows the spheres demonstrating a wide range of sizes. The image also reveals that the surface of the spheres is not smooth. The TEM image in Figure 2a show highly populated 2 D structure of the spheres. A few broken spheres can be seen in Figure 2b (marked by arrows), which indicate the low mechanical stability of the polymer spheres. The higher-mag-

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Figure 1. a) SEM image of poly(3-aminoquinoline) microspheres. b) Higher-magnification SEM image of spheres with various sizes. Scale bars = 10  $\mu m$  (a) and 5  $\mu m$  (b).



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**Figure 3.** Raman spectrum of the product in the range of 1700–1100 cm<sup>-1</sup> indicates the formation of the polymeric product of 3-aminoquinoline with both the quinoid and the benzenoid ring structure.



**Figure 2.** a) TEM image of high-density poly(3-aminoquinoline) microspheres. b) TEM image of a few broken polymer hollow spheres (marked by arrow). c, d) Higher-magnification TEM images of the spheres with the dark outer shell and the light core, which indicate the hollow spherical structure of the polymer. The images also reveal the variation in the shell wall thickness and sphere diameter. Scale bars = 2  $\mu$ m (a), 1  $\mu$ m (b), 200 nm (c), and 100 nm (d).

nification TEM images in Figure 2 c and d provide information regarding the internal structure of the microspheres. Both images show a dark outer shell and a light core of the circles, which indicate the hollow spherical nature of the polymer. Notably, the nanoparticles are absent.

The Raman spectrum of the material within the range 1100–1650 cm<sup>-1</sup> is shown in Figure 3. The spectrum is well characterized by the prominent bands above  $1000 \text{ cm}^{-1}$  (*in-plane* modes). In the range 1300–1400 cm<sup>-1</sup>, two bands appearing at

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The UV/Vis spectrum of the product material shows two prominent absorption peaks at 320 and 600 nm (Figure 4). The



**Figure 4.** The UV/Vis spectrum of the product shows two prominent absorption bands at 320 and 600 nm, which indicates the  $\pi$ - $\pi$ \* transition of the benzenoid rings and the benzenoid to quinoid excitonic transition, respectively. A shoulderlike feature is seen at approximately 450 nm (indicated by a circle), which is due to a polaron–bipolaron transition in the product material.

absorption peak at 320 nm is due to the  $\pi$ - $\pi$ \* transition of the benzenoid rings. The absorption peak at 600 nm is due to the transition from a localized benzenoid highest occupied molecular orbital to a quinoid lowest unoccupied molecular orbital,<sup>[32]</sup> that is, a benzenoid to quinoid excitonic transition.<sup>[33]</sup> The position of the excitonic peak can shift towards a higher-wavelength region because it is sensitive to the nature of the ions present,<sup>[34]</sup> to the solvent<sup>[35]</sup> and to the chemical struc-

ture.<sup>[36]</sup> A shoulderlike feature can be seen at approximately 450 nm (indicated by a circle), which could be due to the presence of a polaron–bipolaron transition in the product material. The Raman spectrum and the UV/Vis spectrum indicate the formation of the polymeric product of aminoquinoline.

During the addition of palladium acetate to 3-aminoquinoline, a radical cation is formed, which is accompanied by the release of an electron. This step is the initiation process of the polymerization reaction. Palladium acetate is an oxidizing agent and can initiate a polymerization process for the monomers of aniline or aniline derivatives,<sup>[1,37]</sup> and a similar kind of such a mechanism is followed in the present reaction. Spectroscopic analysis confirmed that the product has only a head-totail arrangement, not a head-to-head arrangement. The headto-head coupling occurs only under neutral or basic pH conditions. In contrast, 3-aminoquinoline oxidation products obtained in an acidic medium (presence of acetate ions) have predominantly a head-to-tail arrangement.<sup>[2]</sup>

