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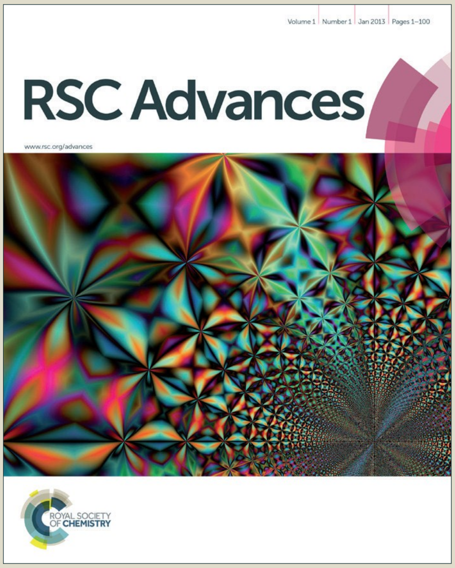

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ARTICLE

Synthesis of polyamides using palladium-on-carbon (Pd/C) as a heterogeneous, reusable and ligand-free catalytic system

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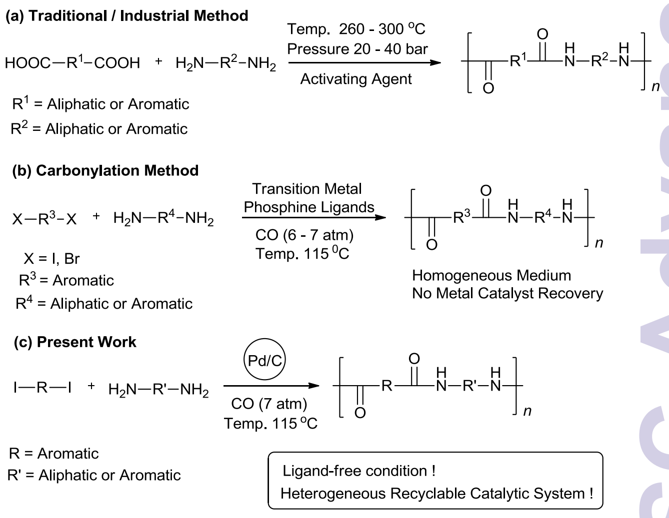
This work reports the synthesis of polyamides using an efficient, ligand free and Pd/C-catalyzed protocol. Various polyamides can be synthesized by carbonylation polycondensation reaction of aromatic diiodides, diamines and carbon monoxide using Pd/C as a heterogeneous and recyclable catalyst. Variation in inherent viscosities observed with the structure of diamine component. Notably this synthetic route does not require any ligand and give high yield of the polyamides. Catalyst Pd/C can be recovered easily and was characterized using XPS analysis. The Catalyst was recycled five times without substantial loss in activity.

Introduction

Polyamide polymers are ideal class of high performance materials that have attracted great industrial interest due to their unique strengths, gas barrier and dye-pickup properties.[1] Their potential application fields are emerging including fibre, film, engineering plastic and PET industries.[2] The presence of strong intermolecular hydrogen bonding interaction due to amide linkage plays the important role for good thermal and mechanical properties.[3] Traditionally or industrially these polymers are prepared by the reaction of aromatic diacids or their suitable derivatives such as acid chlorides and various diamines (Scheme 1).[4] On the basis of academic and industrial interest in these materials, development of alternate synthetic route has been the prime focus for various researchers in recent times. Palladium catalyzed carbonylation-polycondensation reactions are the alternate methods for the synthesis of several high performance polymer like polyamides, polyimides, polyketones, polyesteramides etc. Notably these synthetic methods not only eliminate the use of corrosive, hydrolytically sensitive acid chlorides but also converting the cheap, easily available carbon monoxide gas into useful polymer. Moreover these monomers are difficult to prepare and require a number of synthetic steps. These diiodinated aromatic compounds can be prepared by the direct iodination of various aromatic compounds.[5]

