

Palladium(II)-catalyzed synthesis of polyamides (aramids) from aromatic dichlorides, diamines, and carbon monoxide

Jang Sub Kim, Ayusman Sen *

Department of Chemistry, Pennsylvania State University, University Park, PA 16802, USA

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Abstract

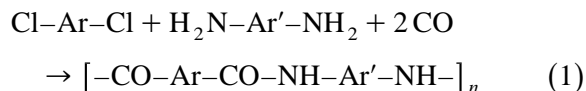
A novel catalytic procedure for the synthesis of polyamides (aramids) from aryl dichlorides, aryl diamines, and carbon monoxide has been developed. Palladium complexes incorporating bulky ligands, such as dippp (dippp = 1,3-bis(diisopropylphosphino)propane), are suitable catalysts for the reaction. Polyamides exhibiting inherent viscosity between 0.10 and 0.40 dl g⁻¹ were obtained. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Palladium complex; Carbonylation; Polyamides; Aramids

1. Introduction

Aromatic polyamides (aramids) constitute a technologically important class of high-strength polymeric materials. These are currently synthesized commercially by the polycondensation reaction between aromatic diacid derivatives and diamines [1,2]. An alternative procedure would involve the catalytic amidocarbonylation of aryl dihalides using diamines and carbon monoxide. Indeed, the palladium-catalyzed synthesis of polyamides through this route starting with aryl dibromides and diiodides has been reported [3–8]. Although relatively unreactive [9,10], the use

of significantly less expensive aromatic dichlorides as starting materials would be far more attractive from a commercial standpoint (Eq. (1)). In this paper, we report the first examples of catalytic formation of polyamides from aryl dichlorides, diamines and carbon monoxide.



2. Experimental section

2.1. Measurements

The ¹H, ³¹P and ¹³C NMR spectra were obtained on a Bruker AM300 FT-NMR spectrometer. The chemical shifts were referenced to

* Corresponding author. E-mail: asen@chem.psu.edu

internal standard in a sealed capillary tube or to the solvent resonance at the appropriate frequency. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Viscosity measurements were carried out by using an Cannon–Fenske capillary viscometer at 25°C. Molecular weight determination by a gel permeation chromatography (GPC) was performed by Scientific Polymer Products (Ontario, NY) with poly(2-vinylpyridine) standard using a Wyatt/Optilab 903 equipment. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN).

2.2. Materials

Bis(diisopropylphosphino)propane (dipp) was prepared by a modified literature procedure [11]. Lithium diisopropylphosphide was prepared from the reaction of diisopropylphosphine and methyl lithium in THF at 0°C. The reaction mixture was stirred at room temperature for 4 h and then 1,3-dibromopropane was added at 0°C. An 85% yield of dipp ligand was obtained. (Dipp)PdCl₂ was synthesized from the quantitative reaction of dipp ligand with (C₆H₅CN)₂PdCl₂ [12,13]. Solvents, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and hexamethylphosphoramide (HMPA) (all from Aldrich) were dried over 4-Å molecular sieves and stored under an argon atmosphere. Pyridine (Aldrich) was dried over KOH and stored under an argon atmosphere. Lithium chloride, calcium hydroxide, sodium ethoxide, tricyclohexylphosphine, tri-*o*-tolylphosphine (all Strem), triphenylphosphine, tri-*t*-butylphosphine, Pd(OAc)₂, 1,4-dichlorobenzene, 1,3-dichlorobenzene, 1,4-phenylenediamine, 4,4'-methylenedianiline, 4,4'-(hexafluoroisopropylidene)diamine, 4,4'-diaminobenzophenone, 1,5-diaminonaphthalene, 4,4'-diaminodiphenylether, 3-aminophenylsulfone, 4-aminophenylsulfone, 4-aminophenyldisulfide, and 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) (all from Aldrich) were used as received.

2.3. Representative polymerization reactions

The reaction mixture was prepared in a dry nitrogen-filled glove box. Polymerization reactions were performed in a 300-ml stirred autoclave manufactured by Parr Instrument.

