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Synthesis and Characterization of Polystyrene Supported Catalytically Active Poly(amidoamine) Dendrimer-Palladium Nanoparticle Conjugates

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SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE SUPPORTED CATALYTICALLY ACTIVE POLY(AMIDOAMINE) DENDRIMER-PALLADIUM NANOPARTICLE CONJUGATES

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□ *Poly(amidoamine) dendrimers were synthesized on cross-linked aminomethyl polystyrene. Palladium complexes of supported dendrimers prepared by ligand exchange method were reduced to dendrimer-nanoparticle conjugates supported on polystyrene resin. The supported nanoparticles were used as heterogeneous catalysts for the Suzuki coupling between aryl boronic acids and aryl halides. Various factors affecting the catalysts performance were studied. Higher generation dendrimers gave well-defined nanoparticles without agglomeration and these particles showed good catalytic performance.*

Keywords Dendrimer, Nanoparticles, Palladium, Polymer-supported catalyst, Suzuki coupling reaction

INTRODUCTION

Nanoscience and nanotechnology have become popular for research and development during the last few years. As an example to explain its potential significance, heterogeneous catalysis was cited as a successful application that has great benefits for the society. Thus, it is reasonable to expect that the advancement in new developments in nanoscience and nanotechnology would have a significant impact on the understanding, practice, and applications of catalysis (1). Among various nanomaterials used in catalysis, metal nanoparticles have found acceptance because of their predominant size-dependant properties and comparatively simple methods of preparation (2, 3). Nanoparticles have many advantages over conventional catalysts. Major advantages are the large surface area and large number of surface atoms of nanoparticles compared to a bulk material. In nanoparticles, the percentage of atoms present on

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the surface are very large compared to the bulk and the surface atoms have vacant coordination sites with which they can form bonds with the approaching substrate, which finally leads to catalysis (4, 5). Generally, metal nanoparticles stabilized by an organic ligand like dendrimers are used for catalysis, since this methodology gives nanoparticles of well defined and controllable size.

Dendrimers are a new class of molecular architecture, which has attracted the attention of the scientific community due to the special features they offer compared to the linear polymers (6–9). Since dendrimers have interior voids of nanometer dimensions, they can hold small molecules or nanoparticles of suitable dimensions, which can fit into the voids (10). This property finds widespread application in catalysis and biomedical research. In addition, dendrimer metal complexes can be reduced to dendrimer metal nanoparticle conjugates that hold nanoparticles of well-defined size and shape and these materials find application in catalysis (11–13).

But removing dendrimer-based catalysts from final reaction mixture after catalysis is generally a tedious process and requires ultrafiltration or chromatographic methods. This difficulty can be avoided by attaching dendrimers to an insoluble support. The best choice of such a support is an insoluble lightly cross-linked polymer resin. Many research groups have proved the success of solid phase synthesis of dendrimers on polymer supports (14–17). Catalysts derived from the dendrimers supported on insoluble supports were shown to be highly efficient and reusable (18–21).

The synthesis and characterization of polymer-supported dendrimer-palladium nanoparticle conjugates is reported here. The supported metal nanoparticles were found to be highly active and reusable catalyst in Suzuki coupling reaction between aryl halides and aryl boronic acids. As a carbon-carbon bond forming reaction, Suzuki coupling plays an important role in the synthesis of pharmaceuticals, natural products, and advanced materials (22–27). A large number of catalysts, both homogeneous and polymer-supported, were reported for Suzuki coupling (28–36). To the best of our knowledge, catalysis by polymer-supported dendrimer-nanoparticle conjugates was not exploited in any such reactions. The nanoparticles showed good catalytic activity along with long shelf life and tolerance of moisture and air.

EXPERIMENTAL

Materials and Methods

Chloromethyl polystyrene (1% DVB cross-linked, 100–200 mesh [75–125 μm], 1.1 mmol Cl atoms per gram) was obtained from Thermax India Ltd as a gift sample. It was washed with methanol, dioxan, and acetone (20 mL \times 2 times) and dried under vacuum prior to experiments. Methyl acrylate was purified according to the literature procedure. All other chemicals were

purchased from different suppliers and used as received. Fourier transform infrared (FTIR) spectra were taken on a JASCO FTIR spectrometer as KBr pellets. Solid state CP-MAS ^{13}C -NMR spectra were recorded on a Bruker 400 MHz instrument with a spinning rate of 7 K (NMR Research Centre, IISc. Bangalore). Solution nuclear magnetic resonance (NMR) spectra were taken on Bruker 300 MHz or 400 MHz instrument with tetramethyl silane (TMS) as internal standard in CDCl_3 . GC/MS was taken on a Varian 1200 L single quadrupole GC/MS with capillary column. MALDI TOF MS was recorded on a Shimadzu Kratos compact analytical MALDI TOF MS using an Nd-YAG laser with an operating wave length of 345 nm. The matrix used was α -cyano-4-hydroxy benzoic acid. Angiotensin II and insulin were used as internal standards. Thermogravimetric analysis was done on a Perkin Elmer Diamond model TG/DTA system using platinum as the standard. SEM micrograph was recorded using Jeol JSM 840 microscope. TEM images were taken on a JOEL 3010 HRTEM operating at electron beam energy of 300 kV. A suspension of the sample in methanol was loaded to the TEM copper coated carbon grid and the solvent was allowed to evaporate at room temperature before recording the images.

