

# Synthesis of Polyamides from Diols and Diamines with Liberation of H<sub>2</sub>

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**ABSTRACT:** The amidation reaction based on catalytic coupling of alcohols with amines previously reported by us, using the pincer complexes **1** and **2** as catalysts, was applied to the generation of polyamides from nonactivated diols and diamines. A range of polymers was prepared, with  $M_n$  up to 26.9 kDa. Unlike the traditional syntheses of polyamides based on carboxylic acid derivatives, which require the use of toxic reagents and generate stoichiometric amounts of waste, this process generates only molecular hydrogen as byproduct. Both aromatic and aliphatic diols and diamines were used. Gel permeation chromatography measurements of the dimethylformamide-soluble polymers and thermal studies of the polyamides were performed. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra are also reported. Thermogravimetric

analyses studies indicate that the aromatic polyamides (with the exception of the pyridine-based polyamide) are more thermally stable than the aliphatic ones. This general, environmentally benign method for the synthesis of polyamides is homogeneously catalyzed under neutral conditions by dearomatized ruthenium-pincer complexes **1** and **2** and proceeds in 1,4-dioxane under an inert atmosphere. Conditions for polyamidation in the absence of solvent are also reported, using the pincer complex **2** as catalyst. © 2012 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 1755–1765, 2012

**KEYWORDS:** alcohol dehydrogenation; amidation; catalysis; catalysts; dihydrogen; homogeneous catalysis; pincer; pincer complex; polyamides; ruthenium complex

**INTRODUCTION** Polyamides are one of the most important polymer classes extensively used in fiber products, plastics, and their derivatives, with many applications including in biomedical studies.<sup>1</sup> Generally, polyamides are synthesized by condensation of diamines and activated dicarboxylic acid derivatives<sup>1(b),2</sup> and/or in the presence of coupling reagents.<sup>3</sup> In some cases, ring opening of small-ring lactams at high temperatures leads to the formation of polyamides.<sup>4</sup> To avoid the use of activators, waste generation, or harsh conditions, the development of atom-economical, efficient, and environmentally benign protocols are desirable.

We have discovered the atom-economical, environmentally benign direct synthesis of amides from alcohols and amines with liberation of H<sub>2</sub> (Scheme 1), catalyzed by the dearomatized pincer complex PNN-Ru(II) **1** (Fig. 1).<sup>5</sup>

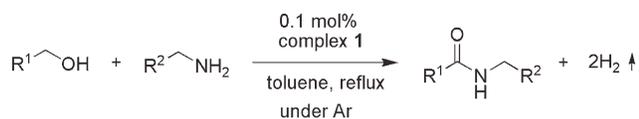
Several reports on amide formation by dehydrogenative coupling of amines with alcohols have appeared previously.<sup>6</sup> Hydrogenation of amides to alcohols and amines catalyzed by Complexes **1** and **2** was also reported by us recently.<sup>7</sup> Complex **1** and the analogous deprotonated (PNP)Ru complexes [PNP = 2,6-bis(di-*iso*-propylphosphinomethyl)pyridine] also catalyze the dehydrogenative coupling of primary alcohols to form esters, the hydrogenation of esters to alcohols, and the

dehydrogenation of secondary alcohols to ketones.<sup>8</sup> Unlike Complex **1**, the analogous PNP complexes catalyze the coupling of amines with alcohols to form imines, rather than amides, with liberation of H<sub>2</sub>.<sup>9</sup> Mechanistically, these catalytic reactions involve a new mode of metal–ligand cooperation, based on aromatization–dearomatization of the pyridine-based core of the pincer ligand.<sup>10</sup> An acridine-based ruthenium-pincer complex catalyzes the dehydrogenative coupling of primary alcohols to acetals or esters and the reaction of alcohols with ammonia to selectively form primary amines.<sup>11</sup> Recently, we have reported the synthesis of amides from esters and amines,<sup>12(a)</sup> as well as the acylation of alcohols with esters, catalyzed by Complex **1**.<sup>12(b)</sup> We have also reported the hydrogenation of ketones and CO<sub>2</sub> catalyzed by Fe pincer complexes.<sup>13</sup>

During manuscript preparation, Zeng and Guan reported the application of the amidation reaction using Catalyst **1** (Scheme 1) for the important atom-economical catalytic polymerization of diols and diamines, leading to novel aliphatic and aromatic polyamides (mostly bearing ether spacers), with number-average molecular weights in the range of 10–30 kDa.<sup>14</sup> Significantly, as the amidation reaction is selective to primary amines, monomers bearing secondary amine

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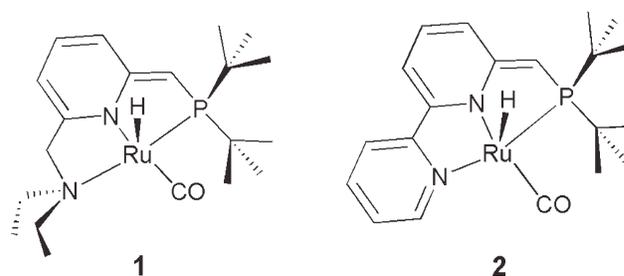
**SCHEME 1** Dehydrogenative coupling of alcohols and amines.

groups led to polyamides incorporating polyamines, without the need for protection–deprotection. Anisole/dimethylsulfoxide (DMSO) mixture was the solvent of choice.

Here, we report the application of the amidation reaction to the synthesis of a variety of polyamides not bearing ether spacers, from simple diols and diamines, under different conditions, using 1,4-dioxane as a solvent. Both Complexes **1** and **2** (Fig. 1) were used as catalysts. Remarkably, using Complex **2** as catalyst, the polyamidation reaction could proceed under solvent-free conditions, and only 0.2 mol % of catalyst was required, representing a “green” reaction. This polyamidation reaction is general, environmentally benign, and atom economical. It proceeds under neutral reaction conditions without the use of activators, condensing agents, or other additives and produces  $H_2$  as the only byproduct (Scheme 2).

