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Template-less synthesis of polymer hollow spheres: an efficient catalyst for Suzuki coupling reaction

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We report here a method for the preparation of polymer hollow spheres in which 3-aminoquinoline (3-AQ) and palladium acetate were used as precursors. During the reaction 3-AQ was oxidized and formed poly(3-AQ). IR and Raman spectra provided information on the chemical structure of the polymer. The oxidation state of palladium was confirmed by X-ray photoelectron spectroscopic analysis. Transmission and scanning electron microscopy were used to determine the size and morphology of the polymer. The palladium–poly(3-AQ) supramolecular system was used as an effective catalyst for the Suzuki coupling reaction of aryl halides in the absence of a phosphine ligand. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: polymer hollow sphere; poly(3-aminoquinoline); Suzuki coupling reaction; IPCF; phenyl boronic acid

Introduction

Conjugated polymers with nano- and micro-structures, such as tubes,^[1] belts^[2] and fibers,^[3] have received growing interest because of their unique physical properties and potential applications in polymeric conducting molecular wires,^[4] chemical sensors or actuators^[5] and gas separation membranes.^[6] In the family of conjugated polymers, polyaniline and related structures are fascinating because of their environmental stability, controllable electrical conductivity, interesting redox properties and ease of synthesis in various sizes and shapes.^[7–13] Conjugated polymer can be prepared either by chemical^[14] or electrochemical^[15] polymerization technique. In situ polymerization and composite formation (IPCF) types of reactions^[16-21] for the synthesis of</sup> 'metal-polymer composite material' have potential advantages in the area of 'synthetic material science' owing to both the polymer and the nanoparticles being produced simultaneously, which facilitates an intimate contact between the particles and the polymer through functionalization.^[22] IPCF is a kind of template-less synthesis route where the nanoparticles are mainly catalyze the direction and orientation of the growth of the polymer chain.

We have reported^[16] on a gold–polyaniline composite material using a phase transfer catalyst, in which polyaniline spheres of several hundred nanometers in diameter were decorated with gold nanoparticles (10–50 nm). An *in situ* protocol has been developed by our group for the synthesis of a copper–poly(o-toluidine) composite material using cupric sulfate as an oxidizing agent.^[12] The copper nanoparticles produced had an average size of 5 nm and were highly dispersed within the polymer matrix. A single step, *in situ* chemical synthetic route for the preparation of a copper– poly(3,5-dimethylaniline) composite material has also been reported in which 7–10 nm diameter copper nanoparticles are highly dispersed within the fiber-shaped polymer.^[20] An IPCF synthetic route for the preparation of a palladium nanoparticle– poly(o-methoxyaniline) composite material has been reported in which Pd-acetate and o-methoxyaniline were used as the precursor. During the reaction, o-methoxyaniline undergoes oxidation and forms poly(o-methoxyaniline) while, at the same time, palladium ions form nanoparticles which, under the reaction conditions used, were stabilized in the polymer matrix.^[18] The fabrication of a poly(3,5-dimethylaniline) nanofiber and palladium nanoparticle (polymer-metal) composite material has also been reported,^[17] where 3,5-dimethylaniline and Pd-acetate were used as precursors of polymer fibers and Pd particles, respectively. A single-step, in situ chemical synthetic route has been described for the preparation of a Pd-[poly(o-aminophenol)] composite material in which highly dispersed Pd nanoparticles of the order of ~2 nm diameter were encapsulated within the polymer matrix.^[23] A similar kind of IPCF type of reaction has been reported with polyaniline and cerium ammonium nitrate (Ce⁴⁺), in which the product formed a polyanilinecerium(III) supramolecular complex.^[24] A similar approach has also been reported for the synthesis of a platinum(II)-phenylenediamine hybrid material with a spherical morphology.^[25]

In the present communication we report on an *in situ* technique for the preparation of a palladium–poly(3-aminoquinoline) supramolecular material by applying an IPCF route using palladium acetate as an oxidizing agent for polymerizing 3-aminoquinoline (3-AQ). During the reaction 3-AQ forms poly(3-AQ) and palladium (II) reduced to palladium(I). The ion–polymer composite material served as an effective and versatile catalyst for Suzuki coupling

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reaction both for aryl iodide and bromide systems in a very efficient way under phosphine-free conditions, which is very important from environmental and economic points of view. The Suzuki reaction is the coupling of an aryl or vinyl boronic acid with an aryl or vinyl halide in the presence of a palladium catalyst. It is a powerful cross-coupling method that allows for the synthesis of conjugated olefins, styrenes and biphenyls. The palladium(I)–poly(3-AQ) supramolecular material has been characterized using various microscopic and optical techniques. X-ray photoelectron spectroscopy (XPS) showed the presence of Pd(I)-like species. We have found that the hybrid material is very active as a catalyst for Suzuki reactions both for aryl iodide and bromide systems.