Solid Phase Synthesis of PAMAM Dendrimer

First, second and third generation PAMAM dendrimer were synthesized on the cross-linked polystyrene. The chloromethyl polystyrene was converted to aminomethyl polystyrene using a standard procedure (37). It was found that the polystyrene support had a loading of 1.0 mmol of amino group per gram of resin obtained by acid-base titration method using 0.1 M HCl. PAMAM dendrimers were synthesized on aminomethyl polystyrene according to a procedure previously reported by the same authors (38).

Synthesis of Polymer-Supported Dendrimer Palladium Complex

The resin carrying the dendrimer (1 g) prepared as above was allowed to swell in acetone (5 mL) in a 25 mL round bottom flask for 30 min. To the swollen polymer PdCl_2 (0.212 g, 1.2 mmol) was added followed by water (5 mL). This reaction mixture was stirred at room temperature for 12 h. The brown colored polymer beads were filtered under vacuum, washed with water (20 mL \times 3), methanol (10 mL \times 3), and acetone (10 mL \times 3) and dried under vacuum for 24 h.

Synthesis of Polymer-Supported Dendrimer Nanoparticle Conjugates

The polymer-supported metal complex prepared as described earlier (1 g) was suspended in methanol (10 mL) taken in a 25 mL round bottom flask

and hydrazine hydrate (1 mL, 20 mmol) was added to it with stirring. The reaction mixture was stirred at room temperature for 2 h to ensure complete reduction. It was filtered under vacuum, washed with methanol (20 mL \times 5), and dried under vacuum for 24 h.

General Procedure for Suzuki Coupling

A 10 mL round bottom flask was charged with aryl halide (1 mmol), aryl boronic acid (1.2 mmol), and Na_2CO_3 (317 mg, 3 mmol). The catalyst (0.02 mmol Pd, 2 mol%) was added to it followed by dioxane (4 mL) and water (1 mL). The reaction mixture was stirred at 100°C. The progress of the reaction was followed by thin layer chromatography (TLC) on silica gel coated plates using hexane-ethyl acetate mixture (10:1 v/v) as eluent. After the completion of reaction the catalyst was filtered off and was washed several times with small portions of ethyl acetate. The combined filtrate and washings were extracted with water in a separating funnel; the organic layer was isolated and dried with 4 Å molecular sieves. The pure product was isolated by column chromatography on a small silica column using hexane-ethyl acetate mixture (10:1) as eluents. All the products were known compounds and were characterized using ^1H NMR spectroscopy. Characterization data of some representative products are given below.

Biphenyl

^1H NMR (CDCl_3) δ 7.29–7.34 (m, 2H), 7.39–7.44 (m, 4H), 7.56–7.59 (m, 4H).

4-Acetyl biphenyl

^1H NMR (CDCl_3) δ 2.64 (s, 3H), 7.42–7.50 (m, 3H), 7.62–7.70 (m, 4H), 8.04 (d, J = 6.60 Hz, 2H).

4-Methyl biphenyl

^1H NMR (CDCl_3) δ 2.34 (s, 3H), 7.19 (d, J = 7.3 Hz, 2H), 7.21– 7.29 (m, 1H), 7.36 (t, J = 6.24 Hz, 2H), 7.42 (d, J = 8.14, 2H), 7.51–7.54 (m, 2H).

4-Nitro Biphenyl

^1H NMR (CDCl_3) δ 7.44 (m, 1H), 7.49 (m, 2H), 7.62 (m, 2H), 7.73 (d, J = 8.80 Hz, 2H), 8.29 (d, J = 8.80 Hz, 2H).

Recycling of the Nanoparticle Catalyst

The catalyst used for the first cycle of reaction was washed well with water, ethyl acetate, and acetone and was dried under vacuum. It was reused for successive reaction cycles. The metal leaching from the catalyst

was estimated after each cycle using inductively coupled plasma with atomic emission spectroscopy (ICP-AES).

RESULTS AND DISCUSSION

Synthesis and Characterization of Polystyrene-Supported PAMAM Dendrimers

Poly(amidoamine) (PAMAM) dendrimers up to third generation, on aminomethyl polystyrene was prepared using a previously reported procedure (38). The synthesis involved double Michael addition of methyl acrylate to the amino group of the polymer followed by transamidation (Fig. 1).

