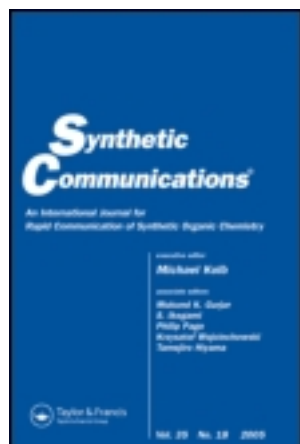


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Polymeric PEG35k-Pd Nanoparticles: Efficient and Recyclable Catalyst for Reduction of Nitro Compounds

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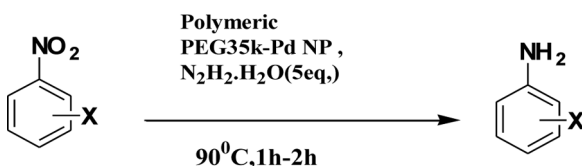
POLYMERIC PEG35k-Pd NANOPARTICLES: EFFICIENT AND RECYCLABLE CATALYST FOR REDUCTION OF NITRO COMPOUNDS

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GRAPHICAL ABSTRACT



X = -CH₃, Cl, OH, NH₂,

Abstract The small size polymeric PEG35k-Pd nanoparticles are key attractions for catalysis due to their large surface to volume ratio, non-toxicity, inexpensive, thermal stability, and recoverability. Polymeric PEG35k-Pd nanoparticles in the absence of phosphine ligands are insensitive to the air and moisture and act as an active heterogeneous catalyst for the reduction of nitroarenes.

Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications[®] to view the free supplemental file.

Keywords Catalysis; palladium; PEG35k; recyclable

INTRODUCTION

Functionalized anilines are industrially important intermediates for pharmaceuticals, polymers, herbicides, and other substances and fine chemicals,^[1,2] so there is a strong incentive to develop chemoselective catalysts for the reduction of nitro groups. Stoichiometric reducing agents such as iron,^[2] sodium hydrosulfite,^[3] tin,^[4] or zinc in ammonium hydroxide^[5] have been successfully used to reduce aromatic nitro compounds. Reduction of aromatic nitro compounds to amines is a very useful synthetic transformation for which a vast array of reagents has been developed.^[6–8] The most general methodology used for this conversion is catalytic hydrogenation,^[9–13] as it is an economical and effective method, particularly in large-scale reactions. However,