2.4. Synthesis of polymer **1a**

In a typical reaction, 30.0 mg (6.62×10^{-5} mol) of (dipp)PdCl₂, 18.2 mg (6.62×10^{-5} mol) of dipp ligand, 2.06 g (13.6×10^{-3} mol) of DBU, 1.0 g (6.81×10^{-3} mol) of 1,4-dichlorobenzene, and 0.74 g (6.81×10^{-3} mol) of 1,4-phenylenediamine were placed in a 50-ml glass liner equipped with a magnetic stirrer and dissolved in 15 ml of DMAc. The liner was put in a 300-ml Parr reactor. The reactor was degassed and filled with N₂ three times and then pressurized with 75 psi (520 kPa) of CO. After stirring at 175°C for 5 h, the unreacted CO was released and the reaction mixture was poured into 100 ml of methanol. The precipitated yellow solid was filtered and washed with 40 ml \times 2 of methanol and then dried under vacuum at 100°C for 5 h to yield 1.51 g (94%) of **1a**. The inherent viscosity of the polymer in 98% sulfuric acid was 0.16 dl g⁻¹, measured at a concentration of 0.92 g dl⁻¹ at 25°C. The IR spectrum (KBr) of the polymer showed bands at 3322 cm⁻¹ (N–H) and 1645 cm⁻¹ (C=O). The ¹³C NMR spectrum showed a resonance for C=O at 173 ppm. Anal. Calcd.: C 70.59, H 4.20. Found: C 67.45, H 4.75.

2.5. Synthesis of **1b**

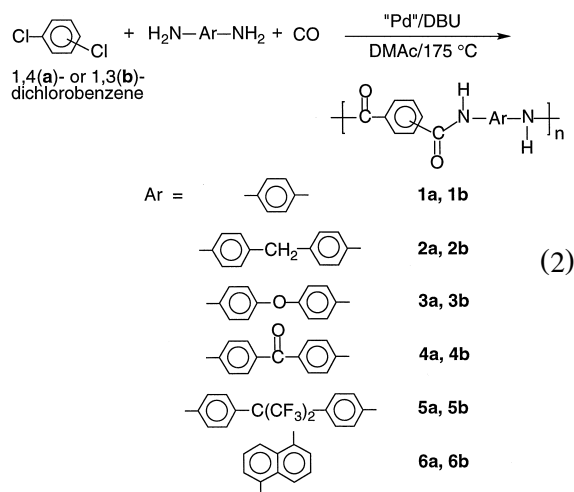
A glass liner (50 ml) was charged with 22.4 mg (1.00×10^{-4} mol) of Pd(OAc)₂, 55.2 mg (2.00×10^{-4} mol) of dipp ligand, 2.06 g (13.6×10^{-3} mol) of DBU, 1.0 g (6.81×10^{-3} mol) of 1,3-dichlorobenzene, 0.74 g (6.81×10^{-3} mol) of 1,4-phenylenediamine, and 15 ml of DMAc. After stirring at 175°C for 20 h inside a

300-ml Parr reactor pressurized with 75 psi (520 kPa) of CO, the reaction mixture was poured into 100 ml of methanol. The precipitated white solid was filtered and washed with 40 ml \times 2 of methanol and then dried under vacuum at 100°C for 5 h to yield 1.60 g (99%) of **1b**. The inherent viscosity of the polymer in 98% sulfuric acid was 0.31 dl g⁻¹, measured at a concentration of 0.92 g dl⁻¹ at 25°C. The IR spectrum (KBr) of the polymer showed bands at 3292 cm⁻¹ (N–H) and 1651 cm⁻¹ (C=O). The ¹³C NMR spectrum showed a resonance for C=O at 173 ppm. Anal. Calcd.: C 70.59, H 4.20. Found: C 68.20, H 4.64.

3. Results and discussion

The procedure that we have developed is based, in part, on Milstein's [14] earlier observation that palladium complexes with bulky trialkyl phosphines were effective catalysts for the carbonylation of aryl chlorides. However, a relatively high temperature, the choice of appropriate base, and the use of amide solvents were found to be extremely important for optimal

polymerization. The synthesis of polyamides is summarized in Eq. (2) and Table 1.