The FTIR spectroscopy was used to monitor the progress of the reaction. The appearance of the absorption band at 1735 cm^{-1} for each half generation was attributed to the CO stretching of the ester groups while peaks at 1648 and 1552 cm^{-1} were due to the CO stretching and the N-H bending/C-N stretching of the secondary amide groups, respectively. The bands at 3394 cm^{-1} , 3344 cm^{-1} , and 1660 cm^{-1} in the IR spectrum are due to the stretching and bending vibrations of the primary amino groups of the polymer-supported dendrimer. It is therefore possible to distinguish between the amide function in the full-generation dendrimers and the ester function in the half-generations. The dendronized resin was characterized using solid state ^{13}C CP-MAS NMR spectroscopy. New peaks at $\delta 173\text{ ppm}$ due to C=O carbon of the dendrimer appeared after the introduction of the dendrimer moiety.

Third generation PAMAM dendrimer was prepared on nitrated aminomethyl polystyrene and the dendrimer was cleaved from the polymer by photolysis. The dendrimer obtained by this method was characterized by

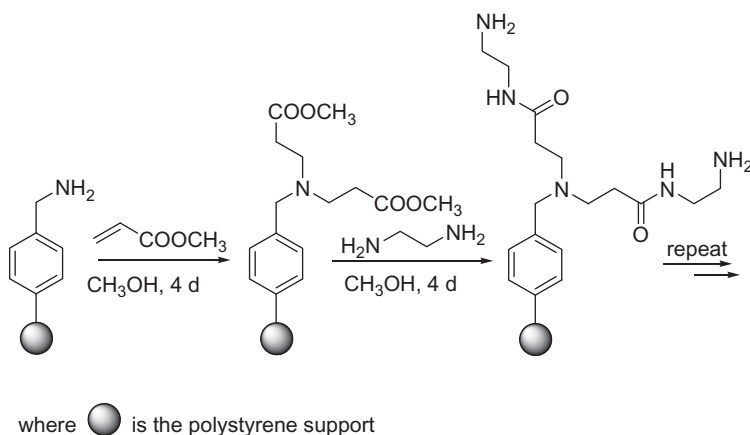


FIGURE 1 General scheme of solid phase synthesis of PAMAM dendrimer.

MALDI-TOF MS. The mass spectra showed a prominent peak at 1615 D (M^+ ion), which confirmed the formation of the third generation PAMAM dendrimer on the polymer. The absence of peaks due to the mass corresponding to lower generation dendrimers clearly indicated that the dendrimer obtained was of good purity and without structural defects.

Estimation of amino groups and CHN analysis showed that the final polymer contained 0.260 mmols of G3 PAMAM dendrimers per gram of the resin. This means there are 2.08 mmols primary amino groups, 1.82 mmols of tertiary amino groups, and 3.64 mmols amide groups per gram of the resin. Thermal analysis of the dendronized polymer showed that it was stable up to 200°C. The polymer showed first weight loss between 200–300°C and this might be due to the decomposition of the dendrimer on the polymer support. Second decomposition occurred between 350–450°C. This might be due to the degradation of the polystyrene support and such degradation is observed in the case of aminomethyl polystyrene itself in the same range of temperature.

Synthesis of Polymer-Supported PAMAM Dendrimer-Pd(II) Complexes

The polymer-supported PAMAM-Pd(II) complexes were prepared by reacting the polymer-supported dendrimer and $PdCl_2$ in water/acetone (1:1) mixture at room temperature under natural pH of the solution for 12 h. On complex formation the yellow colored polymer was turned to a brown one. When water alone was used as the reaction medium the metal intake by the polymer was very low. This may be due to the poor swelling of the dendronized resin in water. Repetition of the reaction in different solvents guided us to choose the aforementioned solvent mixture as the suitable reaction medium (Table 1).

The AAS analysis showed that the resin contained 1.12 mmol of palladium per gram of the resin. Solid state UV-Vis diffused reflectance spectrum of

TABLE 1 Influence of Reaction Conditions on Complex Formation

Entry	Solvent ^a	Temperature °C	pH ^b	Amount of Pd (mmol/g) ^c
1	water	30	natural pH	0.95
2	water + benzene	30	natural pH	0.99
3	water + methanol	30	natural pH	1.09
4	water + dioxane	30	natural pH	1.00
5	water + acetone	30	natural pH	1.12

^aSolvent mixtures were taken in the ratio 1:1 v/v.

^bNatural pH means the pH of the final reaction mixture without any added buffer.

