

Supporting Information

Reversible piperidone derivative amine networks with monomer recovery

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1. Theoretical calculation of thermodynamics

Results

Table S1: The Gibbs energy of formation $\Delta G_{\text{reac}}(c,T)$ at various concentrations c and temperatures T given in kJ mol^{-1} . The reactions are shown in Scheme 2. Two different DFT based methods were used: PBE0-D4/def2-QZVP//def2-TZVP (DCOSMO-RS-out) and M06-2X/def2-QZVP//def2-TZVP (SMD).

		$\Delta G_{\text{reac}}(c,T)$ in kJ mol^{-1}								
Computational method		PBE0-D3(BJ)/def2-QZVP//def2-TZVP (DCOSMO-RS-out)						M06-2X/def2-QZVP//def2-TZVP (SMD)		
Temperature T in K		298.15			333.15			333.15		
concentration c in mol L^{-1}		0.35	1	10	0.35	1	10	0.35	1	10
Product	R									
Hemiaminal	-CH ₂ -CH ₃	25.4	22.8	17.1	31.0	28.1	21.7	24.4	21.5	15.1
	-CO-CH ₃	15.0	12.4	6.7	20.5	17.6	11.2	14.3	11.4	5.0
	-CO-COH	14.9	12.3	6.6	20.4	17.5	11.1	14.0	11.1	4.7
Aminal	-CH ₂ -CH ₃	10.4	7.8	2.1	16.7	13.8	7.5	16.8	13.9	7.5
	-CO-CH ₃	-1.5	-4.1	-9.8	4.7	1.8	-4.6	9.5	6.6	0.2
	-CO-COH	-1.6	-4.2	-9.9	4.6	1.7	-4.6	4.9	1.9	-4.4
Imine	-CH ₂ -CH ₃	-5.7	-5.7	-5.7	-4.8	-4.8	-4.8	9.9	9.9	9.9
	-CO-CH ₃	-14.8	-14.8	-14.8	-14.1	-14.1	-14.1	-0.4	-0.4	-0.4
	-CO-COH	-13.9	-13.9	-13.9	-13.1	-13.1	-13.1	-0.6	-0.6	-0.6
Enamine	-CH ₂ -CH ₃	-5.9	-5.9	-5.9	-5.2	-5.2	-5.2	9.6	9.6	9.6
	-CO-CH ₃	-11.2	-11.2	-11.2	-10.6	-10.6	-10.6	2.2	2.2	2.2
	-CO-COH	-10.7	-10.7	-10.7	-10.1	-10.1	-10.1	1.1	1.1	1.1
Cyclo-Aminal	-CH ₂ -CH ₃	-42.5	-42.5	-42.5	-39.9	-39.9	-39.9	-23.2	-23.2	-23.2
	-CO-CH ₃	-47.3	-47.3	-47.3	-44.7	-44.7	-44.7	-29.1	-29.1	-29.1
	-CO-COH	-47.6	-47.6	-47.6	-45.1	-45.1	-45.1	-31.7	-31.7	-31.7
Enamine-Imine	-CH ₂ -CH ₃	-9.5	-9.5	-9.5	-6.7	-6.7	-6.7	16.0	16.0	16.0
	-CO-CH ₃	-27.9	-27.9	-27.9	-25.6	-25.6	-25.6	-1.8	-1.8	-1.8
	-CO-COH	-32.3	-32.3	-32.3	-29.4	-29.4	-29.4	-3.3	-3.3	-3.3