Various homogeneous catalytic systems along with phosphine ligands are reported for the synthesis of polyamide using aromatic di-halides with diamine compounds under carbonylation method (Scheme 1).[6] Phosphine ligands are very much costly and air sensitive, require tedious work-up procedures to separate it from product and high workup costs which place significant limits on their synthetic applications. In our previous work we have successfully synthesized polyesteramide by using immobilized palladium metal containing ionic liquid on SBA-15 as a phosphine free catalytic system in heterogeneous medium.[7] It is well known that Pd/C as heterogeneous and ligand-free catalyst and well explored for various carbonylation, cross-coupling reactions.[8]

To extend our continued interest in this ligand-free carbonylation[9] polymerization process we have developed an efficient, ligand free protocol for the synthesis of polyamides from carbon monoxide, aromatic diiodides and diamines in the presence of Pd/C catalyst (Scheme 1).



Scheme 1 Comparison of previous traditional, industrial and carbonylation methods with the present work.[1a, 4, 6]

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During the course of our investigation on carbonylation-polycondensation we observed the change in inherent viscosities with different structure of diamines. Advantageously this method, avoids use of the air sensitive phosphine ligand, lower reaction time and easy recovery of Pd/C from the reaction mixture by simple filtration, providing excellent yield of desired polyamides.

Result and Discussion

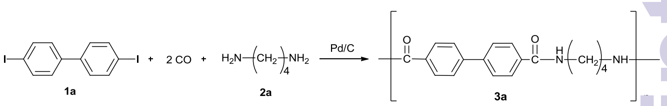
Initially we examined the model reaction between aromatic diiodides such as 4,4'-diiodo-1,1'-biphenyl **1a** and tetramethylenediamine **2a** in the presence of carbon monoxide for the carbonylation-polycondensation reaction using the Pd/C as catalyst. The various reaction parameters such as catalyst loading, solvent, bases, temperature and pressure are screened for the present protocol. Considering the reaction time, yield, and inherent viscosity of the polyamide **3a**, we examined the effect of Pd/C loading on the model polymerization (Table 1). The catalyst loading could be increased to 10 mol% with the increase in the yield of the desired product **3a**, while reducing the catalyst loading results in lower yields and inherent viscosity of the polyamide **3a**. Before proceeding to further investigations, it was important to confirm that the product obtained was **3a**. The infrared spectrum of the product **3a** in KBr pellets showed characteristic frequencies corresponding to amide carbonyl functional groups (around 1630 cm^{-1}) and amide N-H stretch around 3307 cm^{-1}.

The ^{1}H and ^{13}C NMR spectrum of the product **3a** carried out in DMSO solvent. The aliphatic protons appear at 1.25 ($–CH_2–$), 3.23 ($–NH–CH_2–$), and the aromatic protons appear at 7.83 and 7.94. The signal at 8.54 is due to the amide proton (–NH–CO). The ^{13}C NMR spectrum also clearly indicated peaks at 165.6 corresponding to amide carbonyl (-C=O) group. TGA analysis showed that polymer **3a** began to decompose around 320 °C. The DSC analysis of product **3a** showed glass transition temperature at 60 °C and the melting point around 155 °C.

After confirmation of the polymer obtained was desired polyamide, we investigated the effects of different solvents such as *N*-methyl-2-pyrolidone (NMP), dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMAc) for the present carbonylation-polycondensation reaction using the 10% Pd/C-catalyst. The results are presented in Table 2 (entries 1-4). Looking to the yield and inherent viscosity, DMAc appears to be the most suitable solvent for the present protocol (Table 2, entry 4).

Base screening study showed that DBU brings out the highest yield of the product as compared to inorganic and other organic bases (Table 2, entries 5-8). It is observed that inorganic bases are found almost ineffective in these reactions. Highest yield (86%) and highest inherent viscosity (0.36 dLg^{-1}) of polyamide **3a** was obtained by using the DBU as base. The additional advantage of DBU is that it has the ability to swell the resulting polymer apart from acting as an acid acceptor.[3] Next we examined the effect of different CO pressure on reaction profile (Table 2, entries 9-11).