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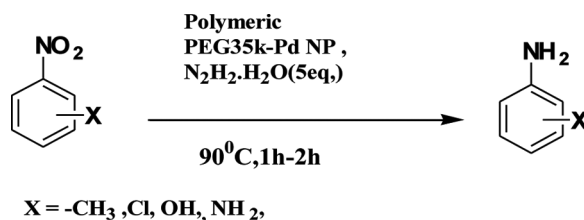
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these reactions have limited utility in the presence of other reducible functional groups.^[14] Catalytic hydrogenation of nitroarenes over heterogeneous catalysts is a simple method for the production of aromatic amines. However, the application of conventional catalytic systems to the reduction of nitroarenes containing other reducible functional groups (e.g., halogen, carbonyl, cyano, benzyloxy, and alkenic groups) is problematic because the reaction is often accompanied by the reduction of these functional groups.^[15–17] It is well known that the catalytic properties of heterogeneous catalysts are dependent on the particle size of the metal and the surface structure of the supports.^[18–20] Now transition-metal nanoparticles are found to be effective catalysts for these chemical transformations because of their large surface area and unique combination of reactivity, stability, and selectivity. In most cases, the use of different catalysts under a wider range of reaction conditions yields the corresponding amine quantitatively, without the production of waste products. Because of the exothermic nature of the reaction and the requirement for a secluded high-pressure system, numerous safety precautions have to be taken. Palladium charcoal system is flammable at room temperature, so these systems have handling problems. Besides this, generally used methods^[21–24] require either strong acid medium, hazardous molecular hydrogen, or high-pressure reactors that corrode the reaction equipment. Compared to the conventionally used methods, contemporary catalytic transfer hydrogenation is a safer and greener way that is attracting more and more attention.^[25–29] Hydrazine hydrate is widely employed as hydrogen donor in catalytic transfer hydrogenation because the hydrazine reduction produces harmless by-products such as nitrogen gas and water. The reduction of aromatic nitro compounds using hydrazine or hydrazine hydrate represents a special variation of the catalytic reduction, where hydrazine is the source of the hydrogen. The hydrogen can be generated by a variety of H-transfer catalysts.^[30–32] Especially with the use of noble metal catalysts, such as Pd, Pt, or Ru, the catalytic hydrazine reduction gives good yields comparable to or better than the catalytic hydrogenation. When hydrogenating halo-nitro aromatics to the corresponding amines, hydrodehalogenation is often an undesired side reaction. The ease with which the hydrodehalogenation occurs depends on the ring position of the halogen.^[33] Therefore, the search continues for a better catalyst for the synthesis of aniline derivatives in terms of mild reaction conditions, operational simplicity, economic viability, and selectivity.^[34] Simple and widely available polymers like such as poly(ethylene glycol) (PEG) as nontoxic, inexpensive, nonionic, thermally stable, recoverable liquid solvents of low volatility have been used for various transformations.^[35–41] Transition-metal nanoparticles have wide-ranging applications in catalysis. However, because of their large surface area and surface energy, they tend to agglomerate during the reactions and therefore need to be stabilized for effective utilization.

RESULTS AND DISCUSSION

Herein, we report for the first time the use of polymeric PEG35k-Pd nanoparticles as catalyst in the reduction of nitroarenes to the corresponding aromatic amines (Scheme 1).

We expect that the present study could accelerate the investigation of polymeric PEG35k-Pd nanoparticles as a catalyst in organic synthesis. A common method to



Scheme 1. Reduction of nitroarenes.

prepare metal nanoparticles involves reduction of metal ions in the presence of stabilizers such as a surfactant and polymers. We report a novel and facile route for the preparation of Pd nanoparticles by exploiting PEG, molecular weight 35000 (MW35k), which was found to act as both reducing agent and stabilizer.^[42] The prepared polymeric PEG35k-Pd nanoparticles can be preserved for months without any change of physical and chemical properties. It was noted that prepared nano-Pd provides the active and recyclable heterogeneous catalyst for the nitro group reduction in the absence of phosphine ligands. The reaction was insensitive to the air and moisture with good yields, and polymeric PEG35k-Pd nanoparticles can be readily recycled more than 8 times (Fig. 1) without deactivation. Polymeric PEG35k-Pd nanoparticles were found to act as efficient reduction catalysts for the conversion of nitroarenes to anilines derivatives in high turn over numbers (TONs) without affecting the reduction of halogen or other functional groups. Control experiments of nitroarene reduction were performed in the absence of polymeric PEG35k-Pd nanoparticles according to the general procedure with reagent hydrazine hydrate at 90–120 °C for 360 min. The reactions did not produce any desired product. This clearly showed that the presence of both polymeric PEG35k-Pd nanoparticles and hydrazine hydrate played important roles in the reduction of nitroarenes in our reaction system. Preparation of polymeric PEG35k-Pd nanoparticles was achieved successfully by the reaction of Pd (OAc)₂ with PEG35k solution in water at room temperature under an open atmosphere. Pd(II) ions reduced to Pd(0) because of the presence of the terminal –OH functional group present in polymer PEG35000 at 90 °C for 2 h (Scheme 2).

