

Supporting Information

Hydrogenative Depolymerization of Silicon-modified Polyureas

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1. Materials and Methods

All experiments were performed under argon atmosphere by using standard Schlenk techniques or in a glove box, if not stated otherwise. Dry THF, 1,4-dioxane, toluene, CH₂Cl₂ and *n*-hexane were purchased from *Acros Organics* (anhydrous, AcroSeal), degassed, and purged with argon prior to use.

Chemicals for the preparation of polymers were purchased from *Sigma*, *Alfa*, *Strem*, *Abcr*, *Acros* and *TCl*. Catalysts **Ru-I – VI** were purchased from *Strem*. **Mn-I – IX**^[1-7], **Fe-I**^[8], **Fe-II**^[9], and **Co-I** and **Co-II**^[10] were prepared according to previously published procedures.

Deuterated solvents were ordered from *Deutero GmbH* and stored over molecular sieves. NMR spectra were recorded using *Bruker* 300 Fourier, *Bruker* AV 300 and *Bruker* AV 400 spectrometers. Chemical shifts are reported in ppm relative to the residual signal of deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet and m = multiplet.

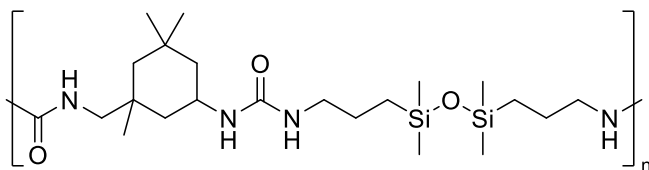
GC analyses were performed on an Agilent 7890B gas chromatograph equipped with HP-5 column (30 m x 0.320 mm x 0.25 μm) and FID detector. The reported yields and conversions were determined using mesitylene or *n*-dodecane as internal standard. Methanol formation for all the investigated reactions was detected.

IR spectra were recorded on a Thermo Scientific™ Nicolet™ iS™ 10 FT-IR-spectrometer. The intensity of the bands is indicated by the following abbreviations: vs (very strong), s (strong), m (medium), w (weak), vw (very weak), broad signals are indexed br (broad).

General procedure for the hydrogenation of polyurea: polyurea **1** (0.25 mmol) was placed into a 4 mL glass vial (VWR 548-0521, 2in1-Kit:4mL) containing a small PTFE-coated stir bar and the vial was introduced into a glovebox (Ar). The catalyst (3 mol% for Mn; 2 mol% for Ru) and potassium *tert*-butoxide (6 mol%, 1.68 mg) were weighed out and added to the vial. The vial was capped with the rubber septum and removed from the glovebox. Under a stream of argon, solvent was added, the vial was subsequently transferred to a Parr Instruments 300mL autoclave, and the autoclave was sealed. The autoclave was purged at least 3 times with hydrogen (20 bar) and ultimately pressurized to the desired pressure. The autoclave was placed into a pre-heated aluminum block and the reaction was stirred (300 rpm) for the indicated time. After the reaction, the autoclave was cooled down in an ice-bath and the pressure was slowly released. The contents of the vial were subsequently analyzed via GC. Upscaling was performed analogously using larger glass vials.

2. Synthesis of Polyureas **1a-d**

2.1 Synthesis of polyurea **1a**



An oven dried round bottom flask (100 mL) equipped with a magnetic stir bar was charged with isophorone diisocyanate (1.11 g, 5.00 mmol) and DMF (30 mL). Then, 1,3-bis(3-aminopropyl)tetramethyldisiloxane (1.30 g, 5.25 mmol) was added to the mixture dropwise under stirring. After the solution has cooled down, it was heated to 60 °C and stirred for 4 h. Afterwards, ice-cold water (30 mL) was added to the mixture. The initially clear solution turned turbid during the precipitation process. The mixture was centrifuged for 3 min at 10,000 rpm to separate the product from the solvent. The product was washed with ethanol and after drying under vacuum (75 °C for 24 h) polyurea **1a** was obtained as a colorless solid (2.01 g; Yield: 86 %). Polyurea **1a** was used without further purification.

¹H-NMR (300 MHz, DMSO-*d*₆) δ = 5.80 – 5.54 (m, 4H), 3.87 – 3.80 (m, 2H), 3.10 (s, 0.80H), **3.05 (s, 0.38H)**, 2.91 (s, 4H), 2.72 (s, 2H), 1.70 (s, 3H), 1.34 (s, 4H), 1.03 – 0.91 (m, 21H), 0.42 (s, 4H), 0.00 (s, 12H) ppm.

NOTE: As shown in **Figure S1**, the strong adsorption peak at around 3294 cm⁻¹ in the spectrum of **1a** should be commonly assigned to NH stretching vibration, and the one at 1577 cm⁻¹ to NH plane-banding vibration. The peak at 2264 cm⁻¹ in the spectra of isophorone diisocyanate should be assigned to the NCO group. It was gone after the reaction, indicating a complete reaction between the isophorone diisocyanate and 1,3-bis(3-aminopropyl)tetramethyldisiloxane. Meanwhile, the peak at 1261 cm⁻¹ should be attributed to the absorption of the Si-CH₃ group in 1,3-bis(3-aminopropyl)tetramethyldisiloxane. After the reaction, the peak showed no change, indicating that the Si-O-Si group is stable under the previously described polymerization conditions.

