Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Effective and Sustainable Depolymerization of Nylon 66 – a Transamidation for the Complete Recycling of Polyamides

Robin Coeck [a] *and Dirk E. De Vos* [a]*

[a] *Centre for Membrane separations, Adsorption, Catalysis and Spectroscopy for sustainable solutions (cMACS), KU Leuven, 3001 Leuven, Belgium*

**Corresponding author: E-mail: dirk.devos@kuleuven.be.*

Table of content

Total pages: 7

Total figures : 3

Total tables: 1

1. Experimental details

1.1. Materials

All materials were used as obtained commercially.

1.2. Reactions

Reactions were performed in a 25 mL pressure Parr batch reactor. In a typical transamidation reaction, the reactor is filled with Nylon 66 (0.566 g; 0.5 M amide bonds), *ortho*-Nb_2O_5 catalyst (0.1 - 0.2 g), and acetamide (10 g). Next, the reactor is sealed, gently purged with N_2 and heated to 85°C (melting point acetamide ≈ 80°C). Next, the reactor is purged with N_2 once more, and pressurized with 3 bar NH_3 under strong stirring (830 rpm). After an appropriate reaction time at a temperature of typically 200°C, the reactor is cooled down in an water bath until 90°C and the pressure is released. While the reaction mixture is still warm (±80°C), octanamide (0.025g, external standard) and 10 ml co-solvent (i.e. methanol or formic acid) were added. Then, the reactor was resealed and stirred for 30 minutes at 60°C. This step is essential to keep the reaction mixture liquid at room temperature and to redissolve any precipitated monomeric (or oligomeric) products. Lastly, the reaction mixture is transferred to one or more glass reaction vials (11 mL) which is/are then sealed and centrifuged. The mixture, with a typically clear to pale yellow color (Figure S 1), is analyzed via GC and/or GC-MS.

Figure S 1 — Centrifuged reaction mixtures after a transamidation reaction of Polyamide 66/Nylon 66 and Polyamide 6/Nylon 6.

1.3. Product analysis and identification

The crude reaction mixtures (described in section 1.2) were quantitatively analysed by gas chromatography (GC). For the main product (i.e. *N,N'*-hexamethylene bis(acetamide)) a calibration curve was recorded. Yields of other products were determined via the effective carbon number method. All products were also identified by gas chromatography coupled to mass spectrometry (GC-MS) with an Agilent 6890 GC, equipped with a HP-5ms column, coupled to a 5973 MSD mass spectrometer.

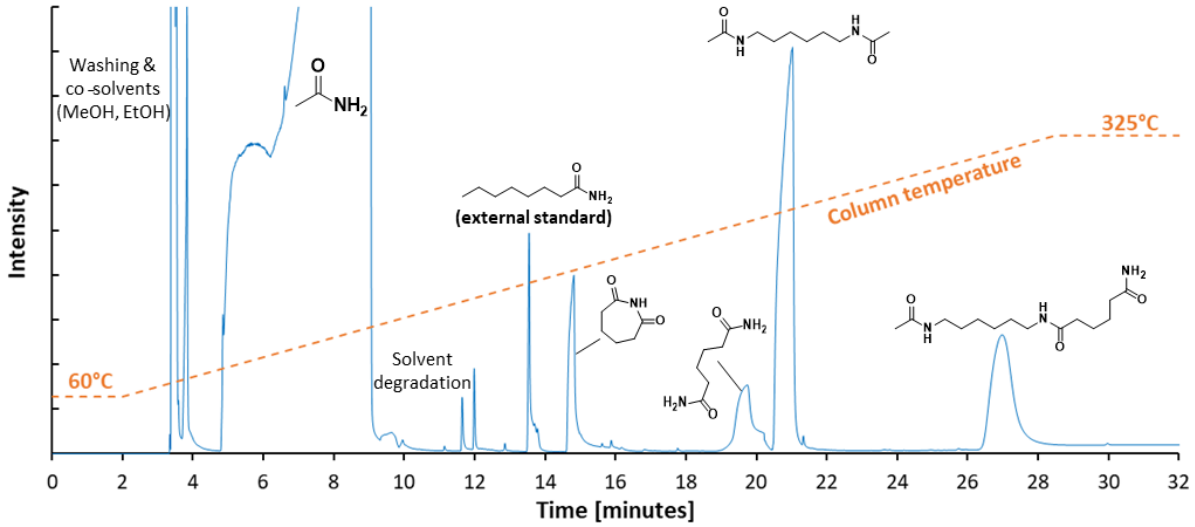


Figure S 2 — GC chromatogram of a crude reaction mixture after a transamidation reaction of Nylon66 with acetamide. Note, during the liquefaction of the reaction mixture with a co-solvent, a significant amount of adipamide reacts to adipimide. The chromatogram corresponds to entry 6, Table 1 of the main text.