## RESULTS AND DISCUSSION

On refluxing 1,4-dioxane solution containing equimolar amounts of 1,6-hexanediol and 1,6-hexanediamine in the presence of 1 mol % of Complex **1** under an argon atmosphere for 3 days, a white solid separated out from the reaction mixture. The solid was filtered off and successively washed with THF:EtOAc (1:1), dichloromethane, and 20% methanol in water. The resultant white solid was dried under high vacuum at 80 °C for 12 h to afford Polymer **3a** in 82% yield (Table 1, Entry 1). The solid was insoluble in MeOH, THF, 1,4-dioxane, and chlorinated solvents, partially soluble in DMSO and dimethylformamide (DMF) on warming. The solid melted at 246–250 °C. The polyamide obtained was dissolved in trifluoroacetic-D acid (TFA-*d*) or trifluoroethanol (TFE) and characterized by NMR spectroscopy. In  $^1H$  NMR, a broad singlet at 2.39 ppm corresponding to four protons is attributed to the presence of  $CH_2C=O$  groups in the polymer. A peak at 180.4 ppm in the  $^{13}C\{^1H\}$  NMR spectrum and an IR band at  $1633 \text{ cm}^{-1}$  confirm the presence of the amide  $C=O$  group. The number-average molecular weight  $M_n$  of the polyamide **3a** was 16.6 kDa as measured by  $^1H$  NMR using TFE as a solvent. The minor peaks adjacent to the major peaks correspond to end groups. The number of repeating monomer units was calculated from the integral value of the end groups and the corre-

**FIGURE 1** Dearomatized Ru-pincer complexes **1** and **2**.

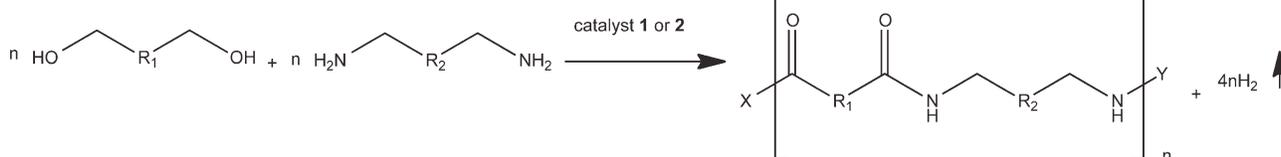
sponding repeating unit. The  $M_n$  value was calculated using the following formula:

$$M_n = (\text{Formula weight of end groups}) + [(\text{Formula weight of repeating unit}) \cdot (\text{number of repeating monomer units})]$$

The polyamide has three possible types of end groups (amine–amine, amine–alcohol, or alcohol–alcohol; Fig. 2) and it might also result in a cyclic form. It was dissolved in TFA:CH<sub>3</sub>CN (1:1), and MALDI-TOF mass spectrum was recorded using 2,5-dihydroxybenzoic acid (DHB) as the matrix<sup>15</sup> (Fig. 3), revealing the highest molecular weight at 4195 Da, which corresponds to 18 monomer units with OH/OH end groups. Because of the insolubility of the polymer in DMF, gel permeation chromatography (GPC) was not performed. The significantly lower average molecular weight obtained by MALDI-TOF is likely a result of the unreliability of this method in cases of high polydispersity (see below).

Notably, the potentially competing polyester formation<sup>8(a)</sup> by dehydrogenative self-coupling of alcohols was not observed under these conditions. This is because the intermediate aldehyde reacts preferentially with the amine, which is a better nucleophile than the alcohol, forming a hemiaminal intermediate (rather than a hemiacetal)<sup>5</sup> followed by its dehydrogenation to the amide (Scheme 3). In addition, it should be noted that Complex **1** also catalyzes the formation of amides by coupling of esters with amines (Scheme 4);<sup>12(a)</sup> hence, even if some ester (or oligoester) were to be initially formed, it would be converted to the polyamide.

The same reaction was performed using the bipyridine-based complex **2** as catalyst. After 3 days in refluxing 1,4-dioxane, polymer **3a** was formed as a white solid and was isolated after workup in 78% yield. Analysis of the solid exhibited a similar MALDI-TOF pattern, and  $^1H$  NMR spectrum as observed with Catalyst **1**. Thus, under these conditions,

**SCHEME 2** Polyamidation using diols and diamines with liberation of  $H_2$ .

**TABLE 1** Catalytic Polyamidation Using Diols and Diamines<sup>a</sup>

Entry	Diols	Diamines	Polyamides	Isolated Yield (%)	Highest $M_w$ by MALDI-TOF (Da)	$M_n$ ( $10^3$ )	PDI
1				82	4,195	16.6 <sup>b</sup>	–
2				88	5,000	10.3 <sup>b</sup>	–
3				82	5,932	ND	–
4				86	7,199	18.7 <sup>c</sup>	2.08
5				80	2,322	ND	–
6				63	1,849	ND	–
7				74	4,583	26.9 <sup>c</sup>	1.98
8				86	3,861	ND	–
9				84	3,734	ND	–
10				78	1,467	ND	–

**TABLE 1.** (Continued)

Entry	Diols	Diamines	Polyamides	Isolated Yield (%)	Highest $M_w$ by MALDI-TOF (Da)	$M_n$ ( $10^3$ )	PDI
11				80	5,200	ND	–
12				66	1,912	ND	–
13				76	4,450	5.3 <sup>c</sup>	3.20
14				88	–	11.3 <sup>c</sup>	2.18
15				77	3,052	5.4 <sup>c</sup>	2.51
16 <sup>d,e</sup>				84	4,951	ND	–

ND = GPC was not performed due to insolubility in DMF.

<sup>a</sup> Complex **1** (0.01 mmol), diol (1 mmol), diamine (1 mmol), and 1,4-dioxane (2 mL) were refluxed at an oil bath temperature of 135 °C in a Schlenk tube under argon for 3 days.

