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Depolymerization of Technical Grade Polyamide 66 and Polyurethane Materials via Hydrogenation

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Abstract: Chemical recycling provides a promising solution to utilize plastic waste. Here, we present a catalytic hydrogenative depolymerization of polyamide 66 (PA 66) and polyurethane (PU). The system features employing Ru pincer complexes at high temperature (200 °C) in THF solution, even technical grade polymers can be hydrogenated with satisfactory yields under these conditions. A comparison of the system with some known heterogeneous catalysts as well as catalyst poisoning tests support homogeneity of the system. These results demonstrate the potential of chemical recycling to regain building blocks for polymers and will be interesting for the further development of polymer hydrogenation

The widespread and increasing use of plastics poses a great challenge for the sustainability of human society. Until now, the majority of these post-consumer polymers are discarded, being either landfilled, incinerated or illegally dumped in the oceans, which causes serious environmental problems.[1] Thus, it is imperative to establish efficient recycling process to avoid the pollution with plastic waste and also to save fossil feedstocks in the monomer synthesis. Although mechanical recycling process (melting and remolding) can prolong the lifetime of polymers, it is still quite limited, for instance, due to high sorting requirements and decreasing material quality in each cycle.[2] On the other hand, chemical recycling, namely decomposing polymers into their monomers, offers a sustainable loop of plastic production, since the monomers obtained by this means can be used to prepare polymers without loss in properties, thus creating an ideal, circular polymer economy.[3] In this regards, pyrolysis, hydrolysis, alcoholysis and aminolysis have been used for the chemical recycling of polyesters, polyamides and polyurethanes.[4] However, these processes suffer from disadvantages such as not being cost competitive, low efficiency of monomer regeneration or generating additional chemical wastes. Therefore, more efficient and sustainable depolymerization process for polymer recycling are required.

Catalytic hydrogenation is a green and sustainable method for functional group transformation, it doesn't produce stoichiometric waste compared to traditional reduction process. Over the past decades, catalytic reductions of carboxylic and carbonic acid derivatives using molecular hydrogen have been investigated extensively.[5] Homogeneous catalysts based on ruthenium,[6] iron[7] manganese[8] and molybdenum[9] were reported. Hydrogenolysis of polyesters and polycarbonates were also realized by several groups.[10] In comparison, hydrogenative depolymerization of polyamides and polyurethanes are much less developed, presumably due to the highly resistant property of these materials. Researchers from Invista described a two-step process where hydrogenation was applied after ammonolysis of polyamides,[11] however, the direct hydrogenation of polyamides is not known until quite recently. During our preparation of this manuscript, Milstein and coworkers published the first example of hydrogenative depolymerization of polyamides (including a polyurethane) with ruthenium pincer complex.[12] Their strategy uses dimethyl sulfoxide (DMSO), which can dissolve polyamide at elevated temperature, as hydrogenation solvent. Due to the deactivating effect of DMSO on Ru catalyst,[13] the turnover number of catalyst was quite limited, thus a two-step approach was adopted in order to improve the overall conversion and yield of the reaction. In addition, decomposition of DMSO at elevated temperature raises potential safety issues.[14] Moreover, in their report, hydrogenation of technical grade polymers was not demonstrated. Here, we disclose our results on ruthenium-catalyzed hydrogenation of polyamides and polyurethanes via cleavage of the C-N bond of amide and carbamate groups. Improved activity, as well as the depolymerization of authentic technical grade samples are achieved.

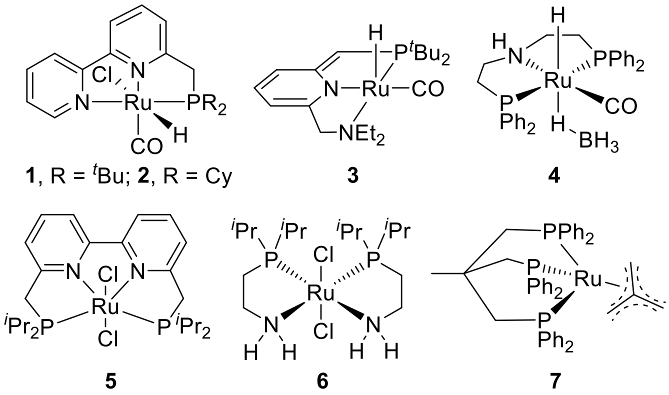
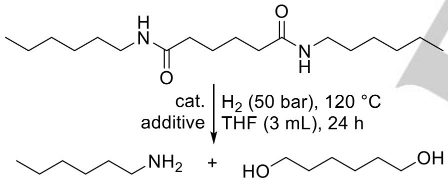