Although the polyamide, **1a**, was formed at 150°C, the maximum yield and inherent viscosity of the product were only achieved above 175°C. No further change in yield and inherent viscosity was observed in the range of 175–230°C. The effect of carbon monoxide pressure was also examined and the highest yield and inherent viscosity for **1a** were obtained in the

Table 1
Synthesis of polyamides^a

Polymer	Time [h]	Yield [%]	η_{inh}^b [dl g ⁻¹]	IR (CO) [cm ⁻¹]	¹³ C NMR ^c [ppm]
1a	5	99	0.16		
1a	20	100	0.16	1645	173
1b	5	85	0.21		
1b	20	99	0.31	1651	173
1b	40	100	0.30		
2a	5	94	0.23	1645	171
2b	20	100	0.17	1654	170
3a	5	81	0.16	1645	170
3b	20	99	0.33	1648	170
4a	5	82	0.20	1647	206, 174
4b	20	93	0.40	1655	205, 175
5a	5	81	0.16	1664	171
5b	20	78	0.22	1664	171
6a	5	78	0.10	1641	173
6b	20	93	0.15	1655	173

^a Monomer (6.81 mmol), Pd(OAc)₂ (0.1 mmol), dippp (0.2 mmol), CO (75 psi, 520 kPa), DBU (14.0 mmol), DMAc (15.0 ml), 175°C.

^b Concentration of 0.92 g dl⁻¹ in 98% H₂SO₄ at 25°C.

^c Resonance of CO group in polyamide.

range 50–75 psi (345–520 kPa) of CO. The choice of base had a significant influence on the polymerization reaction. For example, a small amount (35%) of the polyamide, **1a**, was produced when sodium-*t*-butoxide was employed but the inherent viscosity was low ($\eta_{inh} = 0.05$ dl g⁻¹). On the other hand, the use of NaOAc, triethylamine, pyridine or 2,6-*t*-butylpyridine caused the precipitation of metallic palladium and no polymerization was observed. DBU, a bulky base, was found to be optimal in our studies. Based on the yield of resulting polyamide, **1a**, DMAc was found to be superior to other solvents such as DMF and NMP. HMPA or mixture of HMPA and above solvents caused a reduction of catalytic activity.

Tables 2 and 3 summarize the effect of the phosphine ligand on the yield and inherent viscosity of the polyamide, **1a**. A combination of 1 equiv. of dippip with 1 equiv. of a bulky monodentate phosphine, such as tri-*t*-butylphosphine, tricyclohexylphosphine, tri-*o*-tolylphosphine and triphenylphosphine, was just as appropriate as 2 equivs. of dippip. This is consistent with the known structure of (dippip)₂Pd(0) in which a mononuclear trigonal planar complex is in equilibrium with a binuclear complex having a bridging dippip moiety and a free dippip ligand [15,16].

Judging from the activity (Tables 2 and 3), the catalyst derived from (dippip)PdCl₂ is somewhat more active than that derived from Pd(OAc)₂. For example, the combination of Pd(OAc)₂ and two equiv. of dippip had a cat-

Table 2

Effect of phosphine ligands on synthesis of polyamide, **1a**^a

Phosphine	Yield [%]	η_{inh}^b [dl g ⁻¹]
dippip (2 equiv.)	98	0.16
dippip (1 equiv.) + (<i>o</i> -tolyl) ₃ P (1 equiv.)	99	0.17
dippip (1 equiv.) + (CyH) ₃ P (1 equiv.)	98	0.16
dippip (1 equiv.) + <i>t</i> -Bu ₃ P (1 equiv.)	98	0.15
dippip (1 equiv.) + Ph ₃ P (1 equiv.)	98	0.13

^a Monomer (6.81 mmol), Pd(OAc)₂ (0.1 mmol), CO (75 psi, 520 kPa), DBU (14.0 mmol), DMAc (15.0 ml), 175°C, 5 h.

^b Concentration of 0.92 g dl⁻¹ in 98% H₂SO₄ at 25°C.