<sup>b</sup>  $M_n$  was calculated from <sup>1</sup>H NMR.

<sup>c</sup>  $M_n$  was obtained from GPC analysis.

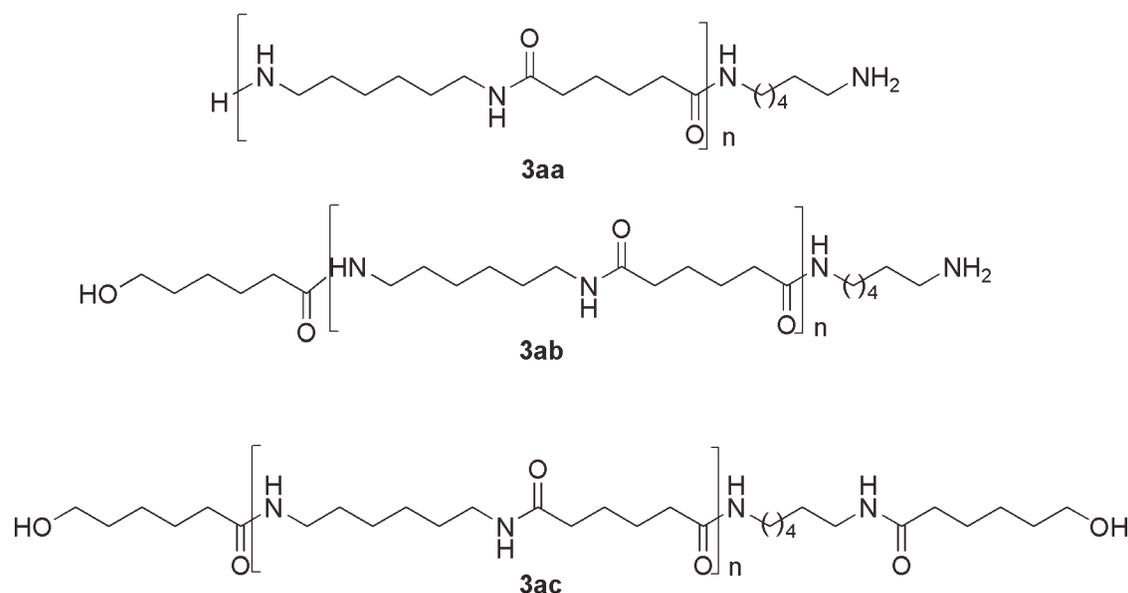
<sup>d</sup> Catalyzed by Complex **2** under solvent-free condition.

<sup>e</sup> Melting point of polyamide = 258–262 °C (252 °C by DSC).

Complexes **1** and **2** exhibit similar catalytic activity in the polyamidation reaction. Interestingly, Complex **2** can catalyze the polyamidation reaction under solvent-free conditions, using a lower catalyst loading. Thus, heating equivalent amounts of 1,6-hexanediol and 1,6-hexanediamine with Complex **2** (0.2 mol %) in the absence of solvent at 130 °C for 14 h followed by heating to 190 °C for 1 h under argon flow and cooling to room temperature resulted in a solid (Table 1, Entry 16). The solid was washed with THF, water, ethanol, and hexane, dried under vacuum for 12 h, and isolated in 84% yield. Its melting point (258–262 °C) was higher than that obtained with Complex **1**. The MALDI-TOF mass spectrum of this solid exhibited a molecular weight of 4951 Da. Although GPC analysis was not possible, due to insolubility of the polymer in DMF, the relative value obtained by MALDI-

TOF and the higher melting point indicate that it has a higher molecular weight than the polymer obtained with Complex **1**. This is likely due to the higher temperatures used and the absence of solvent, allowing polymerization in the melt.

Exploring the scope of the polyamidation reaction, a solution of 1,10-decanediol and 1,6-hexanediamine in 1,4-dioxane was refluxed in the presence of 1 mol % of Complex **1**, resulting in 88% yield of the polyamide **3b** (Table 1, Entry 2). The presence of the amide functional group of **3b** was indicated by an IR absorption at 1637 cm<sup>-1</sup> and a signal at 181.6 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The  $M_n$  value of **3b** was 10.3 kDa based on the <sup>1</sup>H NMR spectrum of TFE solution. The minor peaks adjacent to the major peaks of –NCH<sub>2</sub>–, –CH<sub>2</sub>CO–, and –CH<sub>2</sub>– correspond to end group of respective repeating monomer unit. The  $M_n$  value was