During polymerization, each step involves the release of an electron and that electron is then used to reduce the  $Pd^{2+}$  ion. In general, the released electron reduces  $Pd^{2+}$  to  $Pd^{0}$ , which ultimately forms the palladium nanoparticles<sup>[1,2,38]</sup>; however, in our case we found evidence for the formation of  $Pd^+$  rather than the  $Pd^{0}$  state. The most sensible explanation for this is that the  $Pd^{2+}$  ionic state first forms  $Pd^+$  species, which then coordinates with the lone pair of the nitrogen of quinoline and forms a N–Pd<sup>+</sup> bond. The nitrogen center of aminoquinoline features a basic lone pair of electrons, and this lone pair is not part of the aromatic ring, chemistry similar to that of pyridine. Here, poly(3-aminoquinoline) (PAQ) plays the role of a macroligand that can coordinate with  $Pd^+$ . X-ray photoelectron spectroscopy (XPS) analysis has confirmed the formation of the  $Pd^+$ -like species (Figure 5). The TEM images showed no evidence



Figure 5. XPS spectrum of the palladium–poly(3-aminoquinoline) composite material.

for the formation of palladium nanoparticles. Therefore, to explain our data, the partial reduction of Pd<sup>2+</sup> acetate to Pd<sup>+</sup> species becomes an attractive proposal. This would lead to similar, though not necessarily identical, Pd<sup>+</sup> carbonyl carboxyl-ate complex,<sup>[39]</sup> which can be envisaged as a model for such Pd<sup>+</sup> intermediates.

To identify the chemical state of palladium in the product, XPS measurements were done. The peak corresponding to the Pd 3d<sub>5/2</sub> state resulting from the spin–orbital splitting is posi-

tioned at 335.7 eV, which indicates the presence of  $Pd^{0,[40]}$ , whereas the peak at approximately 337.75 eV can be assigned to the  $Pd^{2+}$  state.<sup>[41]</sup>

The experimentally obtained characteristic peaks corresponding to Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  states from the spin-orbital splitting are shown in Figure 5. Herein, we used only the binding energy value of the Pd  $3d_{5/2}$  line to determine the oxidation state of palladium. The Pd–PAQ sample shows a broad spectrum within the range 334.5–339.0 eV (Figure 5). After deconvolution, two separate peaks appeared at 336.47 and 337.37 eV (Figure 6, inset). As mentioned earlier, the peak at



**Figure 6.** Comparative kinetic study of the Sonogashira reaction involving a) 4-iodonitrobenzene ( $\bullet$ ) and b) 4-iodoniline ( $\blacksquare$ ) with phenyl acetylene catalyzed by the palladium–poly(3-aminoquinoline) hybrid catalyst (0.03 mol% of palladium) at 80 °C.

337.37 eV is due to the presence of unreacted  $Pd^{2+}$  whereas the new peak that appeared at 336.47 eV is due to the presence of  $Pd^+$  in the sample.<sup>[41,42]</sup> We found that not all  $Pd^{2+}$  was converted to  $Pd^+$  and unreacted  $Pd^{2+}$  species could coordinate with chain 'N' of the polymer.<sup>[43]</sup>

XPS analysis indicates that 1.64 wt% of palladium was present on the surface of the polymer matrix. TEM analysis failed to reveal any evidence of the formation of metallic palladium in the sample.

#### Study of catalytic property

The catalytic property of the palladium–polymer complex for a carbon–carbon bond formation reaction was the subject of interest in our investigation. Of the various carbon–carbon bond formation protocols, Sonogashira cross-coupling is one of the important reactions from a standpoint of its versatile applications for the preparation of arylalkynes or conjugated enynes and it is crucial in the synthesis of numerous biologically active compounds.<sup>[44]</sup>

The original protocol of the Sonogashira reaction, a dimetallic-mediated process, which is typically performed in the presence of catalytic amounts of a  $Pd^{2+}$  complex with  $Cu^+$  in an amine solvent, has been repeatedly modified and improved over time to overcome several significant limitations. The most important improvement concerned the elimination of  $Cu^+$ ,

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which is used as a co-catalyst, because it can induce homocoupling reactions of terminal alkynes (Glaser-type reactions).<sup>[22]</sup> A continuation of our work towards the synthesis and catalytic study of a palladium–polymer composite for Heck and Suzuki reactions<sup>[7,8,45,46]</sup> prompted us to study the Sonogashira reaction in a Cu-free situation. By using palladium supported on a PAQ catalyst, we have performed the Sonogashira coupling reaction under Cu-free conditions with excellent yields.