Figure 1. Ruthenium complexes studied in this report

We initiated our study by evaluating a series of ruthenium catalysts (Figure 1), using N,N'-dihexyladipamide as a model substrate as it has very similar structure motif to polyamide 66. When the Milstein's amide hydrogenation catalyst **1**[6] was applied, moderate yields of amine and diol were obtained (Table 1, Entry 1). Changing the substituent on phosphine in complex **1** from *tert*-butyl to cyclohexyl increased the yield slightly (Table 1, Entry 2). The commercially available ruthenium catalyst **3**, which can be operated under base-free conditions, gave a moderate yield (Table 1, Entry 3), while the activated form of Ru-MACHO[15] was inactive (Table 1, Entry 4). A ruthenium complex bearing tetradentate ligand,[6] developed by Saito and coworkers, was tested and satisfactory activity was observed (Table 1, Entry 5). In addition, a ruthenium complex with bis-aminophosphine ligand failed to give the desired products (Table 1, Entry 6).[16] Finally, the Ru-triphos catalyst with acid as additive[6],[10] turned out to be inactive in this hydrogenation (Table 1, Entry 7).

Table 1. Hydrogenation of N,N'-dihexyladipamide with Ru complexes[a]



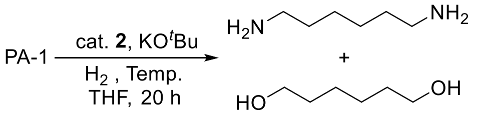
Entry	cat. (2 mol%)	additive (4 mol%)	yield[b,c] (amine)	yield[b,c] (diol)
1	**1**	KO^{t}Bu	77%	64%
2	**2**	KO^{t}Bu	82%	75%
3	**3**	---	63%	47%
4	**4**	---	18%	< 5%
5[d]	**5**	NaH	75%	53%
6	**6**	KO^{t}Bu	0%	0%
7	**7**	$HNTf_2$	0%	0%

[a] Conditions: adipamide (0.5 mmol), cat. (0.01 mmol), additive (0.02 mmol), H_2 (50 bar), THF (3 mL), 120 °C, 24 h. [b] Yields were determined by GC analysis using mesitylene as internal standard. [c] due to the low solubility of N,N´-dihexyladipamide in THF, we were not able to quantify the conversion of the starting material in an accurate manner, as in some reactions solid martial remained. Therefore, only the yield of the products according the amount of used starting material could be quantified accurately via calibrated GC. [d] 0.2 mmol NaH was used

Furthermore, we examined the hydrogenation of N,N'-dicaproylhexamethylenediamine using complexes **1**, **2** and **3**, similar results to the hydrogenation of adipic diamide were observed with complex **2** which showed the highest activity (Table S1, supporting information).

Next, we tested the hydrogenation of a technical grade polyamide 66 sample, Ultramid® A 27[17], using complex **2**. However, no activity was observed at 150 °C under 70 bar of H_2 with different organic solvents (THF, toluene and anisole). We speculated the lack of solubility of polyamide in these solvents at 150°C hampered its hydrogenosis, although, polar solvents like formic acid, *m*-cresol can dissolve polyamide 66 via hydrogen bonding effect; unfortunately, the acidic nature is incompatible with the used catalysts.[18] Besides, for the reasons mentioned above, we also avoided to use DMSO as solvent. Then we turned to a low molecular weight polyamide sample, PA-1. It is noteworthy to mention that this polyamide has excess of amine end group over carboxylic end group, making it a "basic" polymer (Table S2, supporting information). When this polyamide 66 sample was subjected to a hydrogenation pressure of 70 bar, only very low yields of diamine and diol was observed at 150 °C after 20 hours. Gratifyingly, with increased temperature to 200 °C and pressure to 100 bar, satisfactory yields of diamine and diol were obtained. Decreasing the temperature or hydrogen pressure led to reduced activity (Table 2, Entries 3, 4), and the influence of temperature seems to be more significant. Other solvents including toluene, anisole and dimethoxyethane all resulted in inferior yields (Table 2, Entries 5 - 7). In the absence of Ru catalyst, K^{t}OBu or hydrogen, products were not observed, which confirmed the necessity of each component.