^cPolystyrene-supported third generation PAMAM dendrimer was used as ligand.

the complex showed two peaks at 314 and 411 nm and are due to the metal to ligand charge transfer transition and d-d transitions, respectively. Comparison of FTIR spectra of the complex before and after complex formation revealed that the bands at 3394 cm^{-1} and 1660 cm^{-1} due to the stretching and bending vibrations of the primary amino groups of the dendrimer remained unaltered. The carbonyl stretching band of the amide also remained the same before and after the reaction with PdCl_2 . From these observations it can be concluded that the tertiary amines in the dendrimer are responsible for complex formation with the metal ion. Thermogravimetric analysis showed that no considerable weight loss occurred up to 150°C . This indicated that there are no water molecules associated with the polymer-supported complex. In between $150\text{--}300^\circ\text{C}$ approximately 10% weight loss occurred and this might be due to the decomposition of the dendritic part of the resin. After this temperature region, the system showed considerable decomposition and almost complete decomposition occurred in between $300\text{--}450^\circ\text{C}$ leaving 10% residue. It can be concluded from the spectral and thermal analytical data that the complex has a possible structure as shown in Fig. 2.

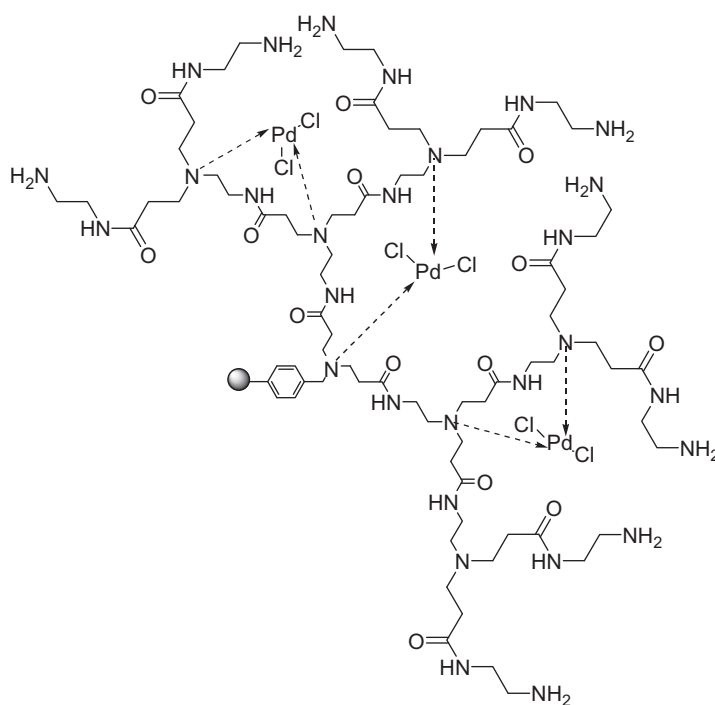


FIGURE 2 Tentative structure of the polymer-supported PAMAM-Pd(II) complex. The size of the polystyrene beads is $75\text{--}125\ \mu\text{m}$ while the size of the dendrimers is approximately $1.5\text{--}2\ \text{nm}$. Only for clarity the polystyrene bead is shown as a small sphere and the dendrimer as a big molecule.

Synthesis of Polymer-Supported Dendrimer-Nanoparticle Conjugates

The polymer-supported PAMAM dendrimer-Pd nanoparticle conjugates were prepared by chemical reduction of the supported dendrimer-Pd(II) complexes using hydrazine hydrate in methanol (Fig. 3).

The efficiency of hydrazine hydrate to reduce Pd(II) complex to nanoparticles is already well established (39). The reagent does not contaminate the products and the excess reagent can be easily removed. Other reducing agents like NaBH_4 were omitted due to the possibility of formation of some borides with palladium (40, 41). Very strong reducing agents like LiAlH_4 were also avoided considering the fact that they may degrade the dendrimer, which will result in the agglomeration of nanoparticles.

Electronic spectrum of the dendrimer-nanoparticle conjugate showed that the peaks at 314 and 411 nm shown by the dendrimer-Pd(II) complex disappeared completely and a continuous absorption band was seen in the visible region. This peak is due to the band structure of palladium nanoparticles (42) (Fig. 4). Thermal analysis showed no considerable variation from that of the metal complex. The amount of residue remained after thermal decomposition was the same as that of complex and it showed that no metal leaching occurred during reduction process (Fig. 5). Since the amount of metal in the polymer is very small the reduction of metal complex to nanoparticle did not influence the thermal stability of the system. Scanning electron microscopy (SEM) images of the polymer-supported dendrimer-Pd nanoparticle conjugate showed that many of the polystyrene beads retained its spherical shape without degradation after the synthetic processes (Fig. 6). This proves the efficiency of lightly cross-linked polystyrene as templates or supports in the preparation of metal nanoparticles.