A solvent-base optimization study was performed initially for the coupling of iodobenzene with phenyl acetylene catalyzed by Pd-PAQ in the presence of toluene and propanol as solvents and Et<sub>3</sub>N, C<sub>5</sub>H<sub>10</sub>NH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> as bases. We found that amine bases (triethylamine and piperi-

dine) were effective for the reaction but inorganic bases ( $K_2CO_3$ ,  $Na_2CO_3$  and  $K_3PO_4$ ) were slow for this system, and toluene produced better results than propanol (Table 1).

We have investigated the coupling of aryl halides with phenyl acetylene in the presence of the Pd-PAQ catalyst (Table 2). Notably, the values within the parentheses are for aryl bromides whereas the values outside the parentheses are for aryl iodides. The high catalytic activity of Pd-PAQ for both the deactivated and activated aryl halides was observed with the formation of the corresponding diphenylethyne compounds with excellent yields. The electron-deficient aryl halide was generally more active than the electron-rich one.[47,48] Aryl halide with electron-withdrawing groups (Table 2, entries 1 and 2) showed higher reactivity than those possessing electron-donating groups (Table 2, entries 3-6). The TOF was as high as 2190  $h^{-1}$  for the coupling of 4-nitroiodobenzene with phenyl acetylene (entry 1) and 0.03 mol% of palladium. A slight decrease in the TOF value to  $2119 h^{-1}$ was recorded when a comparatively weak electronwithdrawing group (-COOH) was attached at the para position of iodobenzene (entry 2) under the same catalytic conditions. The presence of electrondonating groups, such as -CH<sub>3</sub>, -OCH<sub>3</sub>, -OH and -NH<sub>2</sub>, in the iodobenzene ring also lowered the TOF values to 1738, 1547, 1380 and 1214  $h^{-1}$  with a yield of 73, 65, 58 and 51%, respectively (entries 3-6, row a), under the same catalytic conditions. Comparable yield and TOF values were observed for both iodobenzene and bromobenzene on coupling with phenyl acetylene. For the coupling reactions of 4-nitro and 4-carboxy bromobenzene with phenyl acetylene catalyzed by 0.03 mol% of palladium, the yield of the products was 90 and 84% with the TOF value of 2142 and 2000  $h^{-1}$ , respectively (entries 1 and 2). A decrease in both the yield and TOF values was recorded when electron-donating groups, such as -CH<sub>3</sub>, -OCH<sub>3</sub>, -OH and -NH<sub>2</sub>, were attached to the bromobenzene ring (entries 3-6, row a, values within parentheses). The TOF values were found to be 1714, 1451, 1380 and 1190  $h^{-1}$  with a yield of 72, 61, 58 and 50%, respectively, under the same catalytic conditions. An increase in the catalytic concentration (0.05 mol% palladium) improved the yield percentage, whereas TOF values decreased in all the cases (Table 2, entries 4-6, row b). From the above study, we found a high catalytic activity of Pd-PAQ for both the deactivated and activated aryl iodide and bromides with excellent yields when reacted with phenyl acetylene. The activity of aryl halides decreased in the order of I > Br > CI, and the electron-deficient aryl halide was generally more active than the electron-rich one.[47,48] The coupling of 4-nitrochlorobenzene with phenyl acetylene catalyzed by 0.05 mol% of palladium gave a yield of 30% with TOF 428  $h^{-1}$  from the coupled product at 80 °C for 10 h. With the high palladium concentration (0.10 mol% of palladium), a higher yield (50%) was achieved with a TOF value of 357  $h^{-1}$ ; however, with an increase in temperature (100 °C), the TOF



[a] Reaction conditions: aryl benzene (1.0 mmol), phenyl acetylene (1.5 mmol), triethylamine (1.5 mmol), toluene (5 mL). Both iodobenzene and bromobenzene were used for the coupling reaction with phenyl acetylene. The values within the parentheses are for bromobenzene derivatives. Row a: The values were obtained with a catalytic concentration of 0.03 mol% of palladium. Row b: The values were obtained with a catalytic concentration of 0.05 mol% of palladium; [b] TOF = turnover frequency.

value increased to 464  $h^{-1}$  and yield to 65% within the same time period.