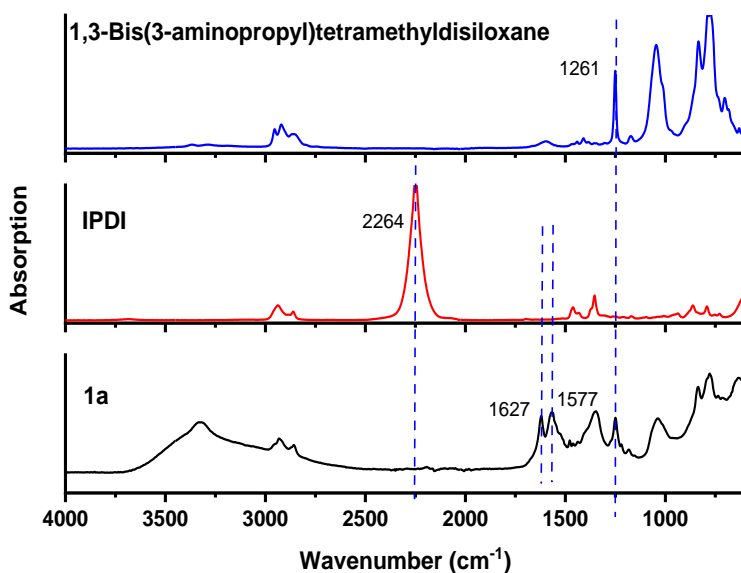


Figure S1. FT-IR spectra of 1,3-bis(3-aminopropyl)tetramethyldisiloxane, isophorone diisocyanate, and polyurea **1a**, respectively.

Determination of the molecular weight: The number molecular weight (*M_n*) of polyureas was determined by end-group analysis using ¹H-NMR spectroscopy.^[11] Therefore, the integral for the CH₂ protons next to the NH₂ end-groups **a** (δ = 3.05 ppm) was compared to the methylenic protons in the repeating units **b** (δ = 0.42 ppm) according to the following equation:

$$M_n = (\text{Integration of peak } \mathbf{b}) / (\text{Integration of peak } \mathbf{a}) * (\text{MW of repeating unit})$$

Where the MW of the repeating unit is calculated as the sum of the molecular masses of the monomers (for **1a** = 470.31 g mol⁻¹).

Thus, for **1a**, $M_n = 4900$ g mol⁻¹.

It is important to note that the M_n calculated using this method only provides a good estimate and can deviate from actual values due to inaccuracy by integrating the NMR signals. This inaccuracy arises from signal overlapping and the low intensity of the signals due to the low concentration of the samples (in some cases) in the deuterated solvents used for the NMR studies. In any case, the eventual mistakes arising from these measurements do not affect the main conclusions of this work.

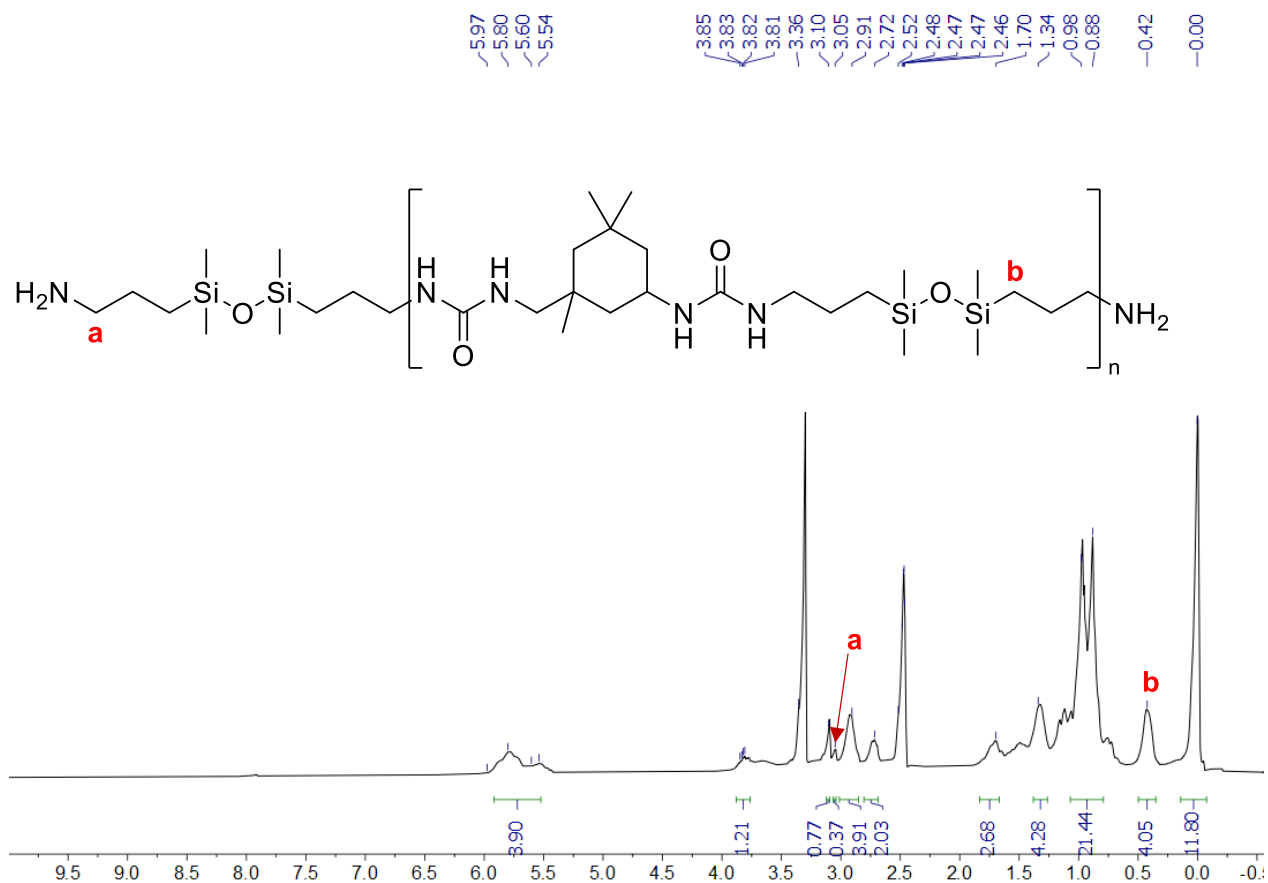
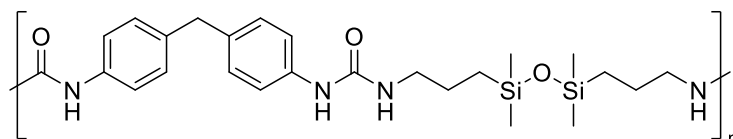