High resolution transmission electron microscopy (HRTEM) images of the sample clearly showed the metal nanoparticles (Fig. 7 and Fig. 8). The

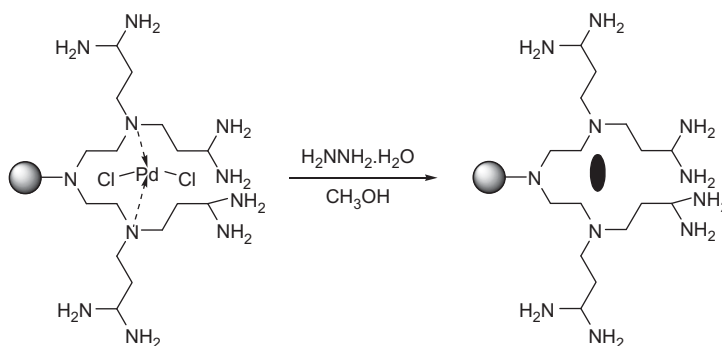


FIGURE 3 General scheme of reduction of dendrimer-Pd complex to dendrimer-Pd nanoparticle conjugates.

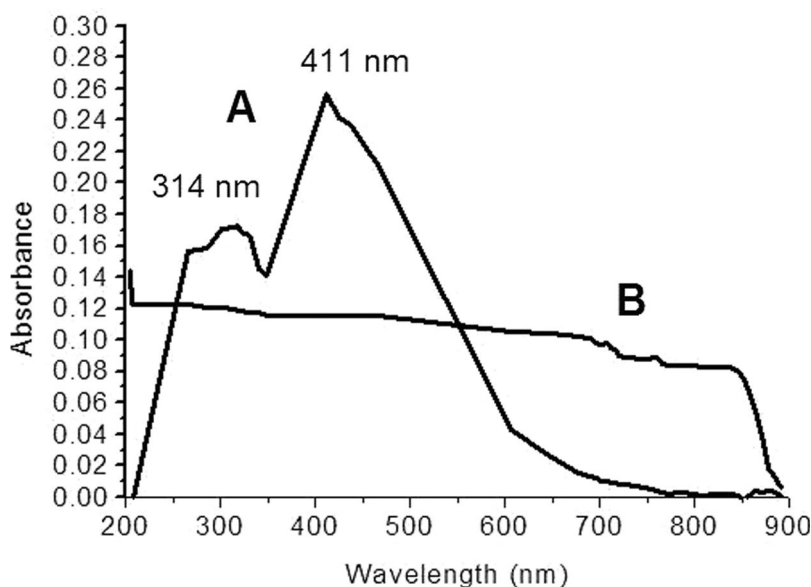


FIGURE 4 Electronic spectra of polymer-supported Pd(II) complex (A) and polymer Pd nanoparticle conjugates (B).

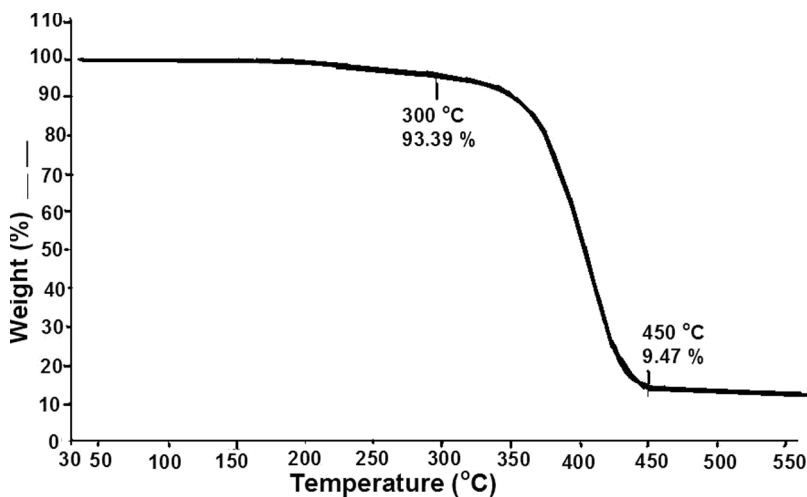


FIGURE 5 Thermogravimetric curve of polymer Pd nanoparticle conjugates.

nanoparticles are of different shapes and this may be due the variation in the co-ordination sphere of the palladium ions taking part in nanoparticle formation. Some of the Pd(II) may complex with tertiary amino groups of the same dendrimer alone, while some others to tertiary amino groups of two neighboring dendrimers. Also, there is difference in the environment of

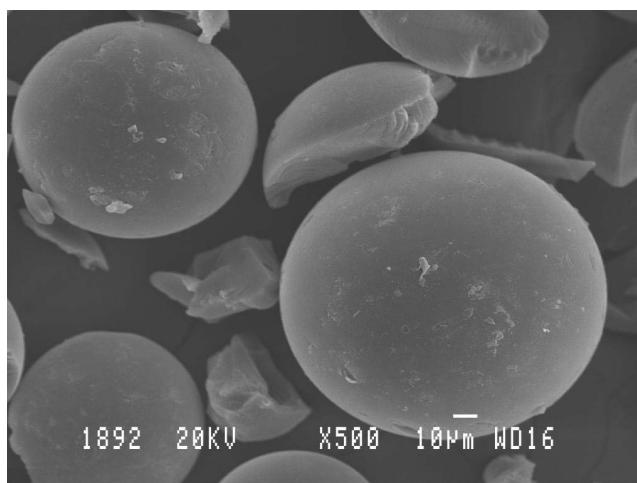


FIGURE 6 SEM image of the polymer beads carrying dendrimer-nanoparticle conjugates.