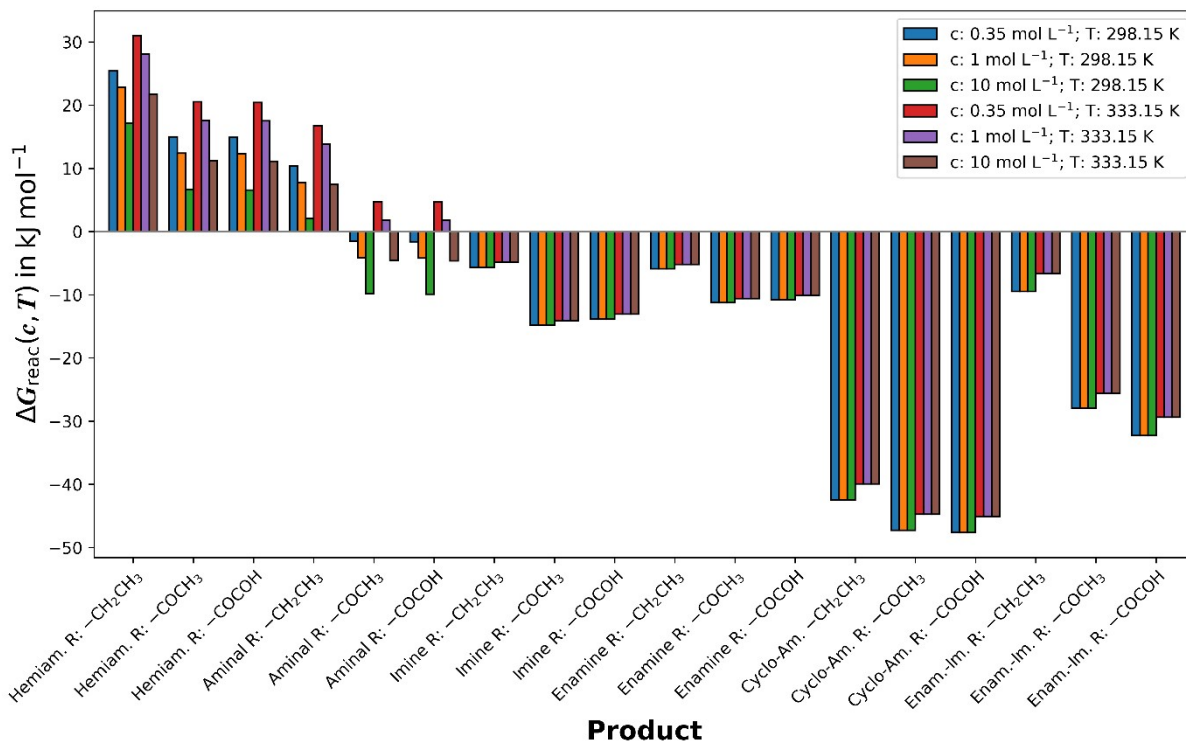


Figure S1: The Gibbs energy of formation $\Delta G_{\text{reac}}(c, T)$ at various concentrations c and temperatures T is presented in kJ mol^{-1} . The reactions are shown in Scheme 2. The data were calculated at the PBE0-D4/def2-QZVP//def2-TZVP (DCOSMO-RS-out) level of theory. Some of the results are also shown in Figure 3 and all of the results in Table S1.