The coupling reaction of phenyl acetylene with the electrondeficient 4-nitroiodobenzene (Table 2, entry 1) and electronrich 4-iodo aniline (Table 2, entry 6, row a) was chosen for the investigation of the kinetics in the presence of the Pd-PAQ catalyst. To achieve maximum yields of the coupling product, a relatively longer time span (10 h) was chosen for a comparative study of the above reactions. Both the reactions were performed at 80 °C in the presence of 0.03 mol% of palladium. From the kinetic study (Figure 6), aryl iodide with an electronwithdrawing group (-NO<sub>2</sub>) showed faster conversion than for aryl iodide with an electron-donating group (-NH<sub>2</sub>). At the beginning of the coupling reaction, the conversion of both 4-nitroiodobenzene and 4-iodoaniline was slow and the rates of the reactions were comparable; however, with time, the reaction between phenyl acetylene and 4-nitroiodobenzene was faster and an 80% of the conversion was achieved within 6 h whereas only 40% of the conversion was achieved for 4-iodoaniline. After that time, a fatigue nature was observed for both the reactions; this is probably due to the deposition of a solid product on the palladium particles, which hinders the access of the reactants to the catalyst surface.

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopic signatures confirm the formation of cross-coupled products. The presence of the methoxy (-OCH<sub>3</sub>) group in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra at 3.8 and at 55.26 ppm clearly indicates that the formation of a crosscoupled product give a homo-coupled product of phenyl acetylene, at which these peaks should have been absent. These data were found to be similar to earlier reported data.<sup>[49,50]</sup>. Furthermore, the formation of the Glaser-type product should give bisphenyl acetylene, and in the NMR spectra the nitro  $(-NO_2)$ ,<sup>[51a]</sup> methyl  $(-CH_3)$ <sup>[51b]</sup> or methoxy  $(-OCH_3)$ <sup>[51c]</sup> substituents should be absent; however, in our cases we obtained only the Sonogashira cross-coupling products, which was confirmed by the NMR spectra of the compounds. In contrast, a Glaser-type product is bisphenyl acetylene and thus the peaks in the <sup>13</sup>C NMR for acetylene 'C' appear at approximately 74 and 81 ppm, which was not found in our case.<sup>[50]</sup>

Although considerable effort has been made to develop the active catalysts for the Sonogashira coupling reaction, most of them have involved the simple aryl halide system. In addition to aromatic systems, we have examined the behavior of the Pd–PAQ catalyst for the Sonogashira coupling reaction with heterocyclic compounds. The study of the Sonogashira coupling reactions using heterocycle-containing substrates has been less popular, and thus the references are less common. Such methods involved a palladium catalyst in the presence of phosphine ligands. A Cu-free Sonogashira coupling of heterocycles with the palladium catalyst along with a phosphine ligand has been reported.<sup>[52,53]</sup> Herein, we have investigated the coupling of heterocycle-containing substrates with phenyl acetylene in the absence of both Cu<sup>+</sup> and a phosphine ligand using the Pd–PAQ catalyst.

As a model reaction, the coupling between 3-bromopyridine and phenyl acetylene was chosen for a solvent-base optimization study. Toluene and 2-propanol were used as solvents and tBuOK, tBuONa, MeONa, Et<sub>3</sub>N, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> as bases with the Pd–PAQ catalyst for the above reaction. We found amine (triethylamine) was effective as a base and 2propanol produced better results as a solvent for the coupling reactions with heterocyclic compounds (Table 3). The results of the coupling reactions of heterocycle-containing substrates with phenyl acetylene are summarized in Table 4. The TOF value was 888 h<sup>-1</sup> for the coupling of 3-bromopyridine and