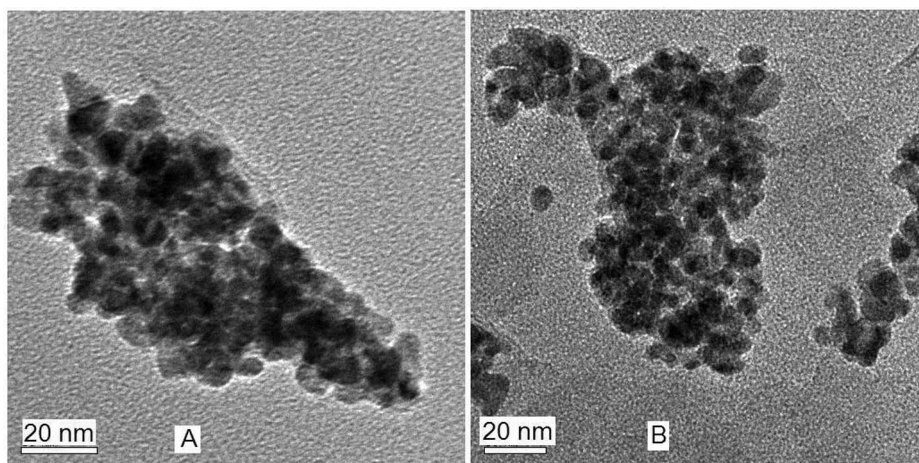


FIGURE 7 HRTEM images of the palladium nanoparticles supported on polymer-supported dendrimers obtained when first (A) and second generation (B) dendrimers were used.

various tertiary amines in the same dendrimer. In the formation of nanoparticles, metal ions from such different environments took part and this results in the formation of nanoparticles with different shape and size. Moreover, the different environmental effects arising due to the morphology of the resin also have considerable effects on controlling the size and shape of the nanoparticles. The resin contains a large number of pores of various sizes and shapes and these pores control the diffusion of the metal ions during complexation and reducing agent during reduction. This regulation of reagents also results in nanoparticles of various size and shape. But it is difficult to prove these

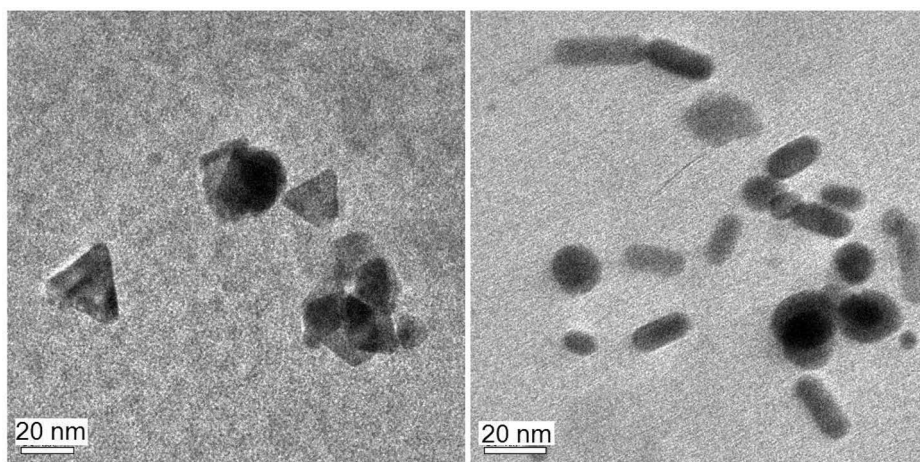


FIGURE 8 HRTEM images of the palladium nanoparticles supported on polymer-supported dendrimers obtained when third generation dendrimer was used.

hypotheses experimentally because of the complex nature of the insoluble polymer supports. Such effects have no role when unsupported dendrimers are used as templates in the synthesis of metal nanoparticles in solution. So nanoparticles of uniform size and shape are obtained under such circumstances. The size of the nanoparticle was high compared to the previous reports in which unsupported dendrimers were used as templates for the synthesis of dendrimer encapsulated nanoparticles (11–13). It is expected that in addition to simple encapsulation, some other mechanism came in to play during the formation of the nanoparticles that regulates their size and shape. So the term “dendrimer encapsulated nanoparticles” was omitted; and the newly prepared material was referred to as dendrimer-nanoparticle conjugates.