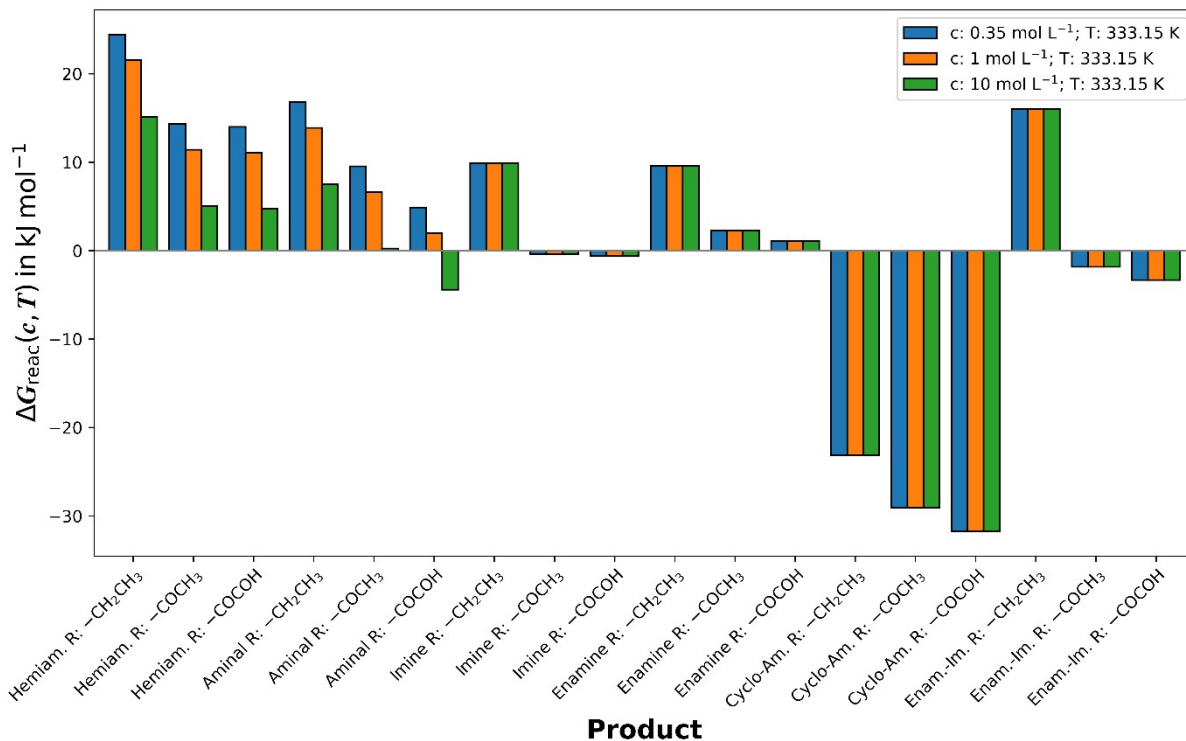


Figure S2: The Gibbs energy of formation $\Delta G_{\text{reac}}(c, T)$ at various concentrations c and temperatures T is presented in kJ mol^{-1} . The reactions are shown in Scheme 2. The data were calculated at the M06-2X/def2-QZVP//def2-TZVP (SMD) level of theory. All of the results are also shown in Table S1.

Coordinates of the molecular structures

The coordinates of all optimised structures can be downloaded from:

****<http://dx.doi.org/10.22029/jlupub-18387>****

The optimised structures are given for PBE0-D3(BJ)/def2-TZVP (DCOSMO-RS) and M06-2X/def2-TZVP (SMD).

2. NMR spectra of monomers

OBP

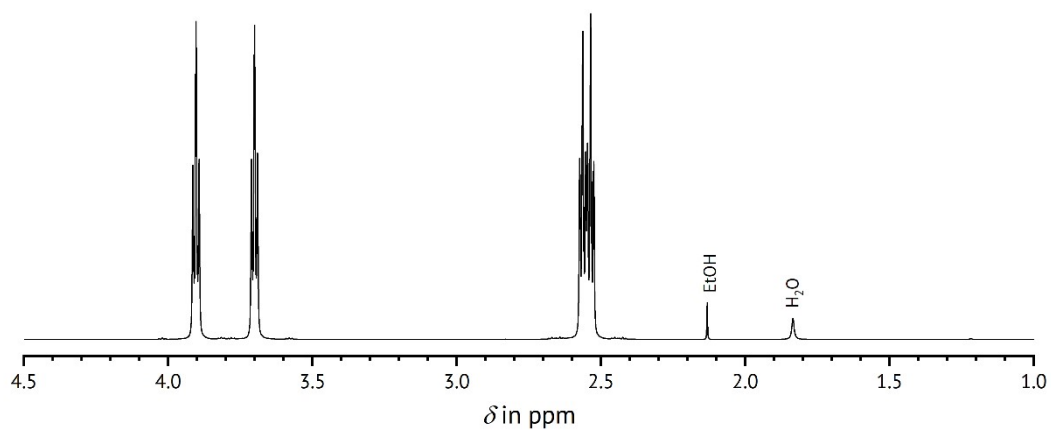


Figure S3: ^1H NMR spectrum of OBP measured in CDCl_3 .