1.4. Catalyst synthesis (and characterization)

Nb_2O_5 was hydrothermally synthesized as described in a previous report by Coeck *et al*.[1-2] To a glass-lined Parr reactor (600 mL) 15 g ammonium niobium oxalate hydrate ($C_4H_4NNbO_9.xH_2O$) was added along with 300 mL deionized water. The reactor was sealed and stirred (500 rpm) for 3 days at 175°C. The resulting precipitate was isolated via filtration and excessively washed with deionized water. Instead of pure white, the precipitate had a very light pale yellow color due to some metal ions leaching from the stirrer and being incorporated into the Nb_2O_5 structure. This hydrothermal synthesis method was repeated 2 more times and the crude Nb_2O_5 from all three runs was combined. Any metal ions on the outer surface of the crude Nb_2O_5 were leached off by stirring the powder in a solution of 5 g citric acid in 250 mL deionized water at 80°C overnight. The wet powder was isolated via centrifugation, decanted and excessively washed with deionized water. After drying the powder overnight at 80°C, the material was calcined in air at 400°C for 4 h after which the *ortho*-Nb_2O_5 was ready to use.

The Nb_2O_5 was characterized with X-ray powder diffraction (XRD) and N_2 physisorption measurements; these results can be found in our previous reports.[1-2]

2. Additional experiments

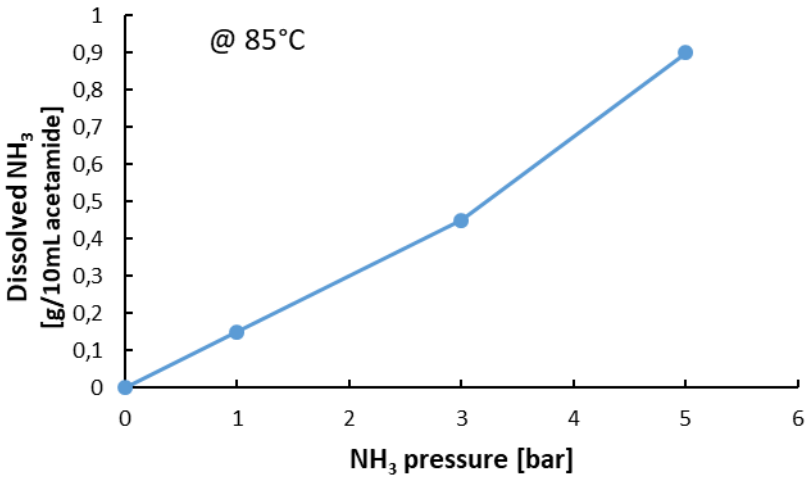


Figure S 3 — Solubility of ammonia (NH_3) in acetamide at different pressures and 85°C.

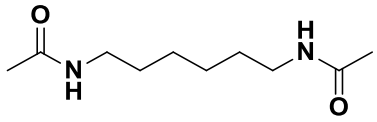
Table S 1— Stability of different acetamide /co-solvent mixtures at room temperature (5 g acetamide, 5 mL co-solvent),

Co-solvent	Water	Formic acid	Methanol	Ethanol	Formamide	Ethylene glycol	Glycerol[a]	HFIP[b]	Acetonitrile
Stability	✓	✓	✓	X	✓	✓	✓	X	✓

X means unstable, ✓ means stable. [a]Very viscous mixture. [b]HFIP: hexafluoroisopropanol

3. Product identification

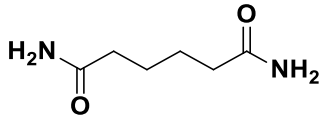
***N*,*N*'-Hexamethylene bis(acetamide) (1, MW = 200 g/mol)**



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.17 (t, 4H, -C-NH-C**H$_2$**-), 1.94 (s, 6H, -C(=O)-C**H$_3$**), 1.57-1.46 (m, 4H, -C-NH-CH$_2$-C**H$_2$**-), 1.41-1.31 (m, 4H, -C-NH-CH$_2$-CH$_2$-C**H$_2$**-).

GC-MS (EI, 70eV): m/z (rel. int, %): 39 (6), 41 (16), 42 (14), 43 (86), 44 (33), 45 (6), 55 (9), 56 (14), 58 (12), 60 (19), 69 (7), 72 (61), 73 (55), 86 (76), 87 (31), 98 (36), 100 (45), 101 (16), 114 (29), 115 (19), 128 (100), 129 (14), 140 (31), 141 (5), 143 (7), 157 (17), 185 (4), 200 (7).

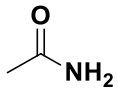
Adipamide (2, MW = 144 g/mol)



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.35 (t, 2H, -C(=O)-C**H$_2$**-), 1.76-1.70 (m, 4H, -C(=O)-CH$_2$-C**H$_2$**-).