[a] Reaction conditions: heterocyclic compounds (1.0 mmol), phenyl acetylene (1.5 mmol), triethylamine (1.5 mmol), 2-propanol (5 mL). Both iodo and bromo heterocyclic compounds were used for the coupling reaction with phenyl acetylene in the presence of 0.10 mol% of palladium (entries 1–6). An increased catalyst concentration (0.175 mol% of palladium) improved the yields for both iodo- (73%) and bromo- (69%) quinolone-based coupled product, and the TOF value has been decreased for both the cases (entries 5 and 6, values with asterisk); [b] TOF=turnover frequency.

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phenyl acetylene (entry 4) with 0.10 mol % of palladium as the catalyst in the presence of triethylamine as a base and 2-propanol as a solvent. A slightly improved value of TOF (908 h<sup>-1</sup>) was achieved with the coupling of 3-iodopyridine and phenyl acetylene (entry 3) under the similar catalytic conditions. The reaction between 2-iodothiophene and phenyl acetylene (entry 1) produced a coupling product with a yield of 88% and a TOF value of 898 h<sup>-1</sup>. The expected trend has also been observed in the case of 2-bromothiophene (entry 2). A relatively low yield of 52% (TOF = 531  $h^{-1}$ ) and 50% (TOF = 510  $h^{-1}$ ) was achieved, respectively, with the coupling of 3-iodo- and bromoquinoline with phenyl acetylene (entries 5 and 6, value without asterisk) in the presence of 0.10 mol% of palladium. To improve the yield of the quinolone-based coupled product, we increased the catalyst concentration. A substantial improvement was achieved in terms of the yields for both iodo- (73%) and bromo- (69%) guinolone-based coupled products (entries 5 and 6, with asterisk) at 120 °C; however, the TOF value decreased for both with the increase in the palladium catalyst concentration to 0.175 mol%. Importantly, there was no increase in their yield with the increased temperature.

In addition to the coupling between aryl and heterocyclic iodo and bromo systems with phenylacetylene, we have studied the coupling behavior of heterocyclic acetylene, 2-ethynylpyridine, with aryl iodide and bromide systems. We again found that triethylamine and 2-propanol were effective, respectively, as a base and as a solvent for the coupling reactions.

The results from the coupling of iodo- and bromoaryls with 2-ethynylpyridine are shown in Table 5. The high catalytic activ-



ity for both the deactivated and activated aryl iodide and bromides was observed with the formation of the corresponding coupling compounds in excellent yields. Aryl iodides and bromides with electron-withdrawing groups (entries 1 and 2) demonstrate higher reactivity compared to those possessing electron-donating groups (entries 3-6). The yield and the TOF values within the parentheses are for bromo derivatives. The reaction of *p*-iodonitrobenzene and *p*-bromonitrobenzene with 2-ethynylpyridine produced the coupling product with a yield of 88 and 84% and the TOF value of 1197 and 1142  $h^{-1}$ , respectively (entry 1). The coupling of 2-ethynylpyridine with aryl halide possessing the activating group showed a decrease in TOF values (entries 3-5); however, in the presence of the  $-NH_2$ group attached to both iodo- or bromo-aryl compounds, the yield and TOF values decreased significantly (entry 6), which is due to the fact that the amine functionality in the 4-bromoaniline (or 4-iodoaniline) could coordinate to the matrix of the catalyst.

We have also studied the Sonogashira coupling reaction between heterocyclic acetylene and heterocyclic halide systems in the presence of triethylamine and 2-propanol. The results from the coupling reaction of iodo- and bromo-substituted heterocyclic compounds with 2-ethynylpyridine are summarized in Table 6. A similar amount of the coupled product was



achieved for thiophene- and pyridine-based heterocyclic compounds (entries 1 and 2). The values within the parentheses are for bromo derivatives. The TOF value of 524 and 509  $h^{-1}$ was achieved, respectively, for the coupling product of 2-iodoand 2-bromothiophene with 2-ethynylpyridine in the presence of 0.175 mol% of palladium at 120 °C for 12 h. Slightly higher TOF values of 529 and 517  $h^{-1}$  were achieved, respectively, for the coupling product of 2-iodo- and bromo-pyridine with 2ethynylpyridine under the same catalytic concentration and temperature conditions, whereas a relatively low TOF values of

frequency.