The generation of the dendrimer showed considerable influence on controlling the size of the nanoparticles. HRTEM images clearly showed that the nanoparticles were agglomerated and individual particles were not well separated when first and second generation dendrimers were used as templates. Since, in the first and second generation dendrimers, nanosized cavities are not well formed due to their smaller size and open structure, they cannot hold the nanoparticles separately and this results in aggregation. The third generation dendrimers have more closed structure and so they can save the nanoparticles from aggregation. This effect is reflected in catalysis also.

Catalytic Activity of Polystyrene Supported Dendrimer-Pd Nanoparticle Conjugates

In order to explore the advantages of preparing nanoparticles stabilized by polymer-supported dendrimers, the prepared system was used as

heterogeneous catalysts in Suzuki coupling reaction between aryl boronic acids and aryl halides (Fig. 9). Since the nanoparticles are attached to an insoluble polymer matrix it is expected that the nanoparticles could easily be separated from the reaction mixture without the loss of nanoparticles.

The model reaction between phenyl boronic acid and 4-nitro iodobenzene was studied in dioxane in the presence of Na_2CO_3 as the base. The amount of the catalyst was varied starting initially from 0.25 mol%. With this low amount of the catalyst loading, the reaction was very slow and gave poor yield. The speed of the reaction as well as yield was increased with increase in the amount of the catalyst and when the amount of catalyst reached 2 mol%, the reaction proceeded at a good pace with good yield (Table 2). The reaction now proceeded at a comparable speed to that of unsupported dendrimer encapsulated nanoparticles (43, 44) but was slower than many homogenous catalysts containing Pd nanoparticles (45). This may be due to the difficulty for the substrates to access the catalytic sites, which are embedded in the polymer-supported dendrimer. The steric hindrance offered by the polymer support may be another reason that retards the interaction between the catalyst and the substrates.

The influence of solvents on the catalytic activity of the nanoparticles was studied in detail. The performance of the catalyst in polar solvents like methanol, ethanol, acetone, dioxane, and tetrahydrofuran (THF) was good while it was poor in nonpolar solvents like benzene and toluene. The good performance of the catalyst in polar solvents can be explained by considering the fact that the polymer matrix that stabilizes the nanoparticles is highly polar due to the presence of a number of amino groups. Due to this

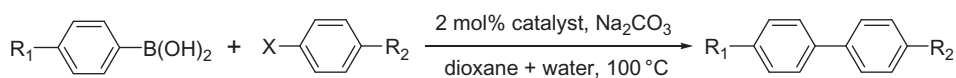


FIGURE 9 General scheme of Suzuki coupling reaction catalyzed by polymer-supported dendrimer-Pd nanoparticle conjugate.

TABLE 2 Influence of the Amount of Catalyst on Suzuki Coupling

Entry	Amount of catalyst (mol%)	Time (h)	%Yield ^{a,b}
1	0.25	12	71
2	0.5	12	78
3	1.0	12	90
4	2.0	12	90

^aReaction condition; 1 mmol 4-nitro iodobenzene, 1.2 mmol phenyl boronic acid, 3 mmol base, 4 mL dioxane, 1 mL water at 100°C.

^bIsolated yield of the product.

the interaction of the polymer with polar solvents is high and it facilitates the interaction between the reactant molecules and the catalysts. On the other hand, the dendritic architecture may get collapsed in nonpolar solvents that prevent smooth interaction between the substrates and catalysts (46).

After optimizing the reaction conditions various aryl halides and aryl boronic acids were allowed to react in the presence of the nanoparticles. The results are summarized in Table 3, which shows that the electronic factors of substrates have no considerable effect on the reaction while steric factors of the substrates do. The yield was low when substrate carrying bulkier substituents like tertiary butyl group was used. This is due to the limited access of bulkier substrates to the catalyst sites due to the steric hindrance offered by dendritic and polymeric backbone. Aryl iodides and bromides gave well to excellent yields while chlorides gave poor yield even after prolonged reaction under refluxing conditions.

Since the dendrimer part of the catalyst contains amide groups, it was assumed that the base employed in the reaction may influence the stability of the catalyst. When a weak base like Na_2CO_3 or triethyl amine was used, it took longer duration for the completion of the reaction but the catalyst was stable even after three cycles and practically no metal leaching was observed. Conversely, when a strong base like NaOH was used, it was observed that a white-colored mass was formed within the reaction vessel after each cycle and some nanoparticles were observed in it. This may be due to the decomposition of the dendrimer part under the strongly basic conditions

TABLE 3 Suzuki Coupling Reaction Between Aryl Boronic Acids and Aryl Halides Catalyzed by Polymer-supported Dendrimer-Pd Nanoparticle Conjugates