Figure S2. Polyurea (**1a**) ¹H-NMR spectrum in DMSO-*d*₆. An explicit representation of the end-groups and the signals used to calculate the M_n (a and b) are also presented

2.2 Synthesis of polyurea **1b**



An oven dried round bottom flask (100 mL) equipped with a magnetic stirring bar was charged with methylene diphenyl diisocyanate (1.25 g, 5.00 mmol) and DMF (30 mL). Then, 1,3-bis(3-aminopropyl)tetramethyldisiloxane (1.30 g, 5.25 mmol) was added to the mixture dropwise under stirring. After the solution had cooled down, the reaction mixture was heated to 60 °C and stirred for 4 h. Afterwards, ice-cold water (30 mL) was added to the mixture. The initially clear solution turned turbid during the precipitation process. The mixture was centrifuged for 3 min at 10,000 rpm to separate the product from the solvent. The product was washed with ethanol and after drying under vacuum (75 °C for 24 h) polyurea **1b** was obtained as a colorless solid (1.98 g; Yield: 80 %). Polyurea **1b** was used without further purification.

$^1\text{H-NMR}$ (300 MHz, DMSO-d_6) δ = 7.92 (s, 1.48H), 5.55 (s, 1H), 2.86 (s, 2.83 H), 2.70 (s, 3.87 H), 2.23 (s, 2H), 2.06 (s, 0.62H), **2.17 (s, 0.29H)**, 1.64 (s, 9H), 1.32 (s, 2H), 1.21 (s, 1H), 0.98 (s, 2H), 0.87 (s, 4H), 0.39 (s, 2H), 0.05 (s, 6H) ppm.

M_n (Calculated by $^1\text{H-NMR}$) = 3800 g mol $^{-1}$.

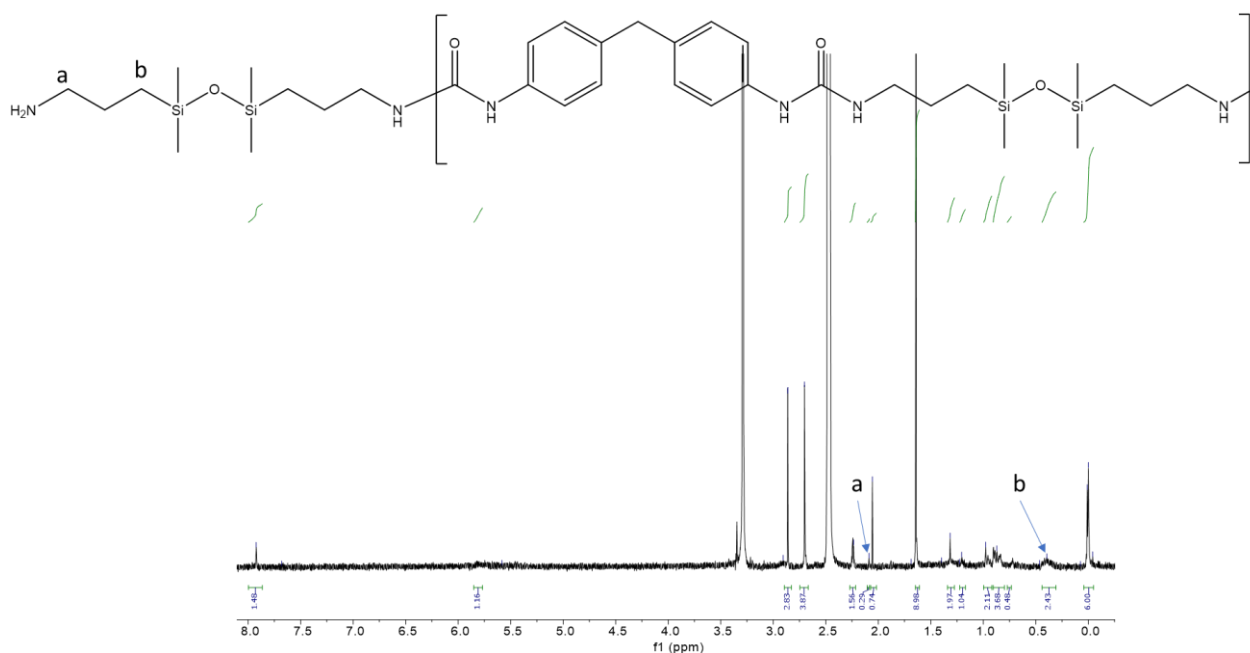
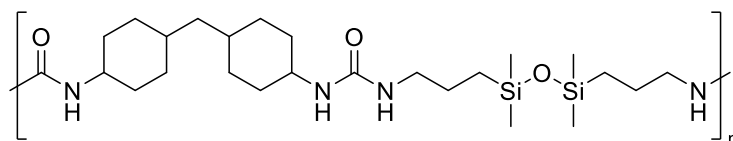