[b] TOF = turnover frequency.

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310 and 298  $h^{-1}$  were achieved, respectively, for the coupled product of 3-iodo- and bromoquinoline with 2-ethynylpyridine.

The original recommendation for the Sonogashira coupling reaction involved a phosphine-based palladium catalyst, a cocatalyst Cu<sup>+</sup>, and an amine base. A Cu-free version of the Sonogashira reaction has been developed to avoid the formation of homocoupling products as mentioned earlier. Herein, we avoid the use of expensive phosphine ligand and Cu<sup>+</sup>. For the Sonogashira coupling reactions, Pd<sup>0</sup> is the active catalyst species that can be of colloidal nature and stabilized by the ligands or polymer present in the system. As mentioned earlier, the XPS analysis did not show any evidence of Pd<sup>0</sup> species in the composite material, which was confirmed by TEM analysis. In the Pd-PAQ composite material, two species of palladium (Pd<sup>+</sup> and Pd<sup>2+</sup>) ions were present in the sample, as confirmed by using XPS analysis. In addition to the acetylene compounds, the amine bases may act as reducing agents and enable the reduction of  $Pd^{2+}$  to  $Pd^{0}$ .<sup>[54-56]</sup> Thus, it is expected that  $Pd^{+}$ could also be reduced to Pd<sup>0</sup> under the same reaction conditions. The proposed mechanism of the Sonogashira coupling reaction is illustrated in Scheme 1. The active palladium cata-



Scheme 1.

Proposed mechanism of the Sonogashira coupling reaction.

lyst reacts with the aryl or heteroaryl halide to produce the aryl or heteroaryl–palladium halide complex  $[R_1Pd^{II}X]$  (**A**), a process of oxidative addition; the complex then couples with alkyne to form an intermediate (**B**), which finally forms the coupling product C through the reductive elimination of Pd<sup>0</sup>.

The recyclability of the Pd-PAQ composite material as a catalyst was also investigated for the coupling of 2-iodothiophene with 2-ethynylpyridine in the presence of 0.175 mol% of palladium. After the first cycle, the product was extracted with ethyl acetate and the residual catalyst was used twice under the same reaction conditions. The results indicated that the used material was also active as a catalyst without a significant loss of catalytic performance. At the end of the third cycle, a yield of 71% was achieved and the TEM images of the used catalyst showed palladium nanoparticles with a wide size distribution. The decrease in the yield was mainly due to the loss of catalyst during the washing process. In every cycle, the fresh reaction mixture had a lower amount of palladium in the catalyst, which thus affects the yield; however, it may not have affected the TOF value, which is difficult to calculate at that stage of the process because the amount of the loss of palladium during the recovery process was unknown. We also did comparative TEM analysis of the catalyst during recyclability tests of the catalyst. We collected the sample for TEM analysis at the early stage of the reaction and found that the nanoparticles were 5–7 nm in size (Figure 7 a), whereas at the end of the third cycle, Ostwald ripening of the particles resulted in a less



**Figure 7.** TEM image of the palladium nanoparticles (5–7 nm in size) in a sample that was collected a) at an early stage of the reaction and b) at the end of the third cycle, which shows that Ostwald ripening resulted in a less dense distribution of larger palladium particles. Scale bars = 20 nm (a) and 0.5  $\mu$ m (b).

dense distribution of palladium particles, which were up to 120 nm in size (Figure 7 b). The enlargement of the palladium particles could be another reason for the deactivation of the catalyst after the end of the third cycle of the reaction. Importantly, the inductively coupled plasma mass spectrometry analysis did not support any kind of leaching of palladium during the recovery process of the catalyst.