Table 1 Effect of dose of Pd/C on the reaction.[a]



Entry	Catalyst	Catalyst loading (mol%)	Yield [%][b]	η_{inh} (dL/g)
1	5% Pd/C	10	59	0.22
2	10% Pd/C	5	57	0.11
3	10% Pd/C	6	71	0.17
4	10% Pd/C	8	80	0.28
5	10% Pd/C	10	86	0.36
6	10% Pd/C	12	87	0.32

[a] Reaction conditions: **1a** (5 mmol), **2a** (5 mmol), CO (7 atm), DMAc (20 mL), agitation: 700 rpm, Temperature 115 °C, Time 70 min; [b] Isolated yield.

The effect of CO pressure showed that reaction could be carried out at 1 atm pressure but gave a higher yield and inherent viscosity of polyamide **3a** at 7 atm of CO pressure. It was observed that the rate of CO adsorption was very high using the 10 mol% Pd/C catalyst. Nearly three atmosphere of CO drop was observed at 115 °C temperature in 15 minute time duration. This might be due to the high surface area of the catalyst. Further increase in CO pressure has no profound effect on yield and viscosity of polyamide **3a** (Table 2, entry 11).

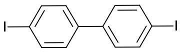
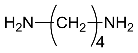
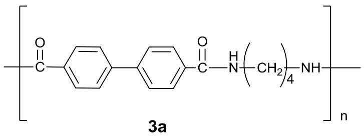
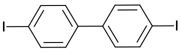
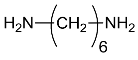
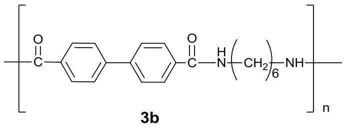
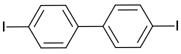
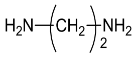
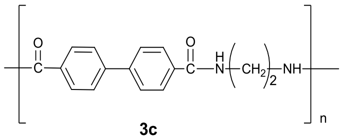
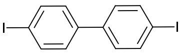
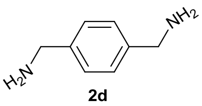
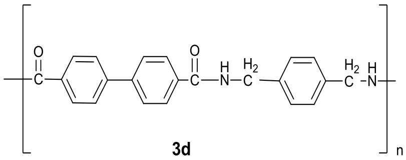
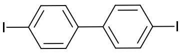
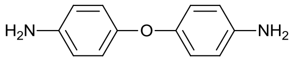
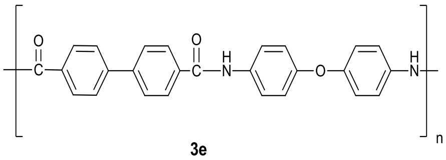
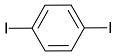
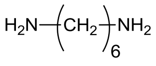
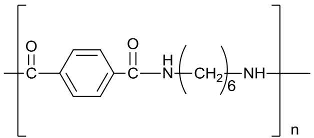
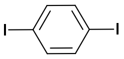
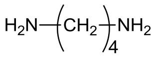
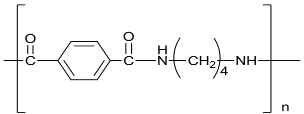
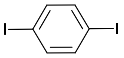
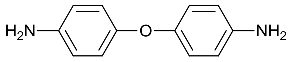
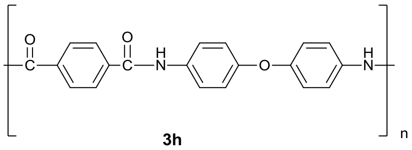
The temperature of the reaction was also important for the effective progress of the Pd/C-catalyzed carbonylation-polycondensation reaction (Table 2, entries 12-14). The inherent viscosity was strongly influenced by temperature. At 115 °C the highest inherent viscosity and CO absorption was observed.