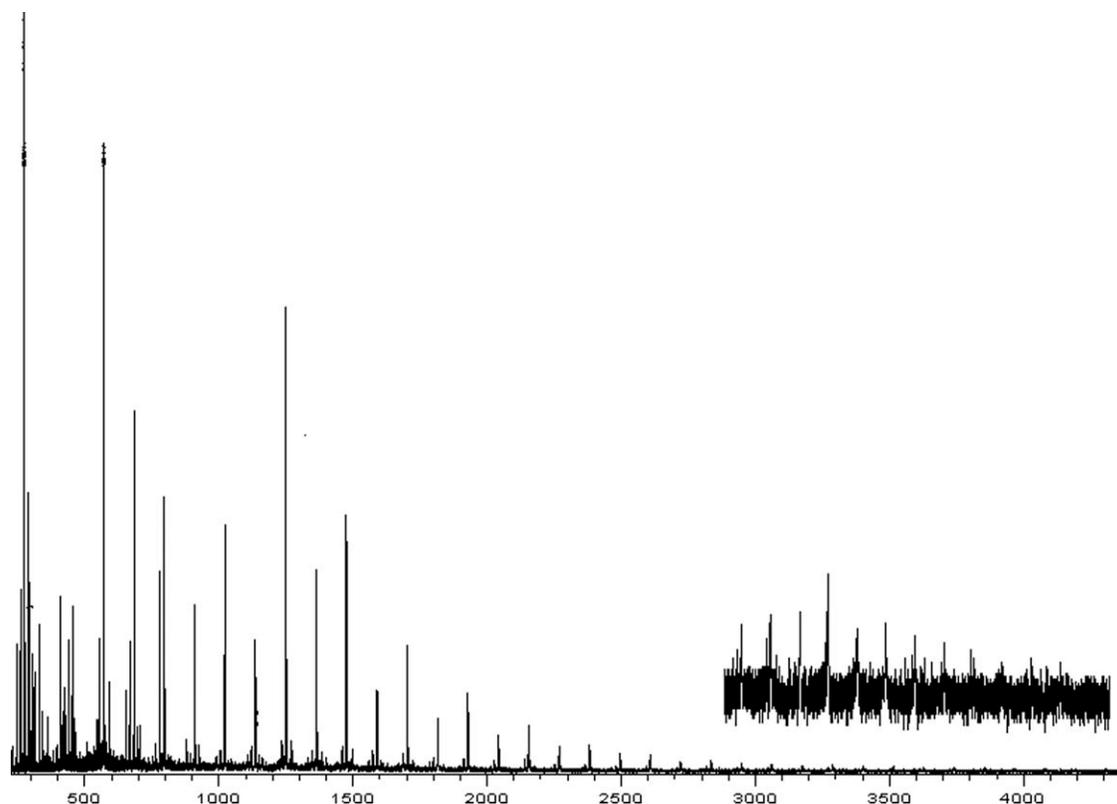


**FIGURE 2** End groups present in polyamide **3a**.

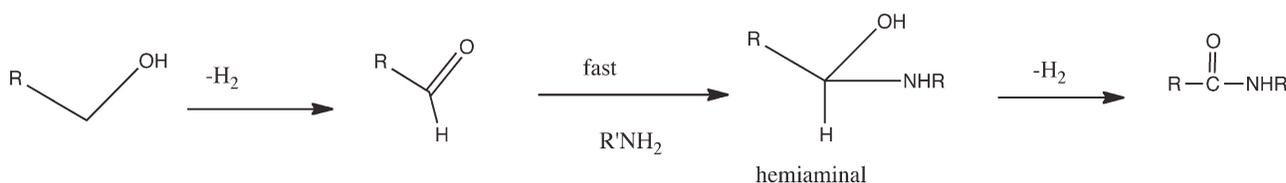
calculated as described above. The MALDI-TOF mass spectrum indicated a molecular weight up to only 4965 Da. Because of the insolubility of the polymer in DMF, GPC was not performed.

Dehydrogenative coupling of benzylic diols with aliphatic diamines leads to polyamides having aromatic and aliphatic

segments. Thus, reaction of 1,3-phenylenedimethanol with 1,6-hexanediamine under similar conditions yielded polyamide **3c** in 82% yield after workup (Table 1, Entry 3). The IR spectrum of the polyamide **3c** showed the presence of the NH group as a broad peak at  $3297 \text{ cm}^{-1}$  and the amide C=O band at  $1631 \text{ cm}^{-1}$ . The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum exhibited the C=O carbon at 165.8 ppm. Polyamide **3c** was



**FIGURE 3** MALDI-TOF spectrum of polyamide **3a** in TFA using DHB matrix.



**SCHEME 3** Amide formation via hemiaminal intermediacy.

further analyzed by MALDI-TOF (Fig. 4), exhibiting a series of peaks in the range of 700–5932 Da. Refluxing a dioxane suspension of polyamide **3c** with or without added 1,3-phenylenedimethanol, and a catalytic amount of Complex **1** did not result in a higher molecular weight. Because of the insolubility of the polymer in DMF, GPC analysis was not performed.

To increase the solubility of the polyamides, ether-substituted aromatic diols were used. Thus, reaction of (5-methoxy-1,3-phenylene)dimethanol and 1,6-hexanediamine gave 86% of polyamide **3d** (Table 1, Entry 4) as a gummy solid and exhibited a mass peak at 7199 Da in the MALDI-TOF spectrum (Fig. 5). Polyamide **3d** was completely dissolved in warm DMF, and the molecular weight was measured using GPC using DMF with 0.1% LiBr (w/v) as the eluent at 50 °C, yielding  $M_n = 18.7$  kDa with PDI of 2.08. The significantly lower molecular weight observed by MALDI-TOF, when compared with GPC, is likely to be a result of the high PDI. As reported,<sup>16</sup> in cases of polydispersities higher than PDI = 1.2, MALDI-TOF leads to under-represented high-mass components with respect to the lower mass components, resulting in significantly lower average molecular weight values.

On refluxing equivalent amounts of 1,4-phenylenedimethanol and 1,6-hexanediamine with 1 mol % of Complex **1**, 88% yield of the crude polyamide **3e** was obtained (Table 1, Entry 6). Successive washings with THF:EtOAc (1:1), dichloromethane, and 20% MeOH in water resulted in 80% yield of the solid after drying under vacuum. IR absorption at  $1626\text{ cm}^{-1}$  and the NMR spectra confirm the presence of amide functionality. MALDI-TOF spectrum of Compound **3e** revealed only oligomeric mixtures in the range of 700–2500 Da (Fig. 6). The mass unit of 2322 Da corresponds to only nine monomer units. The reaction of 1,2-ethylenediamine with 1,4-phenylenedimethanol did not result in significant progress of the polyamidation reaction, giving the polyamide **3f** in 63% yield (Table 1, Entry 6), composed of low-molecular-weight oligomeric mixtures in the range of 600–1900 Da.