#### Conclusions

A new kind of metal ion-incorporated polymer composite material has been reported here. This palladium ion-based polymeric material has potential application in carbon-carbon coupling reactions. The composite material served as an efficient and versatile catalyst for Sonogashira coupling reactions for both aryl and heteroaryl systems under a phosphine-free condition and in the absence of Cu<sup>+</sup>, which is environmentally and economically beneficial. The composite catalyst was found to be stable and could be kept for several years without notable deactivation because the catalytically active species are coordinated and encapsulated by the polymer. We believe that this polymer-based nanocomposite material is a promising candidate for other kinds of carbon-carbon coupling reactions. The combination of easy synthesis route, wide range of application and a long expiry period could make the hybrid material attractive for industrial applications.

## **Experimental Section**

TEM was performed at an accelerated voltage of 197 kV by use of a Philips CM200 transmission electron microscope equipped with a LaB6 source. An ultrathin window energy-dispersive X-ray spectrometer and a Gatan imaging filter attached to the transmission electron microscope were used to determine the chemical composition of the samples.

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For UV/Vis spectra analysis, a small portion of the solid sample was dissolved in methanol and scanned within the range of 300–700 nm with a Varian Cary 1E digital spectrophotometer. The Raman spectra were recorded on a Jobin–Yvon T64000 Raman spectrometer using the green (514.5 nm) line of an argon ion laser as the excitation source. The XPS spectra were collected in an ultra-high-vacuum chamber attached to a Physical Electronics PHI 560 ESCA/SAM system.

#### In situ synthesis of the Pd-PAQ composite

Palladium acetate  $(2.0 \times 10^{-3} \text{ M}, 10 \text{ mL})$  was added dropwise to the aminoquinoline–toluene system. A precipitate appeared slowly at the bottom of the flask. The material was then allowed to settle for an additional 15 min. The whole process was performed at RT ( $\approx 25$  °C). Then, the colloidal precipitation was taken from the bottom of the flask and pipetted onto carbon-coated, Cu TEM grids for SEM and TEM analyses. A small portion of the product was used for Raman and UV/Vis analyses. The rest of the solution was filtered, and the solid mass was dried under vacuum. The solid sample was used as a catalyst for the Sonogashira coupling reaction.

#### General method for the Sonogashira coupling reaction

For a general reaction, aryl halide (1.0 mmol), terminal alkyne (1.5 mmol), base (1.5 mmol) and solvent (5.0 mL) were added to a small round-bottomed flask. The catalyst powder was added to the reactant mixture in the required amount. The mixture was heated to reflux in an oil bath. At the end of the reaction, the reaction mixture was cooled and then diluted with ethyl acetate. The reaction mixture was washed with water and brine, and the combined extract was dried over MgSO<sub>4</sub>. After the evaporation of the solvents, the residue was purified by using flash chromatography.

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**Keywords:** C–C bond  $\cdot$  coupling  $\cdot$  palladium  $\cdot$  polymerization  $\cdot$  Sonogashira reaction

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- [51] a) (4-Nitrophenyl) phenylacetylene: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =8.17-8.19 (d, J=8.8 Hz, 2H), 7.62–7.64 (d, J=8.8 Hz, 2H), 7.53–7.55 (m, 2H), 7.36–7.37 ppm (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =146.97, 132.21, 131.8, 130.21, 129.23, 128.49, 123.57, 122.09, 94.67, 87.53 ppm;

b) Phenyl-*p*-tolylacetylene: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.52 (m, 2 H), 7.42–7.44 (d, *J* = 7.6 Hz, 2 H), 7.32 (m, 3 H), 7.14–7.14 (d, *J* = 6 Hz, 2 H), 2.36 ppm (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.35, 131.54, 131.49, 129.09, 128.29, 128.04, 123.51, 120.22, 89.56, 88.72, 21.47 ppm; c) (4-Methoxyphenyl) phenylacetylene: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45–7.51 (m, 4 H), 7.31–7.32 (m, 3 H), 6.86–6.88 (d, *J* = 8.8 Hz), 3.81 ppm (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.62, 133.03, 131.43, 128.28, 127.90, 123.60, 115.39, 113.99, 89.37, 88.06, 55.26 ppm.

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