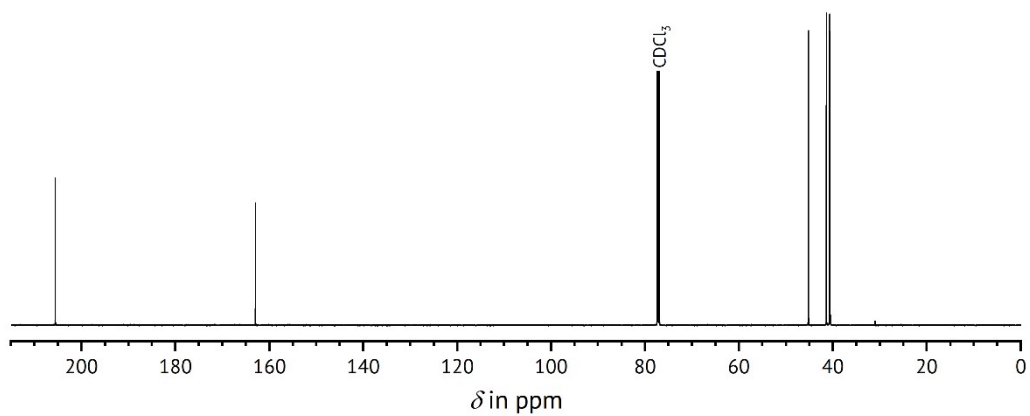


Figure S4: $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of OBP measured in CDCl_3 .

ABP

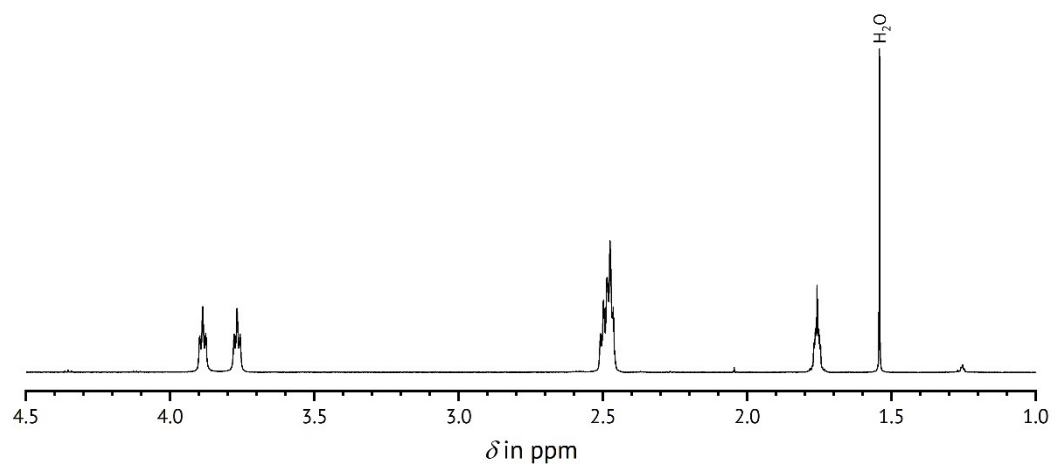


Figure S5: ^1H NMR spectrum of ABP measured in CDCl_3 .