Figure S3. Polyurea (**1b**) $^1\text{H-NMR}$ spectrum in DMSO-d_6 . An explicit representation of the end-groups and the signals used to calculate the M_n (a and b) are also presented

2.3 Synthesis of polyurea **1c**



An oven dried round bottom flask (100 mL) equipped with a magnetic stirring bar was charged with bis(4-isocyanatocyclohexyl)methane (1.31 g, 5.00 mmol) and DMF (30 mL). Then, 1,3-bis(3-

aminopropyl)tetramethyldisiloxane (1.30 g, 5.25 mmol) was added to the mixture dropwise under stirring. After the solution had cooled down, the reaction mixture was heated to 60 °C and stirred for 4 h. Afterwards, ice water (30 mL) was added to the mixture. The initially clear solution turned turbid during the precipitation process. The mixture was centrifuged for 3 min at 10,000 rpm to separate the product from the solvent. The product was washed with ethanol and after drying under vacuum (75 °C for 24 h) polyurea **1c** was obtained as a colorless solid (2.10 g; Yield: 83 %). Polyurea **1c** was used without further purification.

$^1\text{H-NMR}$ (300 MHz, DMSO-d_6) δ = 5.90 – 5.37 (m, 2H), 3.86 (s, 1H), **3.61 (s, 0.4H)**, 2.89 – 2.83 (m, 2H), 1.39 – 1.31 (m, 3H), 1.19 – 0.66 (m, 4H), 0.45 – 0.34 (m, 2H), 0.03 (s, 6H) ppm.

M_n (Calculated by $^1\text{H-NMR}$) = 4700 g mol $^{-1}$.

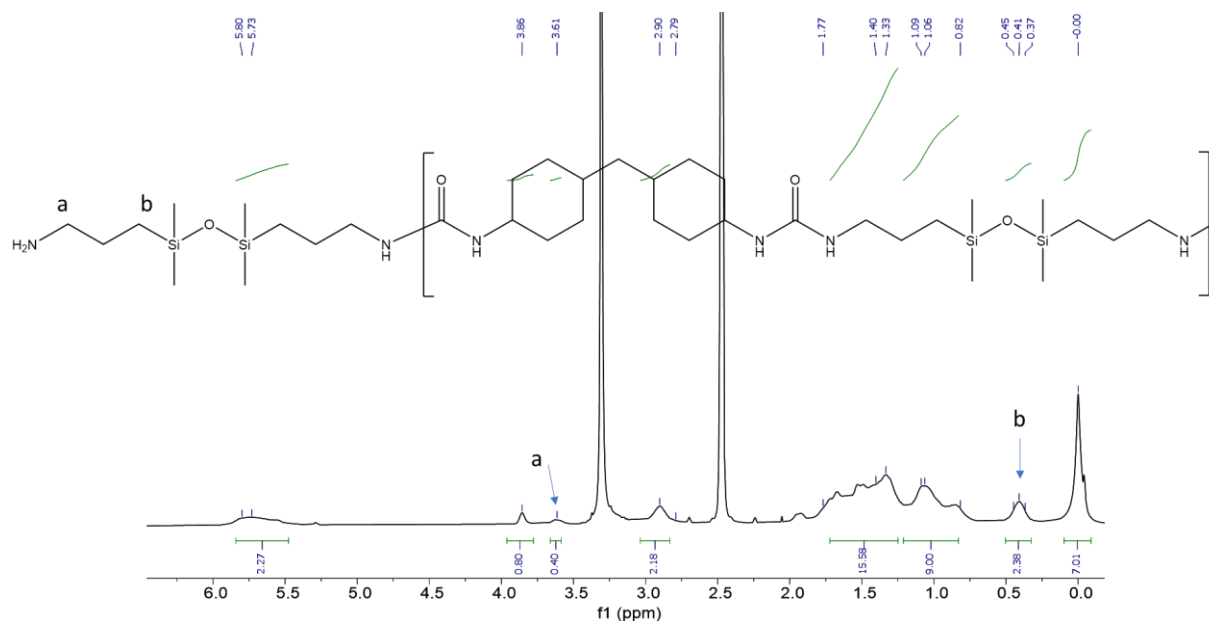
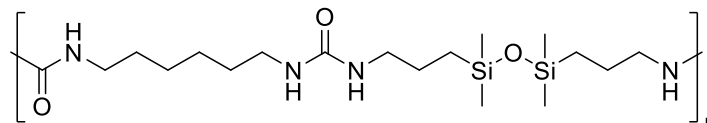


Figure S4. Polyurea (**1c**) $^1\text{H-NMR}$ spectrum in DMSO-d_6 . An explicit representation of the end-groups and the signals used to calculate the M_n (a and b) are also presented

2.4 Synthesis of polyurea **1d**



An oven dried round bottom flask (100 mL) equipped with a magnetic stirring bar was charged with hexamethylene diisocyanate (0.84 g, 5.00 mmol) and DMF (30 mL). Then, 1,3-bis(3-aminopropyl)tetramethyldisiloxane (1.30 g, 5.25 mmol) was added to the solvent dropwise under stirring. After solution had cooled down, the reaction mixture was heated to 60 °C and stirred for 4 h. Afterwards, ice water (30 mL) was added to the mixture. The initially clear solution turned turbid during the precipitation process. The mixture was centrifuged for 3 min at 10,000 rpm to separate the product from the solvent. The product was washed with ethanol and after drying under vacuum (75 °C for 24 h) polyurea

1d was obtained as a colorless solid (1.86 g; Yield: 90 %). Polyurea **1d** was used without further purification.