Results and Discussion

Chemical Structure of the Polymer

IR spectrum study

In the IR spectra (Fig. 1), the groups N-B-N, where B represents a benzenoid ring, and N=Q=N, where Q represents a quinoid ring, absorb at 1510 and 1600 cm⁻¹, respectively. A low-intensity peak at 1340 cm⁻¹ corresponds to the C-N stretching mode of the quinoid ring and confirms the presence of this form in the polymer. The presence of a C-N stretching vibration can be confirmed due to the presence of the band at 1275 cm⁻¹. The aromatic C-H in-plane bending mode was observed in the region of 1215–1040 cm⁻¹.

The out-of-plane deformations of the 1,4 disubstituted rings are located at 880 cm⁻¹. This study indicates that the polymer is neither in the fully oxidized nor the fully reduced state because of the presence of both the quinoid and the benzenoid structure in the resultant material.

Raman spectrum study

In the range $1100-1700 \text{ cm}^{-1}$, the Raman spectrum bands of the product are sensitive to many conformation-dependent features (Fig. 2). The C-C deformation bands of benzenoid ring at 1620 and 1590 cm⁻¹, which are characteristic for semiquinone rings.^[26,27] A strong band at 1463 cm⁻¹ corresponds to the C=N stretching mode of the quinoid units. The band at 1376 cm⁻¹ correspond to the C-N⁺ stretching mode of the delocalized polaronic charge carriers and the high intensity of the band confirms the high concentration of these forms in the product. The band at 1278 cm⁻¹ can be assigned to C-N stretching mode



Figure 1. IR spectrum indicates the presence of both benzenoid and quinoid rings in the product at 1510 and 1600 cm^{-1} respectively.



Figure 2. Raman spectrum of the product in the range $1700-1100 \text{ cm}^{-1}$ indicates the formation of polymeric product of 3-AQ with the presence of both the quinoid and benzenoid ring structure.

of the polaronic units. The 1221 cm^{-1} band, corresponds to C-N stretching mode due to the single bond. The positions of the C-H benzene deformation modes fall at 1175 cm^{-1} , indicating the presence of quinoid rings.

The Raman and IR spectra indicate the formation of polymeric product of 3-AQ with the presence of both the quinoid and the benzenoid ring structure.

UV-visible spectra

The electronic absorption spectrum of poly(3-AQ) has been recorded and Fig. 3 shows two prominent absorption bands. The absorption peak at 320 nm is due to the π - π * transition of the benzenoid rings.

An absorption peak at 600 nm has been observed which is due to the transition from a localized benzenoid highest occupied molecular orbital to a quinoid lowest unoccupied molecular orbital, i.e. a benzenoid to quinoid excitonic transition.^[27] The position of excitonic peak shifts from 560 to 630 nm. It is well known that the position of this peak is sensitive to the nature of the counter-ions and solvent and to the chemical structure of the polymer.^[28]

Morphology of the Polymer

A scanning electron microscopy (SEM) image (Fig. 4A) reveals that the product, poly(3-AQ), is composed of microspheres. A



Figure 3. UV-visible spectrum of the product shows two prominent absorption bands at 320 and 600 nm, indicating π - π * transition of the benzenoid rings and benzenoid to quinoid excitonic transition respectively.

higher magnification SEM image (Fig. 4B) indicates spheres with a wide range of size distribution. In addition, the figure also reveals that the surface of the spheres is not smooth.

A transmission electron microscopy (TEM) image shows the more *in situ* structure of the microspheres (Fig. 5). Figure 5(A) shows a two-dimensional image with a dark shell and light core, indicating the hollow-spherical structure of the polymer. Figure 5 (B) is a single-polymer hollow sphere. A typical energy-dispersive X-ray (EDX) analysis obtained from an electron beam focused onto the various parts of a single sphere yielded Pd X-ray peaks with almost identical intensity. This was found to be the case for all the spheres analyzed. Figure 6 is a representative EDX spectrum from a composite sphere.