Table 2 Optimization of the Pd/C-catalyzed carbonylation-polycondensation reaction.[a]

Entry	Solvent	Base	Press. (atm)	Temp °C	Yield [%][b]	η_{inh} (dL/g)
Effect of Solvent						
1	NMP	DBU	7	115	48	0.10
2	DMSO	DBU	7	115	78	0.30
3	DMF	DBU	7	115	68	0.22
4	DMAc	DBU	7	115	86	0.36
Effect of Base						
5	DMAc	DABCO	7	115	72	0.15
6	DMAc	Et3N	7	115	26	0.08
7	DMAc	Na_2CO_3	7	115	12	0.0[illegible]
8	DMAc	NaOH	7	115	18	0.07
Effect of CO Pressure						
9	DMAc	DBU	1	115	32	0.1[illegible]
10	DMAc	DBU	4	115	81	0.23
11	DMAc	DBU	8	115	86	0.32
Effect of Temperature						
12	DMAc	DBU	7	90	75	0.1[illegible]
13	DMAc	DBU	7	110	78	0.26
14	DMAc	DBU	7	125	83	0.1[illegible]

[a] Reaction conditions: **1a** (5 mmol), **2a** (5 mmol), 10% Pd/C (10 mol%), agitation: 700 rpm, time 70 min; [b] Isolated yield.

Table 3 Pd/C catalysed synthesis of polyamides under ligand free conditions.[a]

Entry	Diiodide	Diamine	Product	Yield[b]	η_{inh} (dL/g)
1	 **1a**	 **2a**	 **3a**	86	0.36
2	 **1a**	 **2b**	 **3b**	79	0.24
3	 **1a**	 **2c**	 **3c**	71	0.15
4	 **1a**	 **2d**	 **3d**	47	0.16
5	 **1a**	 **2e**	 **3e**	73	0.34
6	 **1b**	 **2b**	 **3f**	82	0.17
7	 **1b**	 **2a**	 **3g**	79	0.10
8	 **1b**	 **2e**	 **3h**	72	0.32

[a] Reaction conditions: diiodide (5 mmol), diamine (5 mmol), 10% Pd/C (10 mol%), CO (7 atm), agitation: 700 rpm, temp: 115 °C, time 70 min; [b] Isolated yield.

The low inherent viscosities of the polymers **3a** at low temperature could be because of the low reaction rate (Table 2, entry 12 and 13). At higher temperature, we observed the lower inherent viscosity of polyamide **3a** (Table 2, entry 14).

In order to study the potential and general applicability of developed methodology, various diamines and diiodides were investigated (Table 3). The varieties of polyamides derivatives were prepared using this approach under optimised reaction conditions. The polymers exhibited distinct and characteristic IR frequencies corresponding, amide carbonyl functional groups (around 1630 cm^{-1}) and amide N-H stretching frequency (around 3310 cm^{-1}).

Thermogravimetric analysis (TGA) indicated that all polymers were stable in air up to at least 320 °C (Fig. 1). The NMR spectrum indicates the absence of any amine linkages, at least in detectable amounts, (arising because of competing *N*-arylation reactions) and confirms the structural homogeneity of the polyamide produced by the Pd/C catalysed carbonylation route under heterogeneous and ligand-free condition.

The reusability of Pd/C is a great advantage in decreasing environmental pollution and cost reduction in process chemistry. The effect of reused times of Pd/C on catalytic activity is shown in Table 4. We examined the reuse of Pd/C in the carbonylation-polycondensation reaction using **1a** and **2a** as substrates in the presence of CO at 115 °C temperature. Pd/C could be reused successfully until the five run without significant loss of yield or extension of the reaction time. We also performed the leaching study of palladium metal after first and fifth recycle runs. Pd metal was not detected within the limits of the assay (<1 ppm) by analysis with inductively coupled plasma atomic emission spectrometry (ICP-AES).