Table 2. Hydrogenation of a low molecular weight polyamide 66 (Mw = 8240 g/mol; AEG = 1748 mmol/kg) sample with Ru complex **2**[a]



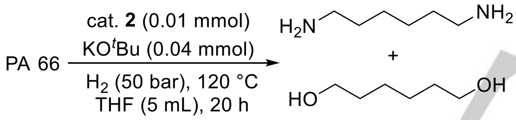
Entry	Temp (°C)	P (H_2) (bar)	Yield / (TONs)[b] (diamine)	Yield / (TONs)[b] (diol)
1	150	70	12% (15)	< 5% (< 7)
2	200	100	78% (98)	62% (78)
3	180	100	60% (75)	35% (44)
4	200	80	70% (88)	47% (59)
5[c]	200	100	59% (74)	32% (40)
6[d]	200	100	69% (86)	49% (61)
7[e]	200	100	70% (88)	46% (58)

[a] Conditions: PA-1 (0.3 g, 1.25 mmol according to the repeating unit of polyamide 66), cat. **2** (0.01 mmol), KO^{t}Bu (0.04 mmol), THF (5 mL). [b] Yields were determined by GC analysis using mesitylene as internal standard. [c] Toluene as solvent. [d] Anisole as solvent. [e] Dimethoxyethane as solvent. TONs, turnover numbers.

To further investigate the effect of the carboxylic acid end group in polyamide 66, three other different samples were tested (Table 3, see Table S2 in supporting information for details). For polyamide PA-2 (Mw = 8750, Table 3, Entry 1), a sample has excess of amine end group as PA-1, moderate yields of diol and diamine were obtained. While polyamide PA-3 (Mw = 2470, Table 3, Entry 2) and PA-4 (Mw = 4090, Table 3, Entry 3), both with an excess of acidic end groups, didn't give any desired products, even though the latter two samples have a lower molecular weight than the first one. The results here clearly demonstrated deactivating effect of excess acidic groups. Fortunately, this is not an important issue for technical grade polyamide hydrogenation, since these materials usually possess a similar amount of carboxylic end groups and amine end groups.[19]

As the hydrogenation was operated under much higher temperature compared to most homogeneous ruthenium catalyzed reactions, it is conceivable that the Ru-pincer complex may decompose and form heterogeneous particles which are responsible for the observed activities.[20] To probe this possibility, several heterogeneous catalysts were examined (Table S3, supporting information). With Ru/C, Raney Ni or Raney Co, desired products were not observed, while Ru nanoparticles on silica, afforded diamine as the only product. Further control experiments revealed that 1,6-hexanediol can be fully converted by Ru nanoparticles on alumina, possible to hexane via deoxygenation. In contrast, the diol remained intact when Ru catalyst **2** was used under the same conditions (Scheme S3, supporting information). Moreover, mercury test disclosed the activity was not inhibited (Scheme S4, supporting information). All these results suggested the system is a homogeneous hydrogenation rather than a heterogeneous one.[21]

Table 3. Hydrogenation of different polyamide 66 [a]