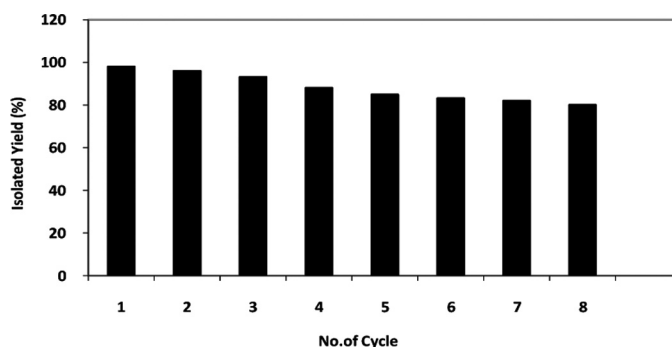
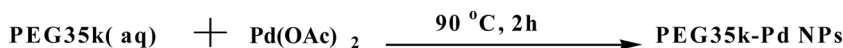


Figure 1. Experiments reusing polymeric PEG35-Pd nanoparticles in the reduction of nitroarenes by hydrazine hydrate.



Scheme 2. Synthesis of polymeric PEG35k-Pd nanoparticles.

Polymer PEG35k was used for the immobilization of palladium metal, where the metal particles could be highly dispersed on the surface of polymer. Polymeric PEG35k-Pd nanoparticle size was found to be 28 ± 4 nm [Polymeric PEG35k-Pd nanoparticles were characterized by quasi elastic light scattering (QELS) and transmission electron microscopy (TEM) (Figs. 2a and 2b. For X-ray diffraction and ultraviolet, see the Supporting Information, available online).

The polymeric PEG35k-Pd nanoparticles were used in the catalytic reduction of the nitro group of nitroarenes derivative (Scheme 1). The reaction of nitroarene derivative was carried out in the presence of the catalyst in $\text{N}_2\text{H}_2 \cdot \text{H}_2\text{O}$ at 90°C temperature (Table 1). All of the Polymeric PEG35k-Pd nanoparticles exhibited good to excellent catalytic efficiency in the reduction of the nitro group. Entry 1 (Table 1) was consumed within 90 min, and high turnover frequencies reached. The selectivity of the reduction of p-chloroaniline (Entry 8, Table 1) was highly dependent on the polymeric PEG35k-Pd nanoparticles. The product yield obtained in the reaction with polymeric PEG35k-Pd nanoparticles was similar to that of commercially available Pt/C, ^[43] producing large amounts of aniline (entry 1, Table 1). Catalytic reduction of other nitroarene derivatives (entries 1–14) was also achieved with high chemoselectivity by using the polymeric PEG35k-Pd nanoparticles. The results shown in Table 1 suggest that the reduction of nitroarenes over polymeric PEG35k-Pd nanoparticles is tolerant toward halogens and other functional groups. Besides the efficiency and selectivity, the reduction over polymeric PEG35k-Pd nanoparticles has two more advantages: Reusability without leaching of palladium species and possible application to produce anilines in gram quantities.

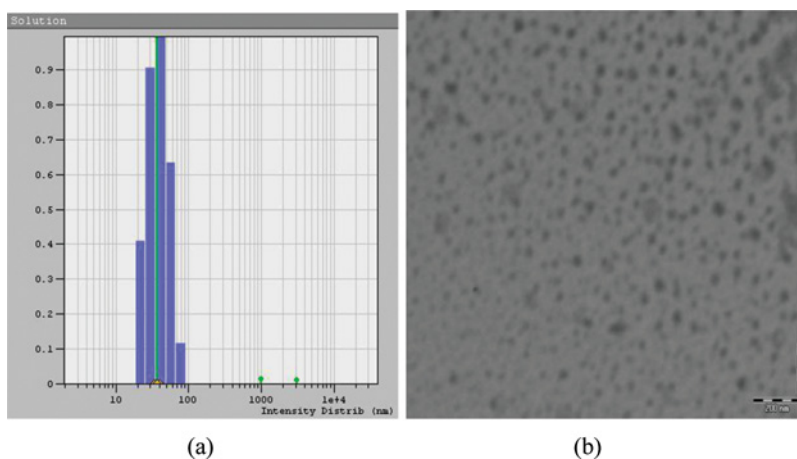
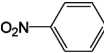
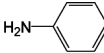
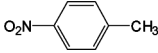