The XPS spectrum and content of each element are shown in Fig. 2a, which proves that the catalyst used in this experiment is composed of elements Pd, C and O. High resolution spectra of element Pd (Fig. 2b) show that 336 eV and 341 eV represent Pd^{2+} in fresh Pd/C catalyst and the two peaks are resulted from spin splitting of Pd(II). It suggests that Pd(II) does exist in the fresh Pd/C catalyst which can promote the carbonylation-polycondensation of diiodides and diamines. For the 1st and 5th recycle catalyst both peaks tend to shift to lower binding energies (334.3 eV and 339.4 eV), which are assigned as 3d$_{5/2}$ and 3d$_{3/2}$ for Pd^0 species suggesting that the catalysts are reduced but the activity of the Pd species remains constant for the reaction. Figure 2c and 2d showed the presence of the carbon and oxygen species in fresh and reused catalyst. For the 1st recycle and the 5th recycle catalysts, in the I 3d region, two intensive peaks appear at 617.8 eV (I 3d$_{5/2}$) and 629.2 eV (I 3d$_{3/2}$), indicating that adsorption of iodide atoms takes place on the surface of carbon (Fig. 2e).

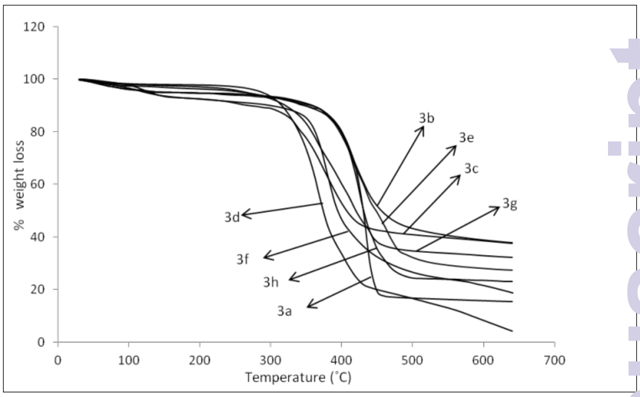
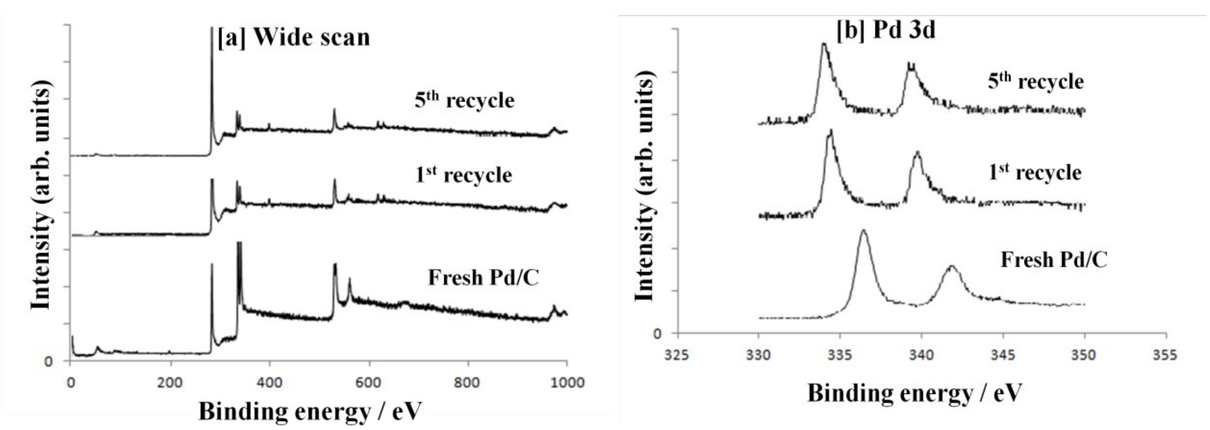


Fig. 1 TGA curves for polyamides prepared by Pd/C catalysed carbonylation-polycondensation reaction

Table 4 Investigation into the reuse of Pd/C.[a]

Entry	Run	Yield[%][b]	η_{inh} (dL/g)
1	1	87	0.36
2	2	87	0.35
3	3	86	0.35
4	4	85	0.34
5	5	85	0.34

[a] Reaction conditions: **1a** (5 mmol), **2a** (5 mmol), 10% Pd/C (10 mol%), CO (7 atm), agitation: 700 rpm, temp: 115 ^{o}C, time 70 min; [b] Isolated yield.