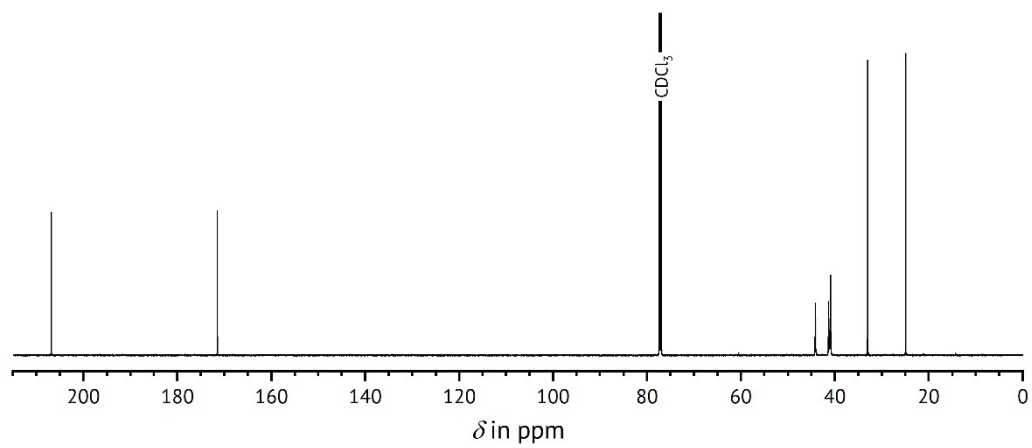


Figure S6: $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of ABP measured in CDCl_3 .

PBP

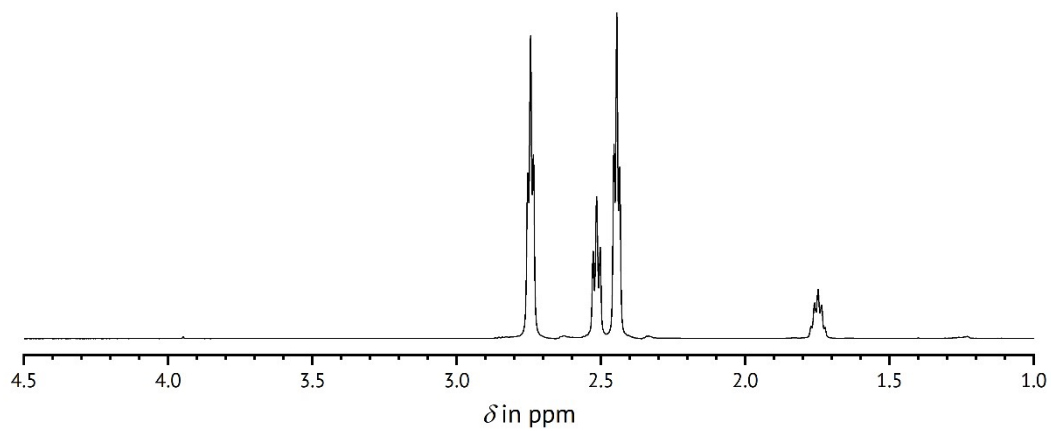


Figure S7: ¹H NMR spectrum of PBP measured in CDCl₃.

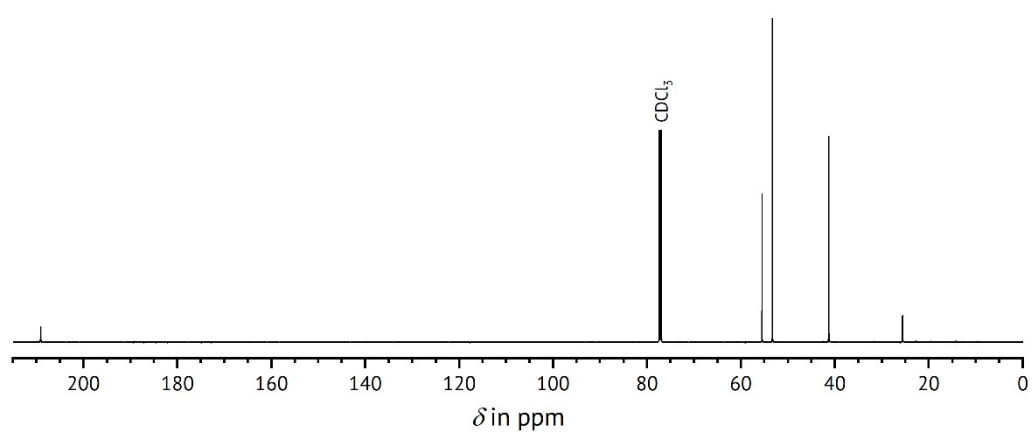


Figure S8: ¹³C-{¹H} NMR spectrum of PBP measured in CDCl₃.