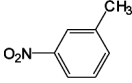
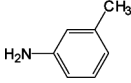
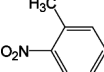
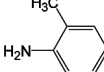
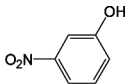
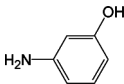
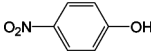
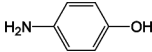
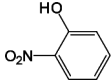
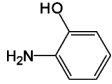
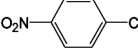
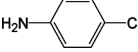
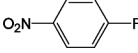
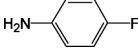
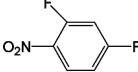
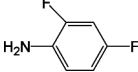
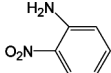
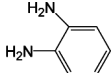


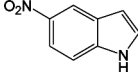
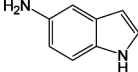
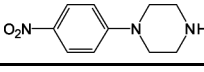
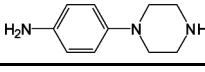


Figure 2. (a) QELS data of PEG35k-Pd: plot of population distribution in percentile size distribution in nanometers. Mean: 36.06, standard deviation: 3.108, polydispersity: 0.007 standard deviation/mean². (b) TEM micrographs of polymeric PEG35k-Pd nanoparticles. (Figure is provided in color online.)

Table 1. Reduction of substituted nitroarenes with hydrazine hydrates in the presence of polymeric PEG35k-Pd NPs to corresponding anilines

Entry	Substrate	Product	Time (min.)	Yield (%)	Reference
1			90	100	[44]
2			100	99	[44]
3			110	97	[44]
4			100	98	[44]
5			120	98	[44]
6			110	98	[44]
7			120	99	[44]
8			90	99 ^a	—
9			90	99 ^a	—
10			80	99 ^a	—
11			70	100 ^a	—
12			60	100 ^a	—
13			90	99 ^a	—
14			100	100 ^a	—

Note. Reaction conditions: All reactions were carried out with nitroarenes (1 mmol), hydrazine hydrate (5 eq), and polymeric PEG35k-Pd NPs (1.0 mol%) at 90 °C for 1–2 h in open atmosphere. Products characterized by ¹H and ¹³C NMR and mass spectroscopic data.

^aIsolated yields.

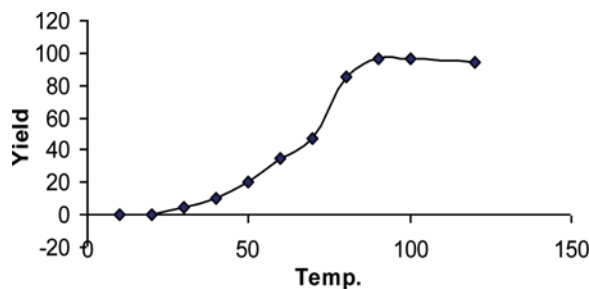


Figure 3. Effect of temperature on product yield with temperature variation. (Figure is provided in color online.)

Temperature Effect

To elucidate the effect of temperature on the reaction conditions, we used different temperature conditions in our nitro reduction to evaluate the scope and limitation of the reactions. We found that polymeric PEG35k-Pd nanoparticles catalyzed reduction of aromatic nitro compounds efficiently at 90 °C. Interestingly, the reaction yield decreases at high as well as low temperature conditions. (Fig. 3).

Optimization of Reaction Conditions

Table 2 shows the optimization of reaction in different conditions. At the high temperature, the reaction yield goes down. Entries 2, 8, and 9 (Table 2) indicate at low temperature, low concentration of hydrazine hydrate and low amount of catalyst loading the reaction yield is poor because of the need for higher activation energy. Entry 3 (Table 2) shows that the polymeric PEG35k-Pd nanoparticles loading 1 mol% at 90 °C and 5 equivalents hydrazine hydrate have greatest activity for direct reduction of nitrobenzene to aniline under mild conditions.