$^1\text{H-NMR}$ (300 MHz, THF-d_8) δ = 5.66 (s, 1H), **5.60** (s, **0.22**), 3.27 (s, 0.24H), 3.24 (s, 4H), 1.35 (s, 2H), 1.22 (d, 2H), 1.16 (d, 2H), 0.46-0.52 (s, 2H) 0.06 (s, 6H) ppm.

M_n (Calculated by $^1\text{H-NMR}$) = 2400 g mol^{-1} .

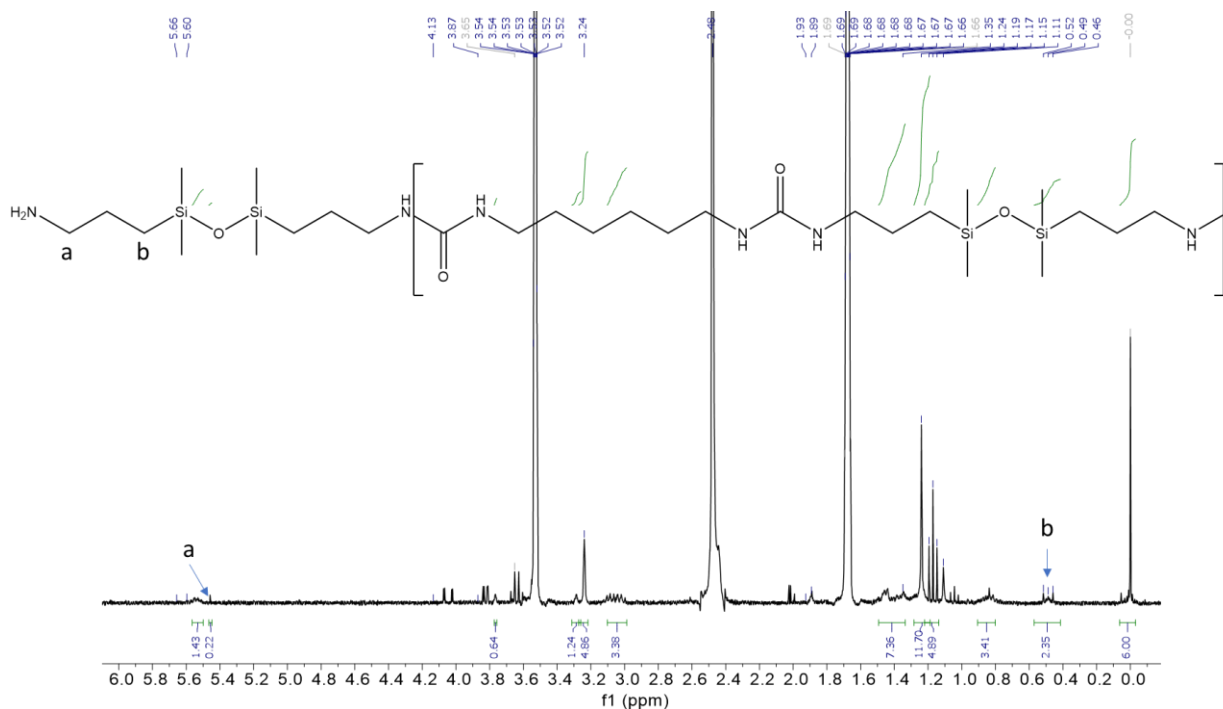


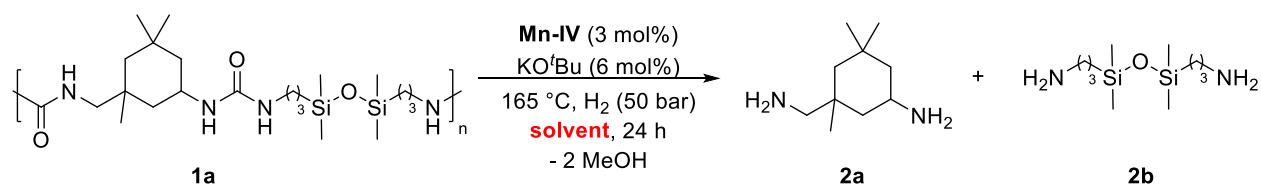
Figure S5. Polyurea (**1d**) $^1\text{H-NMR}$ spectrum in THF-d_8 . An explicit representation of the end-groups and the signals used to calculate the M_n (a and b) are also presented

3. Additional reactions

3.1 Mn-catalyzed hydrogenation of polyurea 1a

In the following tables about the hydrogenative depolymerization, those entries, which were chosen as final reaction conditions, are highlighted for the reader's convenience.