Entry	R ₁	R ₂	X	Base	Time (h)	%Yield ^{a,b}
1	H	NO ₂	I	Na ₂ CO ₃	24	95
2	H	NO ₂	I	NaOH	12	96
3	H	NO ₂	I	Et ₃ N	24	89
4	H	NO ₂	I	KOH	12	95
5	H	H	I	Na ₂ CO ₃	10	92
6	H	H	Cl	Na ₂ CO ₃	48	40
7	H	H	Br	Na ₂ CO ₃	30	85
8	CH ₃	NO ₂	I	Na ₂ CO ₃	12	90
9	H	CH ₃	I	Na ₂ CO ₃	12	92
10	CH ₃	CH ₃	I	Na ₂ CO ₃	24	91
11	H	C(CH ₃) ₃	I	Na ₂ CO ₃	24	72
12	CH ₃	CH ₃	I	Na ₂ CO ₃	24	70
13	H	COCH ₃	Br	Na ₂ CO ₃	24	89
14	CH ₃	COCH ₃	Br	Na ₂ CO ₃	24	85
15	H	NH ₂	Br	Na ₂ CO ₃	24	65

^aReaction condition; 1 mmol aryl halide, 1.2 mmol aryl boronic acid, 3 mmol base, 2 mol% catalyst, 4 mL dioxane, 1 mL water at 100°C.

^bIsolated yield of the product.

employed. The catalyst lost its activity completely after three cycles under this condition. When the reaction was carried out in the presence of the white mass obtained, formation of biphenyl was observed and this is an additional proof that the catalytically active metal nanoparticles were getting detached from the polymer and the catalyst was not stable under strongly basic conditions. HRTEM images of the white mass formed also revealed the presence of palladium nanoparticles (Fig. 10).

To reduce the catalyst's contact with strong base, microwave heating was employed in the place of conventional heating. The reaction was completed within 10–15 min under this condition and no catalyst decomposition was observed even if NaOH was employed as the base. This was due to the faster kinetics of the catalytic process, so that the catalyst was not in contact with the base for a longer time. Such observations were reported previously in which polymer-bound ester groups were hydrolyzed under conventional heating, but not under microwave irradiation under Suzuki coupling conditions (47).

The catalyst was recycled by washing it with water and methanol followed by drying at room temperature under vacuum. The catalyst was used four times without considerable loss of activity but the activity gradually decreased on further recycling (Table 4).

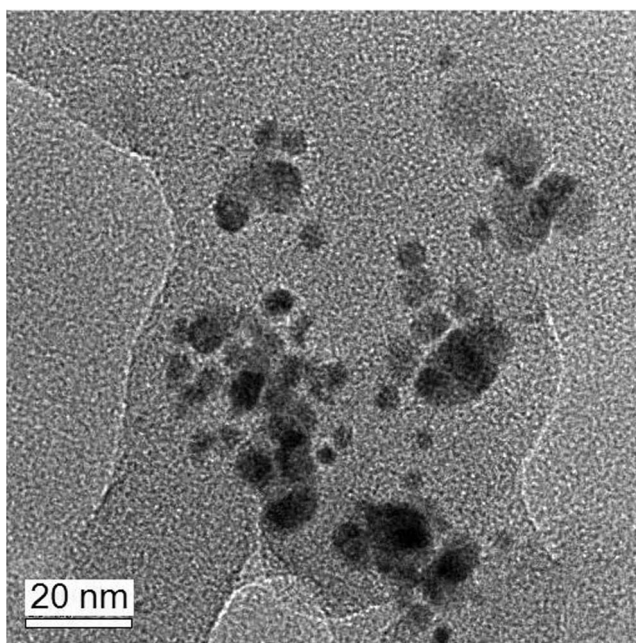


FIGURE 10 HRTEM image of the palladium nanoparticle leached from the catalyst after the decomposition of the dendrimer backbone.

TABLE 4 Recycling of the Catalyst

Entry	No. of cycles	% Yield ^{a,b}	Loading of Pd (mmol/g)
1	1	95	1.12
2	2	95	1.12
3	3	95	1.12
4	4	94	1.10
5	5	91	1.00
6	6	88	0.94

^aReaction condition; 1 mmol 4-nitro iodobenzene, 1.2 mmol phenyl boronic acid, 3 mmol base, 2 mol% catalyst, 4 mL dioxane, 1 mL water at 100°C.

^bIsolated yield of the product.

The stability of the nanoparticles supported on the polymer matrix is relatively high. The system remains stable with no loss of catalytic activity for two years without any special precaution to protect them from air and moisture. After two years there is gradual loss of catalytic activity. It may be due to oxidation of Pd nanoparticles. But the catalytic activity can be retained by treatment with a reducing agent like hydrazine hydrate.

CONCLUSION

Polystyrene-supported poly(amidoamine) dendrimer-palladium nanoparticle conjugates were prepared and characterized. Various factors influencing the size and shape of the nanoparticles were studied. The supported nanoparticles were used as heterogeneous catalysts for the Suzuki coupling reaction between aryl boronic acids and aryl halides. Various factors influencing the catalysts performance were studied. The nanoparticles showed long shelf life without loss of catalytic activity.

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