Table 2. Results of nitrobenzene reduction to form aniline with supported catalyst 1 mol % polymeric PEG35k-Pd nanoparticles at different reaction conditions

No.	Catalyst (mol %)	Temp. (°C)	N ₂ H ₄ · H ₂ O (eq)	Reaction time (min)	Conversion (%)
1	1.0	90	1	120	25
2	1.0	90	4	120	78
3	1.0	90	5	90	100
4	1.0	90	10	120	97
5	1.0	90	5	360	96
6	0.5	90	5	120	85
7	0.5	90	10	360	85
8	1.0	50	5	360	30
9	1.0	80	5	360	85
10	1.0	100	5	120	96
11	1.0	120	5	120	94

Recyclability

To check the reusability of the polymeric PEG35k-Pd nanoparticle catalyst, consecutive cycles were executed, and their results are depicted in Fig. 3. The polymeric PEG35k-Pd nanoparticles could be recycled by separating them from the reaction mixture by mild centrifugation and used as a catalyst for the same reaction again to check for any changes in their catalytic activity. With increasing number of cycles, the catalytic activity of the polymeric PEG35k-Pd nanoparticles decreased, and it was lost after eight cycles. The graphical presentation of the relation between the number of cycles of the reaction and the catalytic activity in terms of yield is presented in Fig. 1.

CONCLUSION

In conclusion, we have developed an exceedingly efficient and highly chemoselective approach to prepare aromatic amines from the corresponding nitroarene compounds using hydrazine hydrate over polymeric PEG35k-Pd nanoparticles. This method is simple and environmentally friendly. The present study opens up the application of polymeric PEG35k-Pd nanoparticles as catalyst in the reduction of nitroarenes. A detailed mechanistic study is now under investigation. Further studies to explore the application of PEG35k-Pd nanoparticles as catalyst in other reactions are under way.

EXPERIMENTAL

Typical Experimental Procedure for Preparation of PEG35k-Pd Nanoparticles

Palladium acetate $\text{Pd}(\text{OAc})_2$ (0.5 mmol) and solid PEG, mol. wt. 35000 (1.0 mmol), were added to water as a solvent. The resulting solution was heated to 90°C and remained at this temperature for 2 h. The color of the solution turned from orange to brown and finally turned black, indicating the formation of Pd(0) metal. Then the mixture of PEG35k and palladium nanoparticles was cooled immediately to ambient temperature to form a solidified mixture. The solids were washed with doubly distilled water (10 ml) and ether (20 ml) and dried under vacuum at room temperature for 5 h to afford the corresponding polymeric PEG35k-Pd nanoparticles. Particle sizes were characterized by QELS, TEM, UV spectroscopic techniques. The average size of polymeric PEG35k-Pd nanoparticles was found to be 28 ± 4 nm.

Typical Experiment Procedure for the Reduction of Aromatic Reduction Compounds

Reduction of nitroarenes was performed in a 10 ml, round-bottom flask in the presence of nitroarenes (entries 1–14) (1.0 mmol), polymeric PEG35k-Pd NPs (1 mol % polymeric PEG35k-Pd NPs), and hydrazine hydrate (5 equivalents) in an open atmosphere at 90°C . After the reaction was completed, polymeric PEG35k-Pd NPs were removed by centrifugation. The solution was filtered through a pad of Celite, and then saturated aqueous NaHCO_3 (10 ml) was added to the filtrate and

extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure, and purified by the column chromatography to give the aniline derivatives. Products were characterized by ^1H NMR and ^{13}C NMR and mass spectra. The removed polymeric PEG35k-Pd NPs were washed with water and diethyl ether, dried under vacuum, and then reused.

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