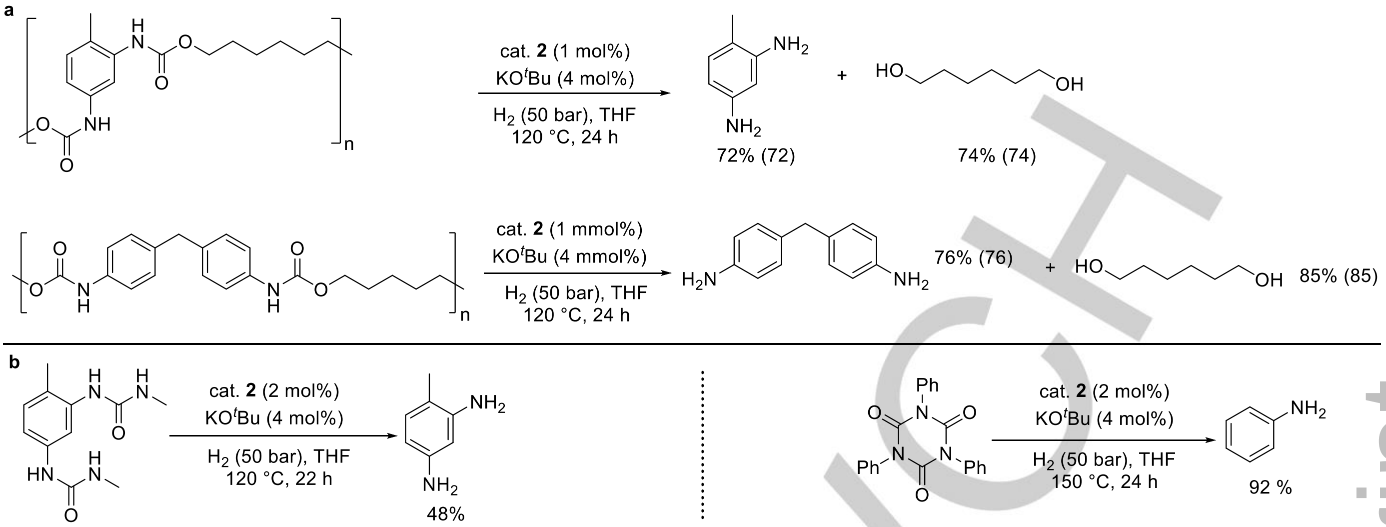


Entry	Polyamide 66	Mol Wt (g/mol)	AEG / CEG[b] (mmol/kg)	Yield[c] (diamine)	Yield[c] (diol)
1	PA-2	8750	1482 / 7.5	62%	37%
2	PA-3	2470	23.3 / 1683	0%	0%
3	PA-4	4090	13.6 / 1286	0%	0%

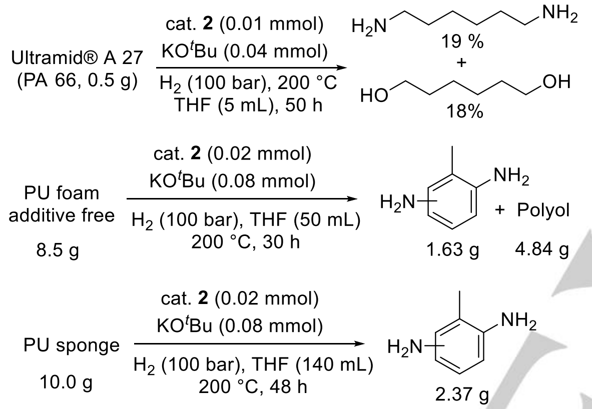
[a] Conditions as showed, polyamide 66 (0.3 g, 1.25 mmol according to the repeating unit of polyamide 66) [b] AEG, amine end group; CEG, carboxylic end group. [c] Yields were determined by GC analysis using mesitylene as internal standard.

After the hydrogenation of polyamides substrates, we also investigated polyurethanes models. Dimethyl toluene-2,4-dicarbamate can be readily hydrogenated (Scheme S1, supporting information), which demonstrated the general feasibility to hydrogenate the main linking group in the polyurethanes. Self-prepared toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) based polyurethanes were depolymerized smoothly (Scheme 1a). Due to the soluble nature of these two polyurethane samples, high yields of monomers were obtained under much milder conditions than the polyamide hydrogenation. This corroborates the results by Milstein and coworkers,[12] indicating that the solubility of substrates has a great influence on reactivity. In addition, two polyurethane-related compounds, a urea and an isocyanurate were tested, which are also present in polyurethanes as linking groups.[22] Both were hydrogenated to give the corresponding aromatic amines with moderate and high yields (Scheme 1b). To the best of our knowledge, this is the first time an isocyanurate was hydrogenated to give corresponding amine. This showed the feasibility that all isocyanate-derived connecting groups in technical polyurethanes can be hydrogenated to the corresponding amines.

Finally, we tested the hydrogenative depolymerization of technical grade polyamide 66 and polyurethane at the high temperature and pressure conditions. To our delight, with Ultramid® A 27 the desired products were observed after 50 hours, albeit in limited amount. Regarding polyurethane, many additives like antioxidants, stabilizers and plasticizers are added during the manufacturing process,[22] which may complicate the system, thus we started with a well-defined polyurethane sample. Satisfyingly, 1 g of additive-free polyurethane was fully converted after 24 hours and 0.2 g of toluenediamine (TDA, as a mixture of 2,4 and 2,6 isomers) was isolated. The reaction can be upscaled to 8.5 g without decrease of activity and 1.63 g of TDA and 4.84 gram of the polyol were obtained respectively (Figure S2, supporting information), corresponding a turnover number of 668. Remarkably, when a commercial household kitchen sponge made of a TDI-based polyurethane was applied, almost full conversion was observed on 10-g scale, and 2.37 g of TDA was isolated, corresponding to a turnover number of 970 according the formed TDA (Figure S8, supporting information). In addition, polyetherols were formed as the other hydrogenation products. As the composition of the polyetherols used for the synthesis of this foam was not known to the authors, we were not able to quantify the yield of the polyetherol unlike in the hydrogenation of the defined foam described above. We could only see by NMR of the crude mixture, that a mixture of polyetherols is formed (use of polyetherols mixtures for technical PU foams is common). Besides TDA, no other products detectable by GC were formed. To the best of our knowledge, this is the first example of hydrogenation of real-life polyurethane materials with such a high efficiency.