GC-MS (EI, 70eV): m/z (rel. int, %): 39 (13), 41 (20), 42 (12), 43 (27), 44 (100), 45 (5), 53 (5), 54 (6), 56 (12), 57 (15), 59 (39), 72 (52), 73 (18), 85 (9), 86 (67), 99 (50), 100 (9), 110 (7), 127 (18), 144 (1).

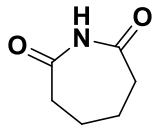
Acetamide (3, MW = 59 g/mol)



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.04 (s, 3H, -C(=O)-C**H$_3$**),

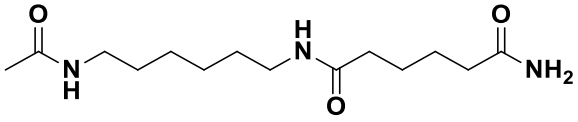
GC-MS (EI, 70eV): m/z (rel. int, %): 40 (6), 41 (9), 42 (29), 43 (57), 44 (100), 59 (90), 60 (5).

Adipimide (4, MW = 127 g/mol)



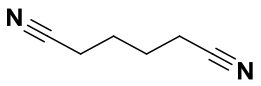
GC-MS (EI, 70eV): m/z (rel. int, %): 38 (3), 39 (18), 40 (7), 41 (24), 42 (12), 43 (22), 44 (60), 51 (4), 52 (5), 53 (7), 54 (51), 55 (37), 56 (4), 59 (100), 60 (3), 68 (3), 72 (5), 82 (21), 86 (12), 110 (3), 126 (0.3).

N^1-(6-acetamidohexyl)adipamide (5, MW = 285 g/mol)



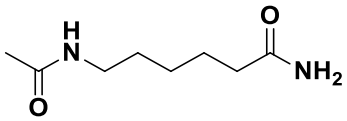
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (10), 41 (33), 42 (17), 43 (65), 44 (43), 45 (5), 53 (7), 54 (19), 54 (19), 55 (66), 56 (21), 57 (6), 58 (20), 60 (17), 67 (5), 69 (11), 70 (6), 72 (51), 73 (46), 81 (6), 82 (62), 83 (11), 84 (7), 86 (87), 87 (36), 98 (72), 99 (9), 100 (100), 101 (21), 110 (34), 114 (48), 115 (14), 127 (8), 128 (83), 129 (17), 139 (22), 140 (61), 141 (8), 142 (17), 143 (27), 153 (15), 154 (8), 156 (10), 157 (23), 159 (5), 167 (20), 168 (10), 181 (14), 185 (17), 195 (81), 196 (13), 200 (9), 213 (10), 224 (33), 225 (5), 227 (26), 267 (7), 284 (0.01).

Adiponitrile (6, MW = 108 g/mol)



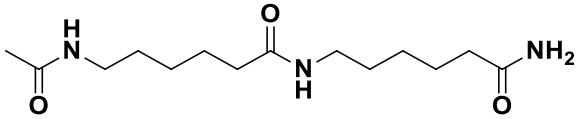
GC-MS (EI, 70eV): m/z (rel. int, %): 38 (7), 39 (26), 40 (17), 41 (100), 42 (7), 51 (8), 52 (14), 53 (7), 54 (60), 55 (26), 64 (5), 66 (7), 68 (75), 107 (1), 108 (0.1).

6-Acetamidohexanamide (7, MW = 172 g/mol)



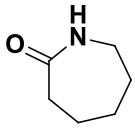
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (10), 41 (23), 42 (16), 43 (73), 44 (65), 45 (6), 55 (16), 56 (12), 57 (10), 58 (8), 59 (35), 60 (16), 67 (6), 69 (12), 72 (100), 73 (31), 86 (23), 87 (15), 100 (17), 101 (26), 111 (8), 112 (25), 113 (12), 114 (32), 128 (6), 129 (56), 155 (4), 172 (2).

6-Acetamido-*N*-(6-amino-6-oxohexyl)hexanamide (8, MW = 285 g/mol)



GC-MS (EI, 70eV): m/z (rel. int, %): 41 (7), 43 (9), 54 (6), 55 (21), 56 (9), 58 (5), 67 (5), 69 (11), 72 (9), 82 (5), 83 (7), 84 (7), 86 (14), 87 (7), 96 (9), 100 (12), 101 (6), 111 (14), 112 (10), 113 (25), 114 (100), 128 (9), 154 (16), 156 (9), 167 (43), 168 (9), 181 (8), 195 (10), 224 (22), 227 (7), 268 (1), 284 (1).