Mechanism of Formation of the Polymer

3-AQ has structural similarity with aniline or aniline derivatives. A wide variety of methods have been applied for the preparation of polyaniline-type compounds by oxidative polymerization of their

monomer.^[29] According to the most widely accepted mechanism, the first step during polymerization involves the formation of a radical cation accompanied by the release of an electron. This step is the initiation process of the polymerization reaction. In the present work, during the addition of palladium acetate to 3-AQ a greenish-yellow precipitation formed. Spectroscopic analysis confirmed that the product only has a head-to-tail-like arrangement rather than a head-to-head arrangement. The head-to-head coupling occurs only under neutral or basic pH conditions. On the other hand, 3-AQ oxidation products obtained in an acidic medium (presence of palladium acetate) have a predominantly head-to-tail-like arrangement.^[29]

During the reaction between $Pd(OAc)_2$ and 3-AQ, the metal salt acts as an oxidizing $agent^{[16,30,31]}$ that can oxidize AQ and form poly(3-AQ). During polymerization, each step involves the release of an electron^[29] and that free electron is then used to reduce the Pd(II) ion. In general, the released electron reduces the Pd(II) to Pd(0), which ultimately forms Pd nanoparticles^[17,18,21] but in this reaction we found evidence of formation of Pd(I) rather than Pd (0) state. The most probable explanation of this event is that



Figure 4. (A) SEM image showing the formation of the poly(3-AQ) microspheres. (B) Higher-magnification SEM image indicates spheres with a wide range of size distribution.



Figure 5. (A) TEM image of the poly(3-AQ) microspheres, focus being at the top of the spheres. (B) Higher-magnification image of a single-polymer hollow sphere, clearly showing the dark shell and the light core, focus being on the background.



Figure 6. EDX analysis resulting from the electron beam being focused onto a spot on a composite sphere.

the Pd(II) ionic state first formed Pd(I) species, which then coordinated with the nitrogen of quinoline to form an N \rightarrow Pd(I) type of bond. XPS analysis confirmed the formation of Pd(I)-like species. There is no evidence for formation Pd nanoparticles from the TEM image.

To identify the chemical state of the polymer-stabilized palladium particles, XPS measurement was carried out. The peak corresponding to 3d_{5/2} state from spin-orbital splitting appearing at 335.7 eV indicates the presence of zero-valent Pd,^[32] whereas the peak around 337.75 eV was assigned to Pd(II) state.^[33] The characteristic peaks corresponding to Pd 3d_{3/2} and 3d_{5/2} states from the spin-orbital splitting are shown in Fig. 7. In this work we used only the binding energy value of the Pd $3d_{5/2}$ line to find the oxidation state of palladium. The Pd-poly(3-AQ) sample shows (Fig. 7) a broad spectrum within the range 334.5-339.0 eV. After deconvolution two separate peaks appeared at 336.47 and 337.37 eV. As stated before, the peak at 337.37 eV is due to the presence of unreacted Pd(II), whereas the new peak that appeared at 336.47 could be due to the presence of Pd(I) in the sample, as supported by other studies.^[33,34] XPS analysis also confirmed that 1.64 wt% Pd was present on the surface of the polymer matrix. TEM (Fig. 5) also confirmed that there was no evidence of formation of metallic palladium in the sample.

Catalytic Performance of Pd-poly(3-AQ) for Suzuki coupling reaction

The reaction reported first by Miyaura and Suzuki^[35] is the crosscoupling reaction between aromatic (or vinyl) halides and boranes, boronic acids or esters to form biaryls. The original recommendation for the Suzuki reaction involved a phosphine-based palladium catalyst, it being commonly believed that one role of the phosphine ligand was the formation of catalytically active zerovalent palladium species.^[36–38] Recently, pre-formed palladium nanoparticles were also used as a catalyst for the Suzuki coupling.^[36–40] Pd anchored with amine and pyridine-based ligands showed remarkable catalytic performance for Suzuki coupling reactions.^[41,42] The Pd–poly(3-AQ) composite material was used as a catalyst for the Suzuki coupling reaction, which is a versatile method for carbon–carbon bond formation, especially when applied to the synthesis of biaryls in organic synthesis. Initially, a solvent-based optimization study was performed for



Figure 7. X-ray photoelectron spectrum of the Pd–poly(3-AQ) composite with peak position at 336.50 eV indicates the presence of Pd(I).

the coupling of phenylboronic acid with bromobenzene. Among the different bases, such as NaOAc, Na₂CO₃, K₂CO₃, Cs₂CO₃, Et₃N and KOH, we found that K₂CO₃ delivered the product with high yields when combined with toluene as a solvent.