Next, we examined the polyamidation reaction using heteroaromatic diol. Reaction of equivalent amounts of pyridine-2,6-diylidimethanol with 1,6-hexanediamine catalyzed by **1** furnished the polyamide **3g** after 3 days of reflux in 1,4-dioxane

(Table 1, Entry 7) as a gummy insoluble solid which separated out from the reaction mixture and after workup gave a yield of 74%. The NMR and IR spectra confirm the presence of the amide carbonyl group and no polyester formation. GPC analysis of polyamide **3g** using DMF exhibits  $M_n = 26.9$  kDa with PDI of 1.98.

Next, benzylic diamines were dehydrogenatively coupled with benzylic diols. Thus, reaction of 1,4-phenylenedimethanol and 1,3-phenylenedimethanamine gave 86% of polyamide **3h** under the same reaction conditions (Table 1, Entry 8). The NMR and MALDI-TOF spectra of **3h** (Fig. 7) reveal high-molecular-weight oligomeric mixtures. The highest mass unit obtained for the polyamide **3h** was 3861 Da, having amine end groups and corresponding to 14 monomer units in the chain. Further heating Compound **3h** in refluxing 1,4-dioxane in the presence of 1 mol% of **1** did not result in the elongation of the polymer chain (due to the insolubility of the polymer in DMF, GPC analysis was not performed).

The polyamidation reaction of 1,4-phenylenedimethanol and 1,4-phenylenedimethanamine afforded a mixture of oligomers **3i** in 84% isolated yield (Table 1, Entry 9). The highest mass unit by MALDI-TOF was 3747 Da, corresponding to 14 monomer units. The reaction of 1,3-phenylenedimethanol and 1,3-phenylenedimethanamine led to **3j** (Table 1, Entry 10) in 78% yield after workup, with a maximum mass unit of 1467, corresponding to 5.5 monomer units. The reaction of 1,5-pentanediol and 1,4-phenylenedimethanamine gave 80% of Compound **3k** (Table 1, Entry 11). Interestingly, **3k** showed a series of mass peaks in the range of 500–5200 Da corresponding to 22 monomer units. The reaction of cyclohexane-1,4-diylidimethanol and 1,4-phenylenedimethanamine gave 66% of Compound **3l** (Table 1, Entry 12), with peaks at 1912 Da corresponding to only seven monomeric units in MALDI-TOF spectrum. Polyamidation of (5-methoxy-1,3-phenylene)dimethanol with 1,4-phenylenedimethanamine using 1 mol % of Catalyst **1** afforded Compound **3m** (Table 1, Entry 13) in 76% yield, with the mass of 4450 Da obtained by MALDI-TOF, corresponding to 15 monomer units. The GPC analysis of **3m** showed a molecular weight  $M_n = 5.3$  kDa. Similarly, the reaction of (5-(hexyloxy)-1,3-phenylene)dimethanol and 1,3-phenylenedimethanamine



**SCHEME 4** Amidation of esters catalyzed by Complex **1**.

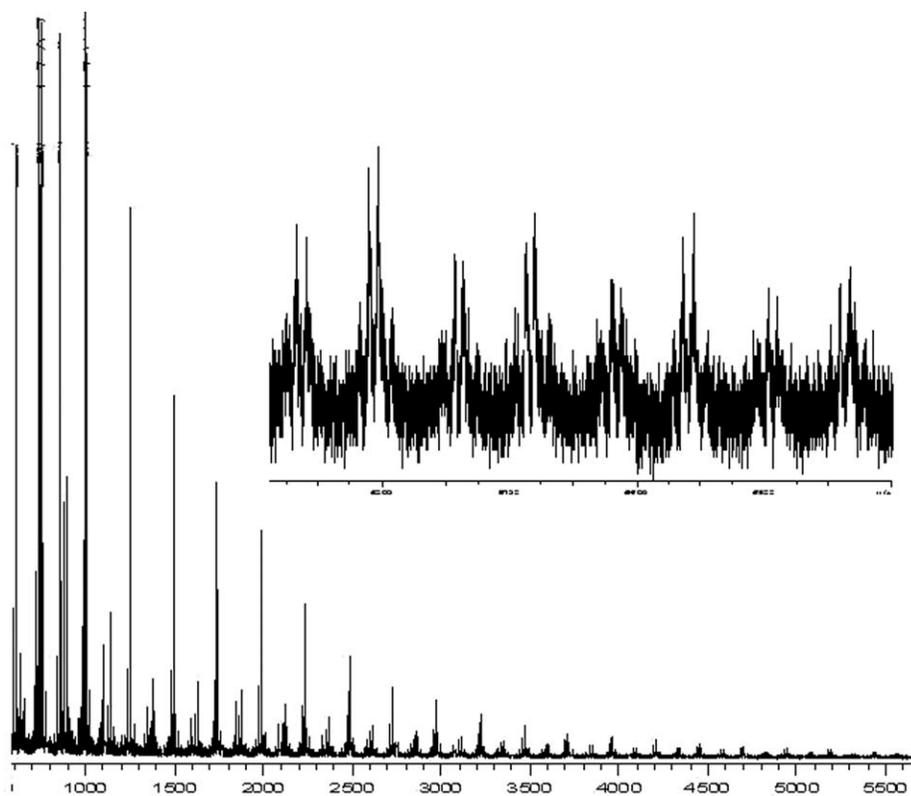


FIGURE 4 MALDI-TOF spectrum of polyamide 3c in TFA using DHB matrix.