1,3-Bis(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)propane hydrobromide (EO₂-PBP)

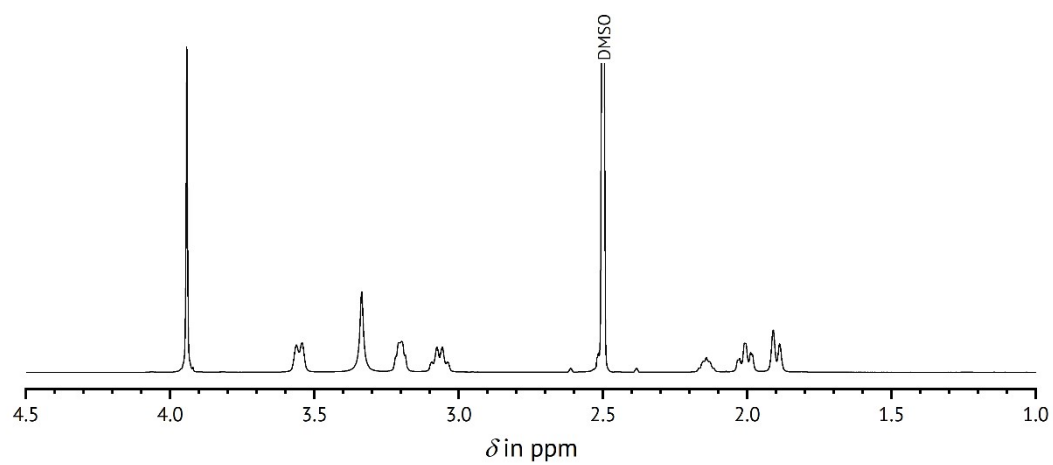


Figure S9: ¹H NMR spectrum of EO₂-PBP measured in DMSO-d₆.

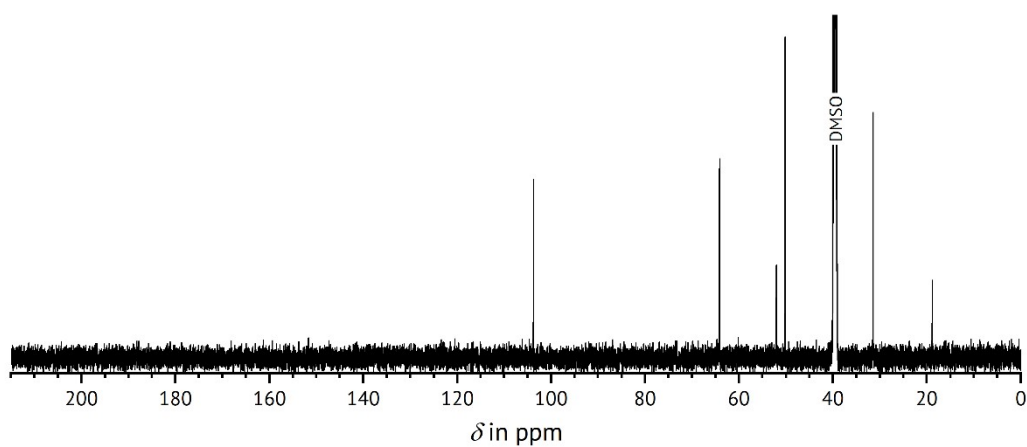


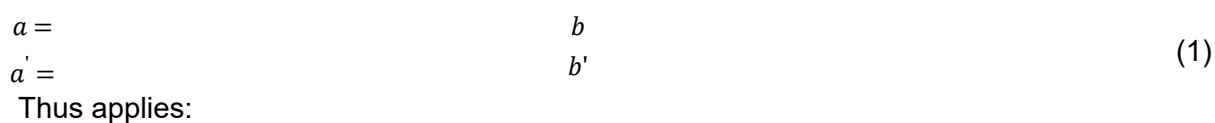
Figure S10: ¹³C-{¹H} NMR spectrum of EO₂-PBP measured in DMSO-d₆.