We have investigated the coupling of aryl bromide and iodide with phenylboronic acid in the presence of a Pd–poly(3-AQ) catalyst (Table 1). High catalytic activity of Pd–poly(3-AQ) for both the deactivated and activated aryl iodide and bromides was observed, with formation of the corresponding biphenyl compounds with excellent yields. Activity of the aryl halides decreases in the order I > Br > Cl and the electron-deficient aryl halide is generally more active than the electron-rich one.^[35] Aryl iodide with electron-withdrawing groups (Table 1, entries 1 and 2) showed slightly higher reactivity than those possessing electron-donating groups (Table 1, entries 3 and 4). A similar trend was also observed in the case of aryl bromide (Table 1, entries 5–8).

It was found that the turnover frequency (TOF) was as high as 2340 h⁻¹ for the coupling of 4-nitroiodobenzene with phenylboronic acid (entry 1) when 0.048 mol% of Pd used as catalyst. A slight fall of TOF value (2240 h⁻¹) was noted when a comparatively weak electron-withdrawing (-COOH) group was attached at the para position of iodobenzene (entry 2) under a similar amount of catalytic influence. Again, in the presence of electron-donating groups (-CH₃ and -NH₂) in the iodobenzene ring (entries 3 and 4) the TOF value dropped to 1908 and 1730 h^{-1} with a yield of 75% and 68%, respectively, under same catalytic conditions to achieve the coupled products. For aryl bromides, a comparable yield could be achieved, like aryl iodides, when 0.073 mol% of Pd was used as catalyst (entries 5-8). We found that 80°C was the ideal temperature for achieving optimum yield. A small improvement in yield was achieved by adding higher amounts of the catalyst, which, whoever, would adversely affect the overall turnover frequency value of the reaction.

In the case of 4-bromoaniline a higher catalyst loading (0.097 mol% Pd) was required to obtain a higher yield of the desired biaryl product (Table 1, entry 9) along with a longer reaction time, but the TOF value further decreased to 954 h⁻¹ (entry 9). This may be due to the fact that the amine functionality in 4-bromoaniline could coordinate to the support source from the catalyst used in the reaction.

The supramolecular material, poly(aminophenol)-supported palladium (I), can also be applied as a catalyst for the synthesis of biaryls from 4-chloronitrobenzene and phenylboronic acid at higher temperature, higher catalyst concentration (0.22 mol% Pd) and longer reaction time. A moderate yield of 42% with a TOF value 195 h⁻¹ was achieved at 100°C for 10 h to obtain the coupled product (entry 10).





Entry	Х	R	Yield (%)	TOF (h^{-1})
1	-1	-NO ₂	92	2340
2	-1	-COOH	88	2240
3	-1	-CH ₃	75	1908
4	-1	-NH ₂	68	1730
5	-Br	-NO ₂	89	1509
6	-Br	-COOH	84	1425
7	-Br	-CH ₃	74	1255
8	-Br	-NH ₂	58	983
9	-Br	-NH ₂	75	954
10	-Cl	-NO ₂	42	195

Entries1–4: iodobenzene and derivatives (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (1.5 mmol), toluene (5 ml) and catalyst concentration 0.048 mol% Pd. Entries 5–8: bromobenzene and derivatives (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (1.5 mmol), toluene (5 ml) and catalyst concentration 0.073 mol% Pd. Entry 9: catalyst concentration 0.097 mol% Pd. Entry 10: 4-chloronitrobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (1.5 mmol), toluene (5 ml) and catalyst concentration 0.22 mol% Pd at 100°C for 10 h.

XPS indicates the presence of Pd(I) and unreacted Pd(II) species in the composite material. Reduction of Pd(II) to Pd(0) by phenylboronic acid has been reported,^[43,44] so reduction of Pd (I) to Pd(0) by phenylboronic acid is also possible. It is believed that for the Suzuki coupling reaction Pd(0) is the catalytic species.^[45,46] The interaction of aryl halide (R¹X) and Pd(0) forms the aryl–palladium halide complex [R¹(Pd²⁺)X], which then couples with phenylboronic acid [R²B(OH)₂] in the presence of a base to produce the [R¹–(Pd²⁺)–R²] intermediate and finally produces the biaryl product (R¹–R²) via the reductive elimination of Pd²⁺ to Pd(0), as outlined in Scheme 1.

The recyclability study was performed for the coupling of 4nitroiodobenzene with phenylboronic acid using 0.048 mol% of Pd catalyst. A 12% drop in product yield was measured after three cycles of the reaction. This fall in catalytic performance of the 'Pd-polymer' composite may be due to applomeration of the palladium particles. It is also important to mention that the study employing inductively coupled plasma mass spectrometry did not support any kind of leaching of palladium during the recovery process of the catalyst. The composite of metal ion and conjugated polymer is not well known as a catalyst from an application point of view. In most cases the reaction between metal salt and monomer ended with the formation of polymer-encapsulated metal nanoparticles.^[18,23,47] In this present study, however, Pd ion-incorporated poly(aminoquinoline) showed it to have excellent catalytic activity and high stability for a longer time period without noticeable deactivation.