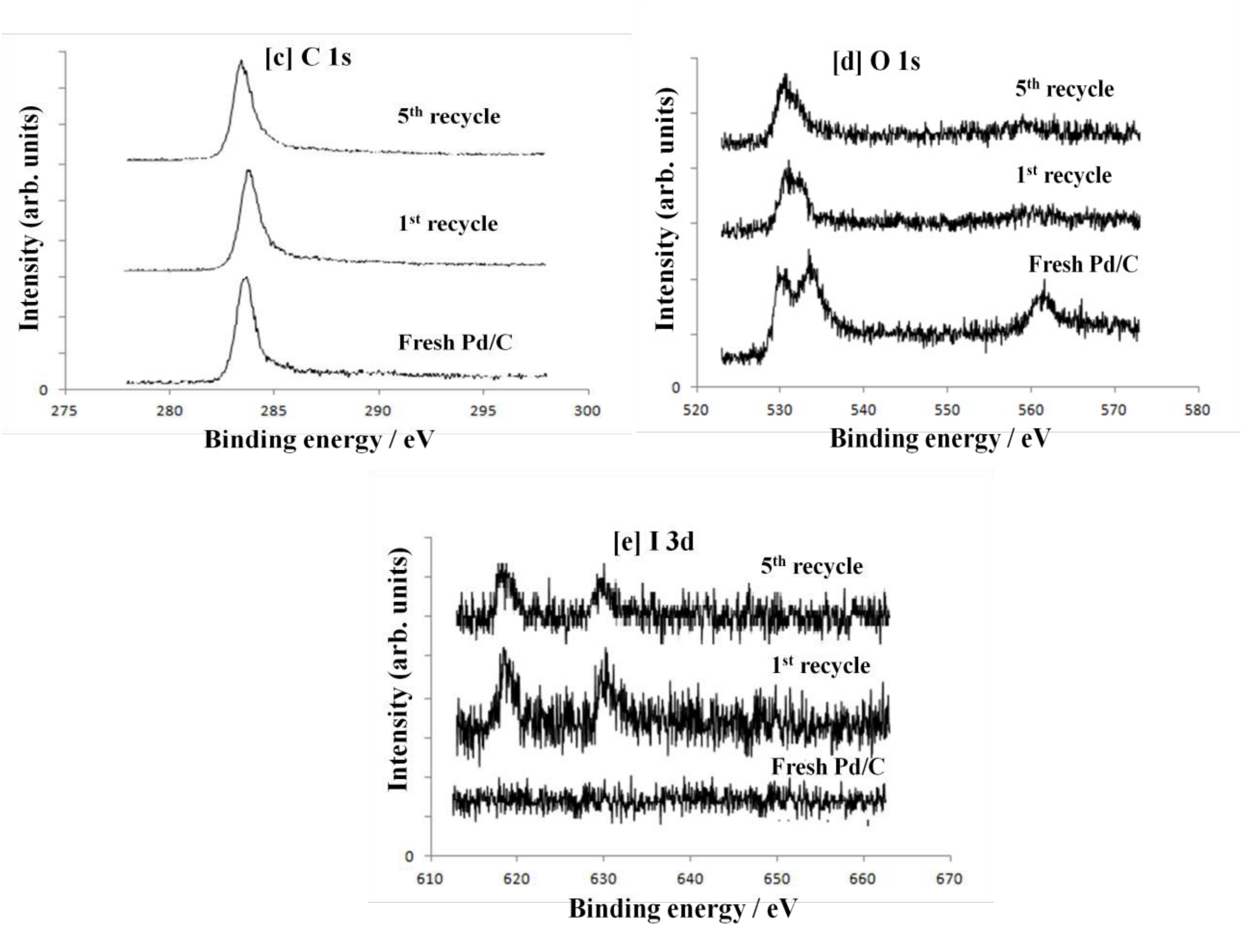


Fig. 2 XPS spectra of the fresh and reused Pd/C catalyst; [a] wide scan; [b] Pd 3d; [c] C 1s; [d] O 1s; [e] I 3d