Table 3

Synthesis of the polyamide, **1a**, by [(dippip)PdCl₂] + phosphine^a

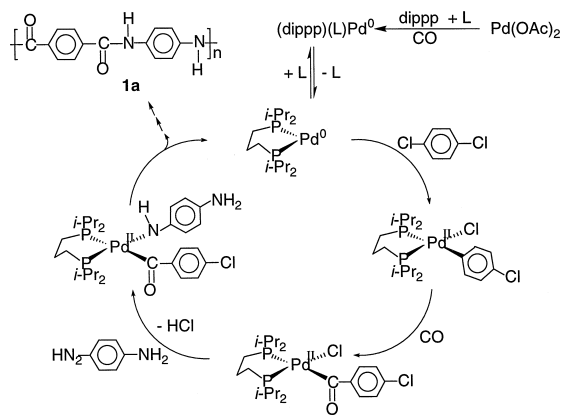
Phosphine	Yield [%]	η_{inh}^b [dl g ⁻¹]
dippip (1 equiv.)	94	0.15
(<i>o</i> -tolyl) ₃ P (1 equiv.)	94	0.15
<i>t</i> -Bu ₃ P (1 equiv.)	85	0.09
Ph ₃ P (1 equiv.)	88	0.10

^a Monomer (6.81 mmol), (dippip)PdCl₂ (6.62 × 10⁻⁵ mol), CO (75 psi, 520 kPa), DBU (14.0 mmol), DMAc (15.0 ml), 175°C, 5 h.

^b Concentration of 0.92 g dl⁻¹ in 98% H₂SO₄ at 25°C.

alytic activity of 3.2 kg mol⁻¹ Pd h⁻¹, while (dippip)PdCl₂ with one equiv. of dippip showed activity of 4.6 kg mol⁻¹ Pd h⁻¹. However, the inherent viscosities for **1a** were generally lower with the latter catalyst system. Thus, the combination of Pd(OAc)₂ and two equiv. of dippip ligand was used in the synthesis of other polyamides (Table 1).

As shown in Eq. (2) and Table 1, a series of polyamides were synthesized starting from 1,3-dichlorobenzene or 1,4-dichlorobenzene, and aromatic diamines in the presence of CO. Those derived from 1,3-dichlorobenzene had a higher solubility and a higher inherent viscosity compared to those formed from 1,4-dichlorobenzene. At the end of reaction, polyamides from 1,4-dichlorobenzene were found to have been precipitated while those from 1,3-dichlorobenzene remained in solution. The reactions involving 1,4-dichlorobenzene were completed within 5 h; no significant change in yield or



Scheme 1.

viscosity was observed with further increase in reaction time. On the other hand, the yield and viscosities of the polyamides derived from 1,3-dichlorobenzene were found to increase with increasing reaction time. For example, the reaction of 1,3-dichlorobenzene, 1,4-phenylenediamine, and carbon monoxide afforded **1b** with $\eta_{inh} = 0.20 \text{ dl g}^{-1}$ after 5 h and $\eta_{inh} = 0.31 \text{ dl g}^{-1}$ after 20 h.

The isolated polyamides are soluble only in sulfuric acid except for **4b** and **5b** which are also soluble in amide solvents such as DMAc and DMF. All polyamides synthesized were characterized by NMR and IR spectroscopy. The IR (KBr) spectra of the polymers showed a CO band at approximately 1644 cm^{-1} and an N–H band at approximately 3300 cm^{-1} . The presence of the carbonyl group was further confirmed by ^{13}C NMR spectroscopy which showed a resonance at 170–175 ppm. The weight average molecular weight (M_w) and number of average molecular weight (M_n) of **4b** with $\eta_{inh} = 0.40 \text{ dl g}^{-1}$ was found to be 30,500 and 15,500, respectively. The polydispersity (M_w/M_n) was 1.97.

Finally, based on past studies [6,17], the probable mechanism for the catalytic formation of polyamide from dichloride, diamine, and carbon monoxide is shown in Scheme 1. The active catalyst is proposed to be a palladium(0) complex formed by a prereduction step. While carbon monoxide is an obvious reductant, phosphines have also been shown to reduce $\text{Pd}(\text{OAc})_2$ [18,19].

Acknowledgements

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