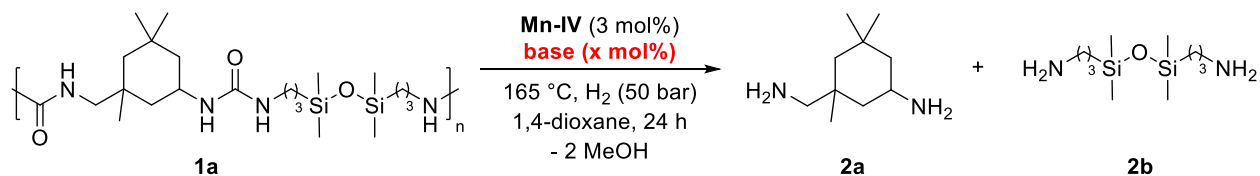
Table S1. Mn-catalyzed hydrogenation of polyurea **1a** in different solvents.^[a]



entry	solvent	yield of 2a (%)	yield of 2b (%)
1	THF	47	38
2	1,4-dioxane	85	79
3	toluene	24	19
4	CH ₂ Cl ₂	39	26
5	DMSO	55	47
6	<i>n</i> -hexane	8	6

[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used with respect to the repeating unit of **1a**), **Mn-IV** (3 mol%, 4.7 mg), KO^tBu (6 mol%, 1.7 mg), solvent (2 mL), 165 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

Table S2. Mn-catalyzed hydrogenation of polyurea **1a** in the presence of different bases.^[a]

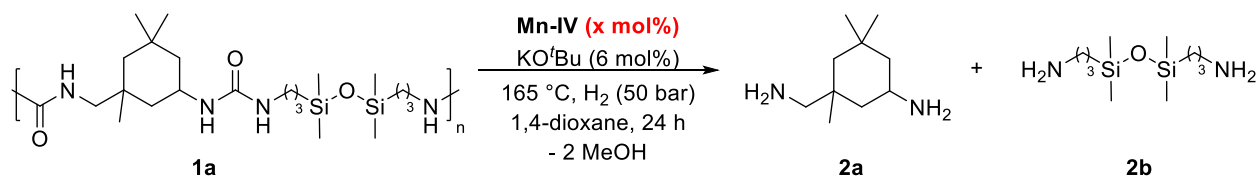


entry	base (x mol%)	yield of 2a (%)	yield of 2b (%)
1	KOH (6)	16	14
2	KO ^t Bu (6)	85	79
3	KO ^t Bu (10)	75	71
4	KO ^t Bu (3)	34	25
5	K ₂ CO ₃ (6)	<5	<5
6	Cs ₂ CO ₃ (6)	17	13
7	NaH (6)	22	16

[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Mn-IV** (3 mol%, 4.7 mg), base (x mol%), 1,4-dioxane (2 mL), 165 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

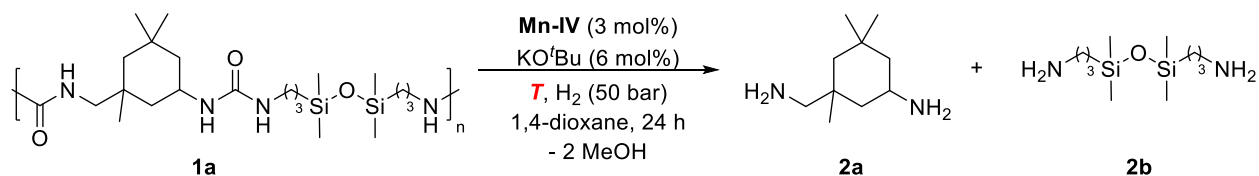
Note: Higher base amounts will cause more side reactions. *N*-formylation of amine has been observed.

Table S3. Mn-catalyzed hydrogenation of polyurea **1a** using various catalyst loadings.^[a]



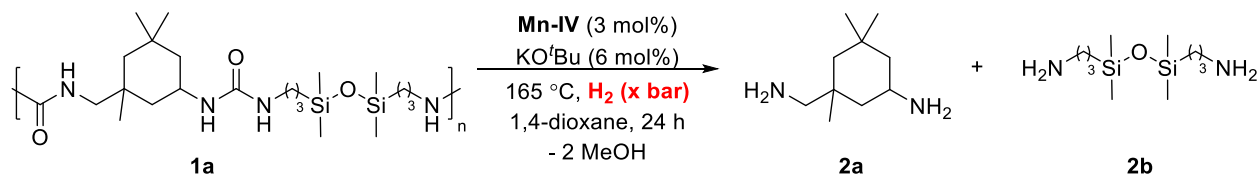
entry	Mn-IV (x mol%)	yield of 2a (%)	yield of 2b (%)
1	4	86	77
2	3	85	79
3	2	63	61
4	1	32	24

[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Mn-IV** (x mol%), KO^tBu (6 mol%, 1.7 mg), 1,4-dioxane (2 mL), 165 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

Table S4. Mn-catalyzed hydrogenation of polyurea **1a** at different temperatures.^[a]

entry	T/ °C	yield of 2a (%)	yield of 2b (%)
1	180	72	68
2	165	85	79
3	150	66	61
4	140	41	38
5	130	26	25
6	120	13	9

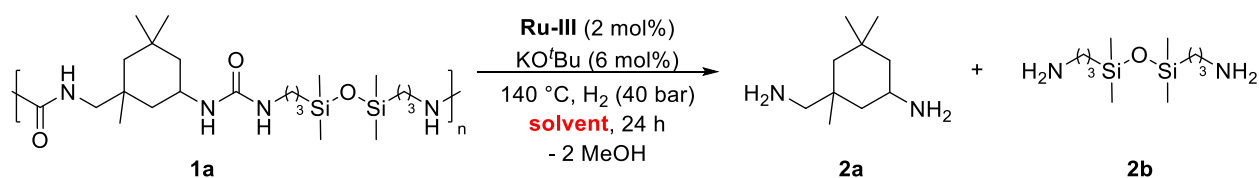
[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Mn-IV** (3 mol%, 4.7 mg), KO^tBu (6 mol%, 1.7 mg), 1,4-dioxane (2 mL), x °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