Scheme 1. a) Hydrogenation of polyurethane models, 1 mmol of substrates was used (according to the repeating unit of polyurethanes), yields were determined by GC analysis , TONs were given in parentheses. b) Hydrogenation of two polyurethane related compounds, yields were determined by GC analysis.



Scheme 2. Hydrogenation of technical grade PA 66 and PU samples.

In conclusion, we report here an improved system for hydrogenative depolymerization of polyamide 66 and polyurethane. Key to success is the employment of high reaction temperature to enhance the solubility of polymers. For the first time, technical grade polyamide 66 and polyurethane were hydrogenated. Although the overall efficiency of the system, especially for the hydrogenation of polyamide 66 still need to be improved for practical application, as well as the recycling of the catalyst needs further investigation, we believe these results will be relevant for the further development of plastic recycling based on hydrogenation.

Experimental Section

All reactions were carried out under an Ar atmosphere using standard Schlenk and high-vacuum-line techniques or in a Braun inert atmosphere glovebox filled with Ar.

Complex **2** was prepared via a similar procedure reported for the synthesis of complex **1**:[6c] RuHCl(CO)(PPh$_3$)$_3$ (476.2 mg, 0.5 mmol) and the PNN ligand (201.6 mg, 0.55 mmol) were placed in a 25 mL Schlenk tube equipped with a magnetic bar, 12 mL of THF was added. The tube was put into a 70 °C oil bath and stirred for 7 h. After cooled to room temperature, solvent was removed via filtered cannula, solid was washed by THF (3 x 5 mL), dried under vacuum. Orange solid, 240.0 mg, 91% yield

CCDC 2042476 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/.

Procedure for polyamide and polyurethane hydrogenation

Inside an Ar glove box, the polymer sample, Ru catalyst, KO^{t}Bu and solvent were put into a Premex autoclave (60 or 200 mL depending on solvent amount) equipped with a Teflon insert and a magnetic stirring bar. The autoclave was sealed and taken out of the glove box, charged with H$_2$, and was put into a preheated aluminum block. The reaction was stirred for indicated time and cooled to room temperature, pressure was carefully released, mesitylene was added as an internal standard and an aliquot amount of crude product was submitted for GC analysis. In case of the larger scale hydrogenations given in scheme 2, the products were isolated by column chromatography (for details see the supporting information).

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Keywords: depolymerization • polyamide 66 • polyurethane • hydrogenation • Ru pincer complexes

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[22] G. Brereton, R. M. Emanuel Jr, R. Lomax, K. Pennington, T. Ryan, H. Tebbe, M. Timm, P. Ware, K. Winkler, T. Yuan, Z. Zhu, N. Adam, G. Avar, H. Blankenheim, W. Friederichs, M. Giersig, E. Weigand, M. Halfmann, F.-W. Wittbecker, D.-R. Larimer, U. Maier, S. Meyer-Ahrens, K.-L. Noble, H.-G. Wussow Polyurethanes in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2020**

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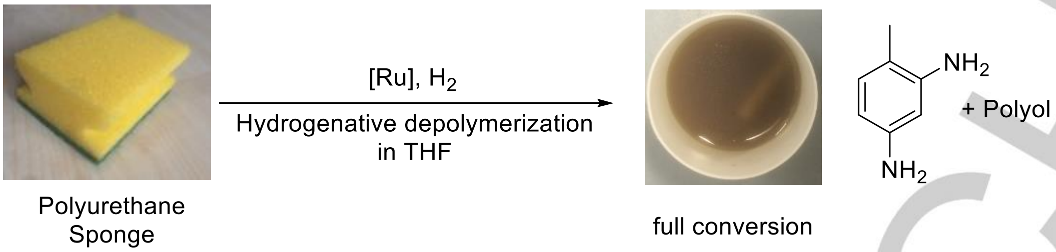

A Ru-pincer complex is developed for the hydrogenative depolymerization of polyamide 66 and polyurethane. The system features high reaction temperature with THF as solvent, technical grade polymers were hydrogenation to give substantial amount of products. Remarkably, turnover numbers close to 1000 is obtained for the hydrogenation of a household kitchen sponge.

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