Conclusions

In conclusion, we have described an economical and easily available palladium based catalyst (Pd/C) for the synthesis of polyamide by carbonylation-polycondensation reactions. The catalyst was isolated by simple filtration process and recycled up to five recycle providing the excellent yield of the desired product. The carbonylation route proposed here eliminates the need for diacid derivatives and provides a cleaner synthetic route for the synthesis of polyamide using Pd/C as a heterogeneous and reusable catalyst. XPS studies of recycle catalyst shows the presence of active palladium species on carbon surface. Though this proposed protocol offers a possible alternative to conventional methods of preparing polyamides, the low inherent viscosity of the polymer is the limitation at present. We are currently investigating the potential application of this low viscosity polyamide polymer by blending with other polymers. The protocol would be practical for use as an economical synthetic method and offer an alternative synthetic strategy for the practical construction of polyamide derivatives.

Experimental section

Materials and Methods

The Pd/C was commercially purchased from Sigma-Aldrich (10 wt.% loading, matrix: activated carbon support, Product Number: 205699, Brand: Aldrich) and were used as such. All the chemicals and solvents were purchased from different commercial sources like sigma Aldrich, S.D Fine chemicals and Lancaster (Alfa-Aesar) were used as received without further purification. The IR spectra were recorded with FT-IR using KBr pellets. The DSC and TGA were performed on the Perkin Elmer instrument. Inherent viscosity (η) was measured at a concentration of 0.5 g.dL^{-1} in DMAc at 30 ^{o}C. The ^{1}H and ^{13}C NMR spectra were recorded with 300 MHz FT-NMR spectrometer using DMSO solvent. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. The XPS of Pd/C was measured using a PHI5000 Versa Probe with a monochromatic focused (100×100 μm) Al Kα X-ray radiation (15 kV, 30 mA) and dual beam neutralization using a combination of Argon ion gun and electron irradiation.

General experimental procedure for polyamide synthesis by carbonylation-polycondensation reaction

Aromatic diiodides (5 mmol), diamine (5 mmol), 10% Pd/C (10 mol%), DBU (10 mmol) and DMAc (20 mL) were added to a 100-mL stainless steel autoclave. The autoclave was closed and was flushed thrice with high purity nitrogen. The reactant mixture was heated up to 115 °C with low stirring. After stabilization of reactor temperature, the autoclave was pressurised with 7 atm of CO. The reaction mixture was stirred with a mechanical stirrer (700 rpm) for 70 minutes. After cooling it to room temperature, the pressure carefully released. The reactor was washed with DMAc to isolate trace of product and catalyst if present. Then the reaction mixture was filtered and the filtrate was poured in 350 mL of distilled water. The precipitate was filtered and dried in vacuum. The compounds were characterized by various techniques such as FT-IR, ^{1}H, ^{13}C NMR and TGA.

Typical Procedure for Reuse of Pd/C

After the dissolution of reaction mixture in DMAc, reaction mixture was passed through a filter paper. The recovered Pd/C was washed with DMAc (5 × 10 mL) to remove trace amounts of product if present and finally with methanol (5 × 2.5 mL). The resulting Pd/C was dried in vacuum, and used for catalyst recyclability experiment.

Characterisation data of the products

[3a] IR (KBr): 3307, 1629 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 8.54 (br. NH), 7.94 (ArH), 7.83 (ArH), 3.23 (CH), 1.25 (CH); ^{13}C NMR (75 MHz, DMSO) δ 165.6 (C=O), 141.5, 133.9, 127.8, 126.6, 29.1, 26.1; Anal. Calcd. (%): Theoretical: C (73.46), H (6.12), N (9.52) Experimental: C (73.25), H (5.92), N (9.63).

[3b] IR (KBr): 3313, 1629 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 8.59 (br. NH), 7.98 (ArH), 7.84 (ArH), 3.28 (CH), 1.52 (CH), 1.32 (CH); ^{13}C NMR (75 MHz, DMSO) δ 165.7 (C=O), 141.5, 134.0, 127.9, 126.7, 29.1, 26.2, 26.1; Anal. Calcd. (%): Theoretical: C (74.53), H (6.83), N (8.69) Experimental: C (74.41), H (6.97), N (8.45).