Scheme 1. Recommended mechanism of Suzuki coupling reaction.

Scaling up of the catalyst, working with different derivatives as well as in heterocyclic systems, the effect of solvent, temperature and the reaction kinetic studies are all currently under investigation in our laboratory. The material described here also has potential as a catalyst for other carbon–carbon bond formation reactions and this will be reported elsewhere.

Conclusion

The present article reports on the synthesis of a functional polymer with a unique hollow sphere-like morphology using palladium acetate as an oxidizing agent. During the reaction, palladium acetate reduced to Pd(I) species and formed a complex with poly(aminoquinoline). The ion–polymer composite material served as an effective and versatile catalyst for Suzuki coupling reaction both for aryl iodide and bromide systems in a very efficient way under phosphine-free conditions, which is very important from environmental and economic points of view. The composite catalyst was found to be very stable and could be kept for several years without noticeable deactivation.

Experimental

Materials

3-AQ, palladium acetate and all the other chemicals were purchased from Sigma-Aldrich and used without further purification. All the solvents used in this work, including toluene, were supplied by Merck.

Characterization Techniques

Instrumentation

TEM was carried out at an accelerated voltage of 200 kV using a Philips CM200 transmission electron microscope equipped with an LaB6 source. An ultrathin windowed energy-dispersive X-ray

spectrometer and a Gatan imaging filter attached to the microscope were used to determine the chemical composition of the samples.

SEM studies were undertaken in an FEI FEG Nova 600 Nanolab at 5 kV instrument. As a precaution to prevent possible charging, the samples were sputter coated with a thin uniform layer of Au–Pd prior to viewing.

For UV–visible spectra analysis, a small portion of the solid sample was dissolved in methanol and scanned within the range 300–700 nm using a Varian CARY 1E digital spectrophotometer. Raman spectra were acquired using the green (514.5 nm) line of an argon ion laser as the excitation source. Light dispersion was carried out using the single spectrograph stage of a Jobin-Yvon T64000 Raman spectrometer. Power at the sample was kept very low (0.73 mW) and the laser beam diameter at the sample was ~1 μ m. IR spectra in the region 800–1700 cm⁻¹ were obtained from a PerkinElmer 2000 FT-IR spectrometer operating at a resolution of 4 cm⁻¹. The sample was deposited in the form of a thin film on a sodium chloride disk. X-ray photoelectron spectra were collected in an ultra-high-vacuum chamber attached to a Physical Electronics 560 ESCA/SAM instrument.

In situ synthesis of a Pd-poly(3-AQ) composite

In a typical experiment 0.35 g 3-AQ was added to 15 ml toluene in a 50 ml conical flask. The flask was then shaking manually with appropriate precautions. Palladium acetate (Pd(OAc)₂) in toluene (10 mL) having a concentration of 2.0 \times 10⁻³ M was added slowly dropwise to the aminoquinoline-toluene system. A greenish-yellow color developed at the bottom of the conical flask. The solution was kept under static conditions for a further 10 min. A precipitation slowly formed at the bottom of the flask. The material was then allowed to settle for an additional 15 min. The whole process was carried out at room temperature (~25°C). The amount of product obtained after the reaction between 3-AQ and Pd(OAc)₂ was 0.31 g. Subsequently, the colloidal precipitation was taken from the bottom of the flask and pipetted onto lacey, carbon-coated, copper TEM grids for SEM and TEM analysis. The rest of the solution was filtered, washed with distilled water and kept under vacuum overnight. A small portion of the dried powder was used for Raman, IR and UV-visible analysis. The remaining portion was used for the study of the catalytic properties of the materials.

Procedure for Suzuki coupling reactions catalyzed by the Pd-poly(3-AQ) composite

In a typical experiment, aryl halide (1.0 mmol), phenylboronic acid (1.5 mol), K_2CO_3 (1.5 mmol) and the Pd–poly(3-AQ) composite catalyst (required amount) were added to toluene (5 ml) in a small round-bottom flask having a magnetic stirring bar. The reaction mixture was placed on an oil bath at 80°C and stirred for 8 h. The reaction was monitored by thin-layer chromatography. Subsequently, the mixture was extracted with ethyl acetate and diluted with Et₂O, filtered through a pad of silica gel and purified by flash chromatography on silica gel.

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