Table S5. Mn-catalyzed hydrogenation of polyurea **1a** at different hydrogen pressures.^[a]

entry	H ₂ (x bar)	yield of 2a (%)	yield of 2b (%)
1	50	85	79
2	40	73	71
3	20	42	35
4	10	22	17

[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Mn-IV** (3 mol%, 4.7 mg), KO^tBu (6 mol%, 1.7 mg), H₂ (x bar), 1,4-dioxane (2 mL), 165 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

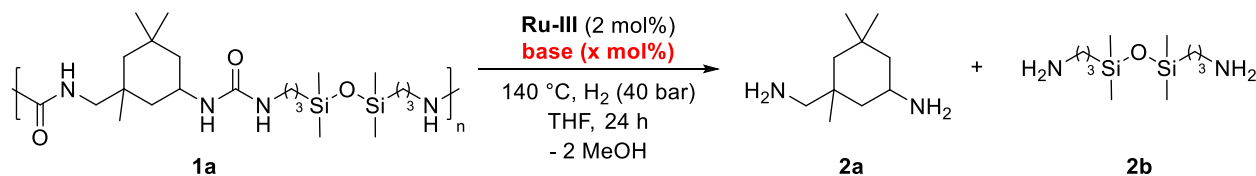
3.2 Ru-catalyzed hydrogenation of polyurea **1a**

Table S6. Ru-catalyzed hydrogenation of polyurea **1a** in different solvents.^[a]

entry	solvent	yield of 2a (%)	yield of 2b (%)
1	THF	84	81
2	1,4-dioxane	80	73
3	toluene	37	24
4	CH ₂ Cl ₂	45	39
5	DMSO	10	7
6	<i>n</i> -hexane	16	13

[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Ru-III** (2 mol%, 3.0 mg), KO^tBu (6 mol%, 1.7 mg), solvent (2 mL), 140 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

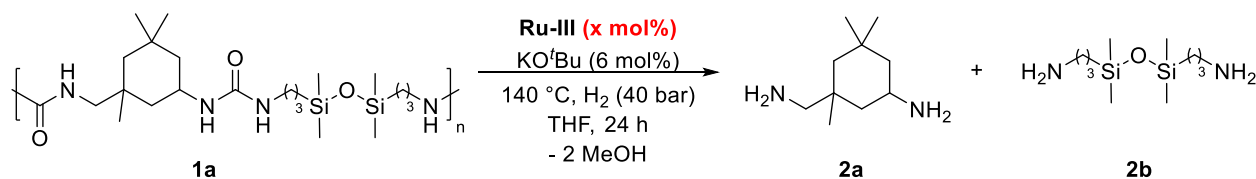
Table S7. Ru-catalyzed hydrogenation of polyurea **1a** in the presence of different bases.^[a]



entry	base (x mol%)	yield of 2a (%)	yield of 2b (%)
1	KOH (6)	29	17
2	KO ^t Bu (6)	84	81
3	KO ^t Bu (3)	55	51
4	K ₂ CO ₃ (6)	<5	<5
5	Cs ₂ CO ₃ (6)	32	35
6	NaH (6)	45	33

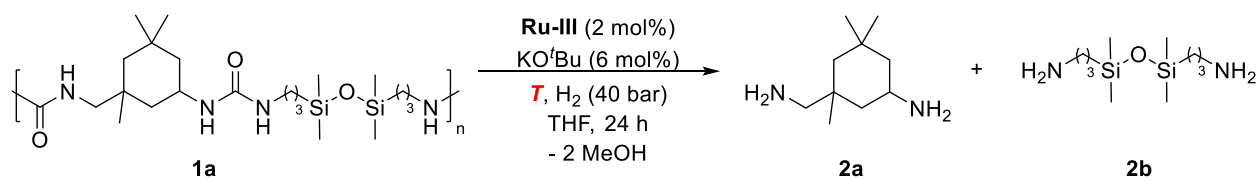
[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Ru-III** (2 mol%, 3.0 mg), base (x mol%), THF (2 mL), 140 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

Table S8. Ru-catalyzed hydrogenation of polyurea **1a** at various catalyst loadings.^[a]



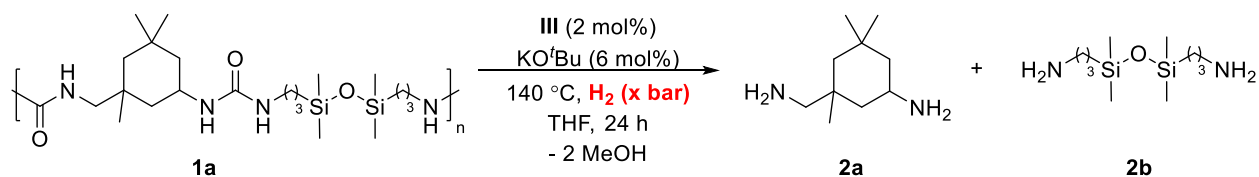
entry	Ru-III (x mol%)	yield of 2a (%)	yield of 2b (%)
1	3	87	83
2	2	84	81
3	1	48	44

[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Ru-III** (x mol%), KO^tBu (6 mol%, 1.7 mg), THF (2 mL), 140 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

Table S9. Ru-catalyzed hydrogenation of polyurea **1a** at different temperatures.^[a]

entry	T/ °C	yield of 2a (%)	yield of 2b (%)
1	165	89	83
2	150	86	80
3	140	84	81
4	130	62	55
5	120	33	27