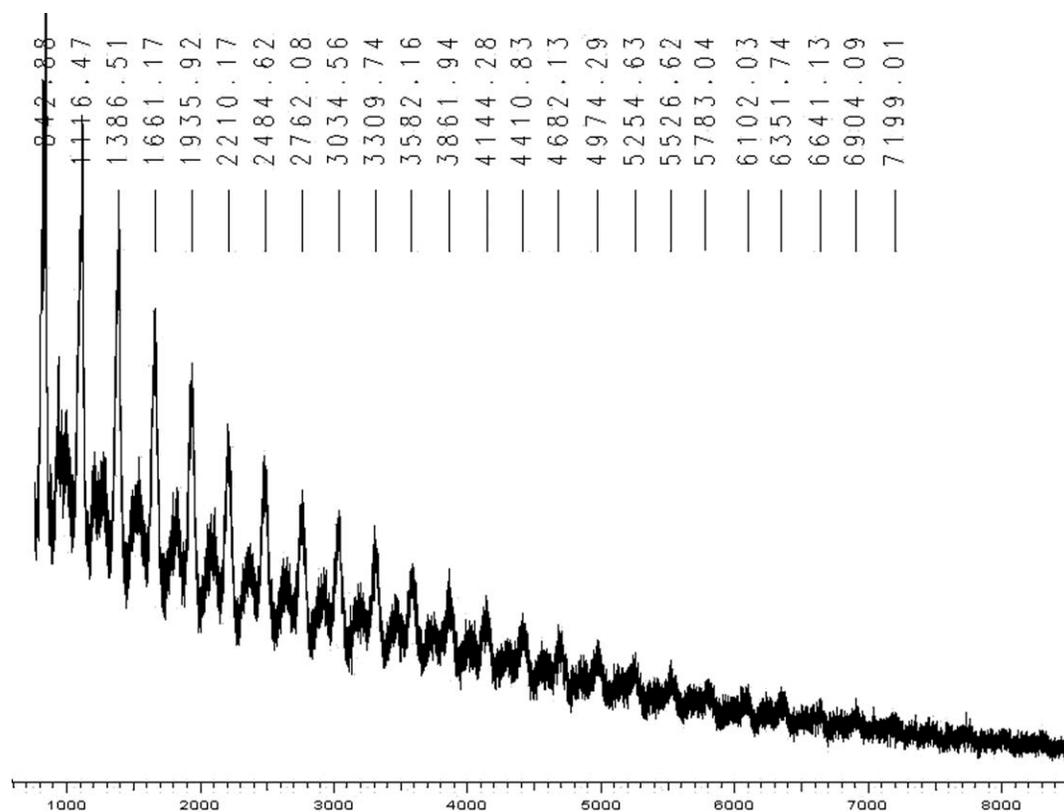


FIGURE 5 MALDI-TOF of polyamide 3d in 50% TFA/dichloromethane using DHB-NaI matrix.

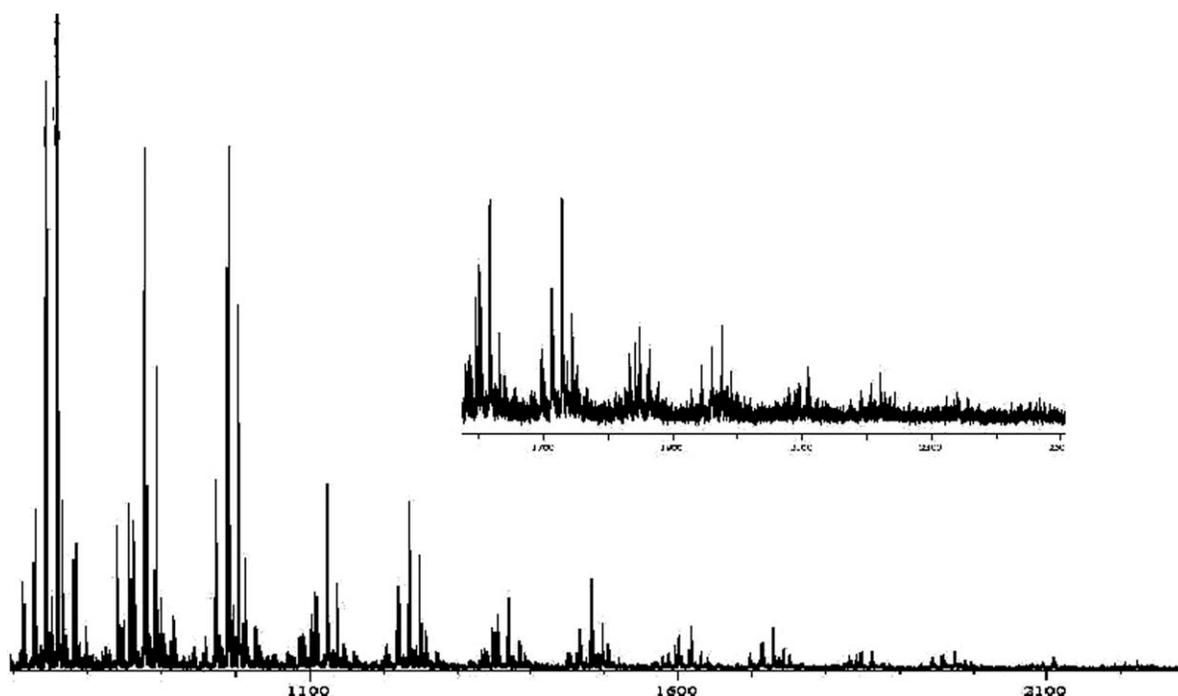


FIGURE 6 MALDI-TOF spectrum of **3e** in TFA using DHB matrix.

gave 88% of the polyamide **3n** (Table 1, Entry 14), with  $M_n = 11.3$  kDa based on GPC analysis. The reaction of (5-(hexyloxy)-1,3-phenylene)dimethanol and 1,4-phenylenedimethanamine gave 77% of the polyamide **3o** (Table 1, Entry 15), with a mass of 3052 Da corresponding to eight monomers based on the MALDI-TOF spectrum.

The results of polyamidation reactions are summarized in Table 1. Thermogravimetric analyses (TGA) of the various polyamides were performed. Weight losses of 30 and 50% occurred at similar temperatures for each polymer (Fig. 8

and Table 2). The aliphatic polyamide **3a** exhibited 83% weight loss at 495 °C and was, as expected, less thermally stable than the arene-based polyamides **3d,m,n** (except **3g**), which exhibited 62–70% weight loss at 680 °C (Table 2). The pyridine-based polyamide **3g** was less stable and exhibited 92% weight loss at 520 °C.