[3c] IR (KBr): 3294, 1647 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 8.69 (br. NH), 7.95 (ArH), 7.86 (ArH), 3.30 (CH); ^{13}C NMR (75 MHz, DMSO) δ 166.1(C=O), 141.6, 133.8, 127.9, 126.7, 29.2; Anal. Calcd. (%): Theoretical: C (72.18), H (5.26), N (10.52) Experimental: C (71.74), H (5.34), N (10.15).

[3d] IR (KBr): 3296, 1647 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 9.12 (br. NH), 8.04 (ArH), 7.85 (ArH), 7.31 (ArH), 4.48 (CH); ^{13}C NMR (75 MHz, DMSO) δ 164.7 (C=O), 141.7, 138.1, 133.8, 130.0, 128.0, 127.2, 42.4; Anal. Calcd. (%): Theoretical: C (77.19), H (5.26), N (8.18) Experimental: C (76.55), H (5.88), N (7.76).

[3e] IR (KBr): 3309, 1644 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 10.30 (br. NH), 8.08 (ArH), 7.92 (ArH), 6.93 (ArH), 6.84 (ArH); ^{13}C NMR (75 MHz, DMSO) δ 164.8 (C=O), 154.1, 148.8, 141.9, 133.9, 128.4, 126.8, 122.1, 120.1; Anal. Calcd. (%): Theoretical: C (76.84), H (4.43), N (6.89) Experimental: C (76.35), H (4.92), N (7.37).

[3f] IR (KBr): 3303, 1644 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 8.56 (br. NH), 7.90 (ArH), 3.26 (CH), 1.52 (CH), 1.32 (CH); ^{13}C NMR (75 MHz, DMSO) δ 165.5 (C=O), 136.8, 127.1, 29.1, 26.2, 26.1; Anal. Calcd. (%): Theoretical: C (69.42), H (5.78), N (11.57) Experimental: C (69.01), H (5.86), N (11.13).

[3g] IR (KBr): 3307, 1630 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 8.58 (br. NH), 7.89 (ArH), 3.30 (CH), 1.56 (CH); ^{13}C NMR (75 MHz, DMSO) δ 165.5 (C=O), 136.7, 127.1, 29.3, 26.7; Anal. Calcd. (%): Theoretical: C (67.28), H (4.76), N (13.08) Experimental: C (66.53), H (5.12), N (12.46).

[3h] IR (KBr): 3306, 1613 cm^{-1}; ^{1}H NMR (300 MHz, DMSO) δ 10.42 (br. NH), 8.09 (ArH), 7.05 (ArH), 6.90 (ArH); ^{13}C NMR (75 MHz, DMSO) δ 164.7 (C=O), 153. 144.8, 134.5, 127.6, 122.2, 120.5; Anal. Calcd. (% Theoretical: C (72.72), H (4.42), N (8.48) Experimental: C (71.51), H (5.12), N (9.06).

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Table of contents entry/ Graphical abstract

Synthesis of polyamides using palladium-on-carbon (Pd/C) as a heterogeneous, reusable and ligand-free catalytic system

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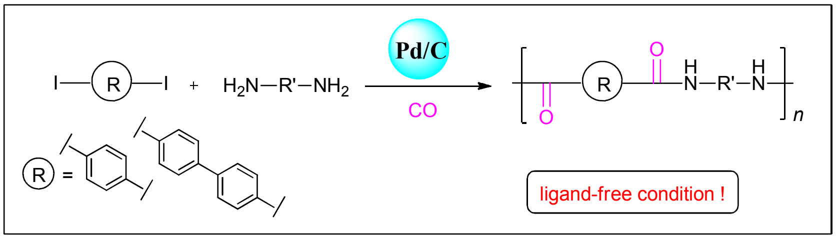

Polyamide has been synthesized by the carbonylation-polycondensation reaction of aromatic diiodides and diamines in the presence of Pd/C as a heterogeneous, phosphine-free and reusable catalytic system. The catalyst solves the basic problem of catalyst recovery and furnishes good to excellent yield of polyamide.