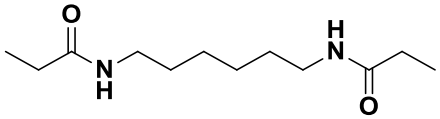
Caprolactam (9, MW = 113 g/mol)



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.22-3.15 (m, 2H, -NH-C**H**$_2$-), 2.48-2.39 (m, 2H, -C(=O)-C**H**$_2$-), 1.82-1.48 (m, 6H, -NH-CH$_2$-(C**H**$_2$)$_3$-CH$_2$-C(=O)-).

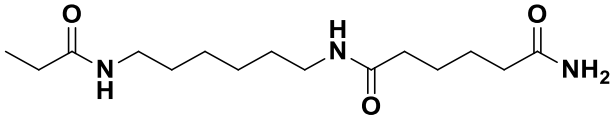
GC-MS (EI, 70eV): m/z (rel. int, %): 38 (5), 39 (12), 41 (45), 53 (7), 55 (100), 56 (91), 57 (9), 67 (10), 68 (7), 84 (53), 85 (58), 113 (98), 114 (5).

***N*,*N'*-Hexamethylene bis(propionamide) (10, MW = 228 g/mol)**



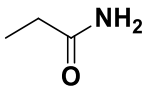
GC-MS (EI, 70eV): m/z (rel. int, %): 41 (15), 42 (7), 43 (6), 44 (30), 55 (17), 56 (17), 57 (80), 58 (17), 69 (6), 72 (9), 74 (20), 82 (4), 84 (4), 86 (77), 87 (49), 98 (59), 99 (7), 100 (100), 101 (32), 114 (61), 115 (19), 128 (19), 129 (5), 142 (96), 143 (47), 144 (4), 154 (39), 155 (5), 156 (7), 171 (27), 199 (20), 228 (12).

***N*^{1}-(6-propionamidohexyl)adipamide (11, MW = 299 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (8), 41 (25), 42 (10), 43 (8), 44 (36), 53 (6), 54 (15), 55 (54), 56 (19), 57 (55), 58 (18), 69 (8), 70 (5), 72 (11), 73 (7), 74 (13), 81 (5), 82 (49), 83 (9), 84 (6), 86 (60), 87 (37), 98 (65), 99 (8), 100 (100), 101 (26), 110 (27), 114 (55), 115 (14), 126 (5), 127 (7), 128 (23), 129 (5), 139 (16), 140 (10), 142 (59), 143 (40), 153 (12), 154 (32), 156 (14), 167 (11), 168 (6), 171 (14), 181 (8), 185 (5), 195 (57), 196 (10), 199 (9), 207 (20), 214 (5), 224 (33), 225 (5), 227 (6), 241 (17), 252 (11), 281 (1).

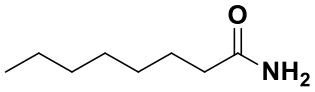
Propionamide (12, MW = 73 g/mol)



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) =2.34 (quart, 2H, -C(=O)-C**H$_2$**-), 1.24 (t, 3H, -C**H$_3$**).

GC-MS (EI, 70eV): m/z (rel. int, %): 99 (7), 73 (60), 72 (14), 70 (34), 57 (21), 56 (5), 55 (7), 44 (100), 42 (6).

Octanamide (13, MW = 143 g/mol)

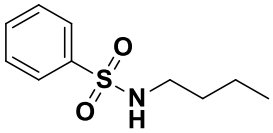


GC-MS (EI, 70eV): m/z (rel. int, %): 39 (10), 41 (22), 42 (10), 43 (23), 44 (38), 55 (12), 57 (9), 59 (100), 60 (5), 72 (31), 73 (13), 86 (9), 100 (5), 114 (4), 143 (0.5).

Acetonitrile (14, MW = 41 g/mol)

GC-MS (EI, 70eV): m/z (rel. int, %): 38 (17), 39 (23), 40 (56), 41 (100), 42 (6).

***N*-Butylbenzenesulfonamide (15, MW = 213 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 213 (6), 171 (9), 158 (1), 157 (14), 142 (7), 141 (100), 132 (1), 125 (2), 106 (1), 116 (16), 97 (1), 78 (11), 77 (93), 74 (2), 65 (2), 52 (2), 86 (54), 51 (22), 49 (6), 41 (6).

4. Acknowledgements

R. Coeck and D. E. De Vos would like to thank VLAIO and Flanders Industry Innovation Moonshot for research funding. R. Coeck would also like to thank Amber Van Peteghem and Pablo De Guinea Echevarria for acquiring difficult to obtain scientific literature.

5. References

[1] R. Coeck, A. De Bruyne, T. Borremans, W. Stuyck and D. E. De Vos, *ACS Sustain. Chem. Eng.*, 2022, **10**, 3048–3056.
[2] R. Coeck, M. Houbrechts and D. E. De Vos, *Chem. Sci.*, 2023, **14**, 7944–7955.