## EXPERIMENTAL

### Materials

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were of reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenoneketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glove box over 4-Å molecular sieves. Complexes **1<sup>B(a)</sup>** and **2<sup>7</sup>** were prepared according to literature procedures. MALDI-TOF mass spectra were recorded on Bruker REFLEX<sup>TM</sup> reflector time-of-flight instrument with SCOUT<sup>TM</sup> multiprobe (384) inlet and gridless delayed extraction ion source, using DHB as the matrix, and the polyamide was dissolved in dichloromethane/TFA (1:1) or acetonitrile/TFA (1:1). Analytical GPC was performed using a Varian PrepStar 218 HPLC pump, Varian ProStar model 356-LC RI detector using a OH-pak SB-803 HQ column from Shodex, to determine molecular weights and molecular weight distributions,  $M_w/M_n$ , of linear polymer samples with respect to poly(ethylene glycol) standards purchased from Aldrich. DMF with 0.1% LiBr (wt/v) was used as the eluent at a flow rate of 1.0 mL/min with column temperature at 50 °C.

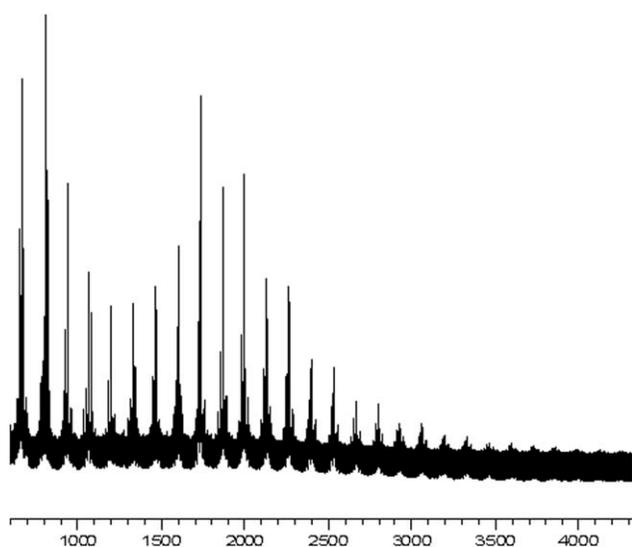


FIGURE 7 MALDI-TOF spectrum of polyamide **3h** in TFA using DHB matrix.

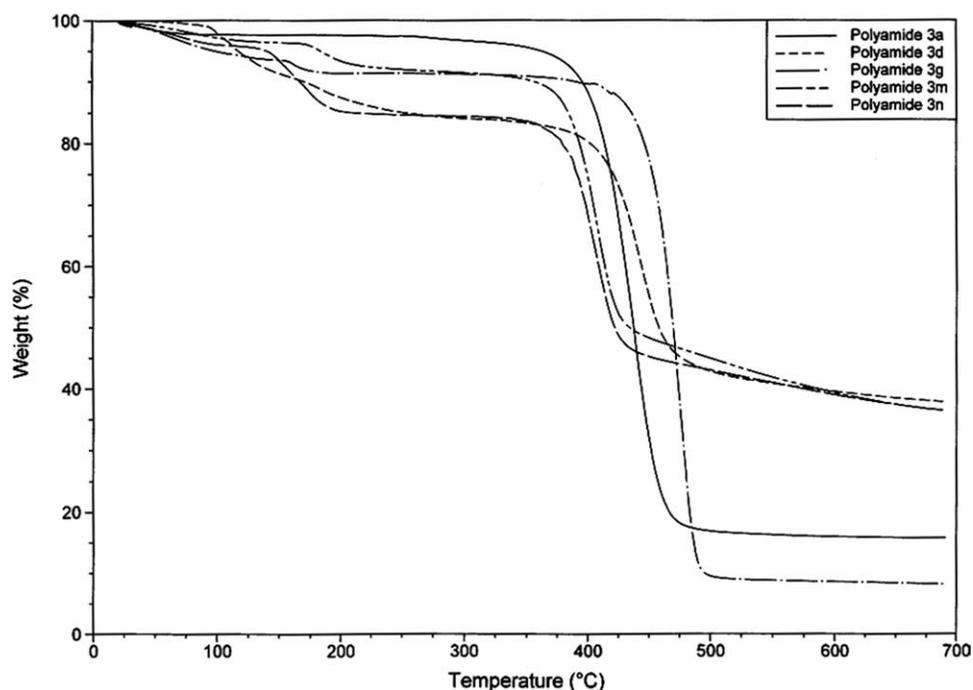
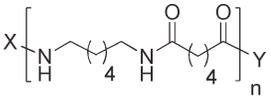
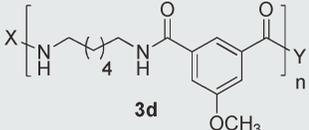
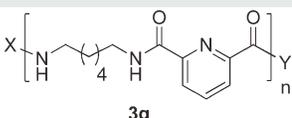
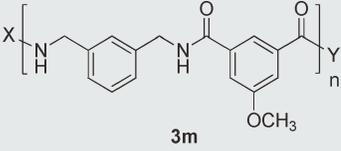
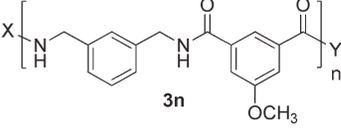


FIGURE 8 TGA of polyamides 3.

TABLE 2 Thermal Studies of Polyamides 3 at Various Temperatures by TGA

Entry	Polyamides	$M_n$ ( $10^3$ )	Temperature (°C) at % Weight Loss				
			5%	10%	30%	50%	70%
1	 <p>3a</p>	16.6	360	395	425	437	551 595 (83%)
2	 <p>3d</p>	18.7	120	170	430	458	680 (62%)
3	 <p>3g</p>	26.9	100	380	458	470	478 520 (92%)
4	 <p>3m</p>	5.3	180	350	402	430	680 (64%)
5	 <p>3n</p>	11.3	140	170	400	420	680 (64%)

Thermal studies were performed on TA instruments SDT Q 600, with heating rate of 20 °C/min under nitrogen gas flow.