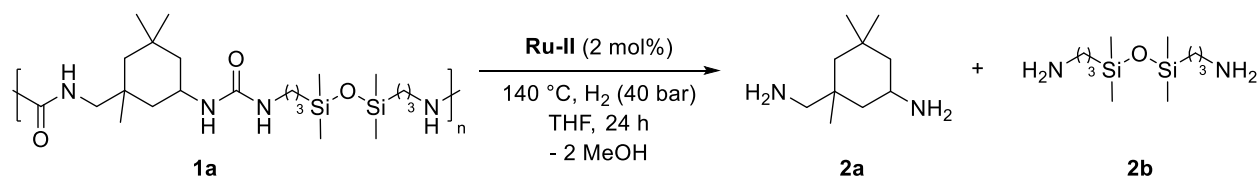
[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Ru-III** (2 mol%, 3.0 mg), KO^tBu (6 mol%, 1.7 mg), THF (2 mL), x °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

Table S10. Ru-catalyzed hydrogenation of polyurea **1a** at different hydrogen pressures.^[a]

entry	H ₂ (x bar)	yield of 2a (%)	yield of 2b (%)
1	60	85	83
2	40	84	81
3	20	62	55
4	10	33	27

[a] Reaction conditions: **1a** (118 mg, 0.25 mmol of substrate was used according to the repeating unit of **1a**), **Ru-III** (2 mol%, 3.0 mg), KO^tBu (6 mol%, 1.7 mg), H₂ (x bar), THF (2 mL), 140 °C, 24 h. The conversion and yields were determined by GC using mesitylene as internal standard.

3.3 Comparison of Hydrogenation of Polyurea **1a** using Ru-II vs Ru-III



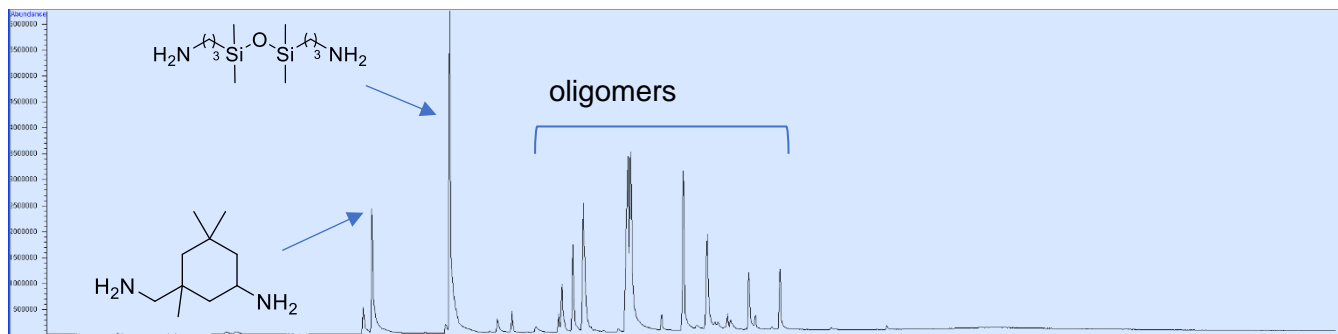


Figure S6. GC-MS chromatogram of crude reaction mixture

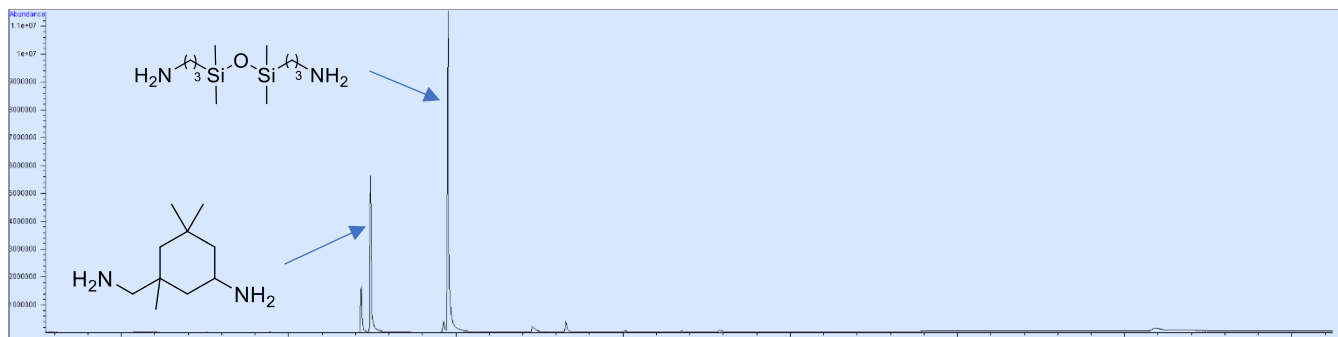
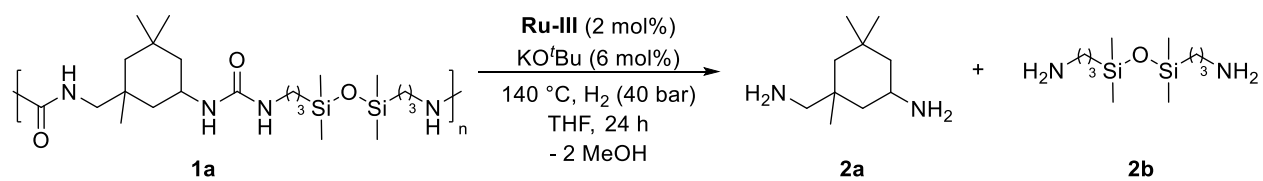


Figure S7. GC-MS chromatogram of crude reaction mixture

4. References

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