### General Procedure for the Polyamidation Reactions of Diols and Diamines

Complex **1** (0.01 mmol), diol (1 mmol), diamine (1 mmol), and 1,4-dioxane (2 mL) were added to a Schlenk flask under an atmosphere of nitrogen in a Vacuum Atmospheres glove box. The flask was equipped with a condenser, and the solution was refluxed outside the glove box with stirring in an open system under argon for 3 days. After cooling to room temperature, the solid was filtered off and successively washed with THF:EtOAc (1:1), dichloromethane, and 20% methanol in water to give the product polyamide. The resulting solid was dried under vacuum at 80 °C for 12 h. Finally, the solid was analyzed by IR, NMR, and MALDI-TOF.

### Characterization of Polyamide **3a**

IR (KBr pellet): 3304, 2935, 2859, 1633, 1536, 1474, 1276  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (TFA-*d*): 1.08 (broad s, 4H), 1.34 (broad s, 4H), 1.52 (broad s, 4H), 2.39 (broad s, 4H), 3.17 (broad s, 4H);  $^{13}\text{C}\{^1\text{H}\}$ NMR (TFA-*d*): 26.8, 27.8, 29.5, 35.0, 44.5, 180.4. MALDI-TOF (matrix: DHB (2,5-dihydroxybenzoic acid), solvent acetonitrile: TFA): *m/z* = 569–4195 Da.

The spectrum of polyamide **3a** shows a series of peaks at 569 [**3aa** +  $\text{H}^+$  ( $n = 2$ )], 795 [**3aa** +  $\text{H}^+$  ( $n = 3$ )], 909 [**3ab** +  $\text{H}^+$  ( $n = 3$ )], 1022 [**3c** ( $n = 4$ )], 1135 [**3ab** +  $\text{H}^+$  ( $n = 4$ )], 1247 [**3aa** +  $\text{H}^+$  ( $n = 5$ )], 1361 [**3ab** +  $\text{H}^+$  ( $n = 5$ )], 1474 [**3ac** ( $n = 6$ )], 1588 [**3ab** +  $2\text{H}^+$  ( $n = 6$ )], 1700 [**3ac** ( $n = 7$ )], 1814 [**3ab** +  $2\text{H}^+$  ( $n = 7$ )], 1926 [**3ac** ( $n = 8$ )], 2041 [**3ab** +  $3\text{H}^+$  ( $n = 8$ )], 2153 [**3ac** +  $\text{H}^+$  ( $n = 9$ )], 2266 [**3ab** +  $2\text{H}^+$  ( $n = 9$ )], 2379 [**3ac** +  $\text{H}^+$  ( $n = 10$ )], 2494 [**3ab** +  $4\text{H}^+$  ( $n = 10$ )], 2606 [**3ac** +  $2\text{H}^+$  ( $n = 11$ )], 2720 [**3ab** +  $4\text{H}^+$  ( $n = 11$ )], 2832 [**3ac** +  $2\text{H}^+$  ( $n = 12$ )], 2947 [**3ab** +  $5\text{H}^+$  ( $n = 12$ )], 3058 [**3ac** +  $2\text{H}^+$  ( $n = 13$ )], 3170 [**3ab** +  $\text{H}^+$  ( $n = 13$ )], 3288 [**3ac** +  $6\text{H}^+$  ( $n = 14$ )], 3402 [**3ab** +  $8\text{H}^+$  ( $n = 14$ )], 3515 [**3ac** +  $7\text{H}^+$  ( $n = 15$ )], 3625, 3739 [**3ac** +  $5\text{H}^+$  ( $n = 16$ )], 3840, 3853, 3966 [**3ac** +  $5\text{H}^+$  ( $n = 17$ )], 4079 [**3ab** +  $6\text{H}^+$  ( $n = 13$ )], 4195 [**3ac** +  $9\text{H}^+$  ( $n = 18$ )].

See Supporting Information for the characterization data of all synthesized polyamides.

### CONCLUSIONS

A variety of polyamides having aliphatic–aliphatic, aromatic–aromatic, aliphatic–aromatic, and aliphatic–heteroaromatic spacers were obtained in good yields using nonactivated/nonether-linked diols and diamines, with liberation of  $\text{H}_2$ . The heteroaromatic polyamide **3g** gave the highest number-average molecular weight ( $M_n = 26.9$  kDa); lower but still reasonable molecular weights were obtained for the aliphatic **3a** ( $M_n = 16.6$  kDa) and aromatic **3d** ( $M_n = 18.7$  kDa) compounds. These numbers are similar to the ones obtained by Zeng and Guan (10–30 kDa).<sup>14</sup> Polydispersities were in the range of PDI = 1.98–3.2. Molecular weights were determined by GPC and NMR in case of the soluble polymers. MALDI-TOF spectra of insoluble polyamides were also obtained; however, because of the high polydispersity (PDI) of the

polymers, the observed highest molecular weights by MALDI-TOF were significantly lower than the actual molecular weights determined by GPC, as reported in other cases.<sup>17</sup> Thermal stability of the polyamides was explored by TGA, with the aromatic polyamides being more stable than the aliphatic ones, as expected, with the exception of the pyridine-based polymer **3g** which was least stable; however, the reason is unknown at this stage. Notably, using the bipyridine-based pincer catalyst **2**, the polyamidation reaction can be performed in the absence of solvent, representing a “green” reaction. Together with the results reported by Zeng and Guan,<sup>14</sup> the new polymerization reaction emerges as a synthetically useful and general method for the preparation of a variety of polyamides under mild, neutral conditions, using no toxic reagents, not requiring preactivation of the substrates, and generating no waste.

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