3. Determination of diol contents

For a measure of electrophilicity the content of ketone and the respective diols in presence of an excess of water were calculated by use of proton NMR experiments. Therefore, a sample of all three bispiperidones, as well as a sample of commercially available 1,4-cyclohexanedione were dissolved in deuterated water and ^1H NMR experiments were conducted. Defined signals that could be assigned clearly to either the ketone or diol species were integrated and the diol content p_{diol} calculated. Signal assignments were confirmed via 2d NMR spectroscopy.

In the following NMR spectra, signal assignment, integrals and calculation pathways are shown. It needs to be considered, that three species, the bis-ketone, the ketone-diol and the bis-diol are in equilibrium with each other. For simplification, only 6-membered rings bearing either ketone or diol were differentiated.

Protons were assigned as shown in Scheme S1. Each signal integral of a , a' , b and b' equals the same number of protons per molecule.



Scheme S1: Proton assignment of ketone and diol species.

OBP

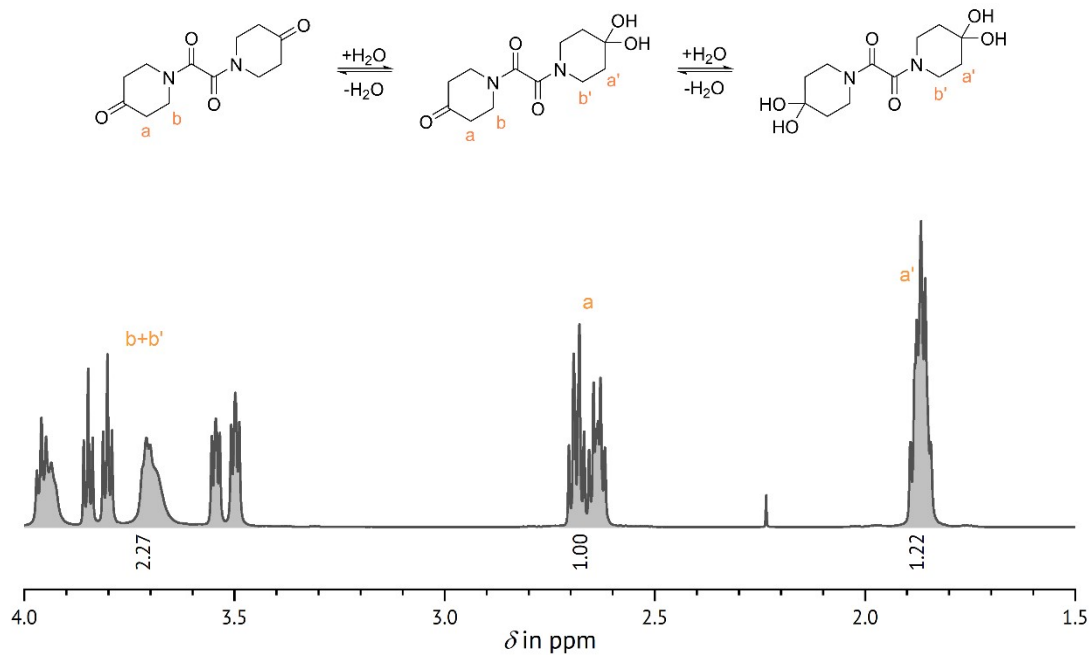


Figure S11: 1H NMR spectrum of OBP in D_2O to determine diol content by integration of proton signals as measure for electrophilicity

It was found that the integral assigned to protons $a = 1.00$ and the integral assigned to protons $a' = 1.22$.

$$p_{diol} = \frac{a'}{a + a'} \quad (2)$$

$$p_{diol} = \frac{1.22}{1.22 + 1.00}$$

$$p_{diol} = 55\%$$

A diol content of 55% was found.

ABP

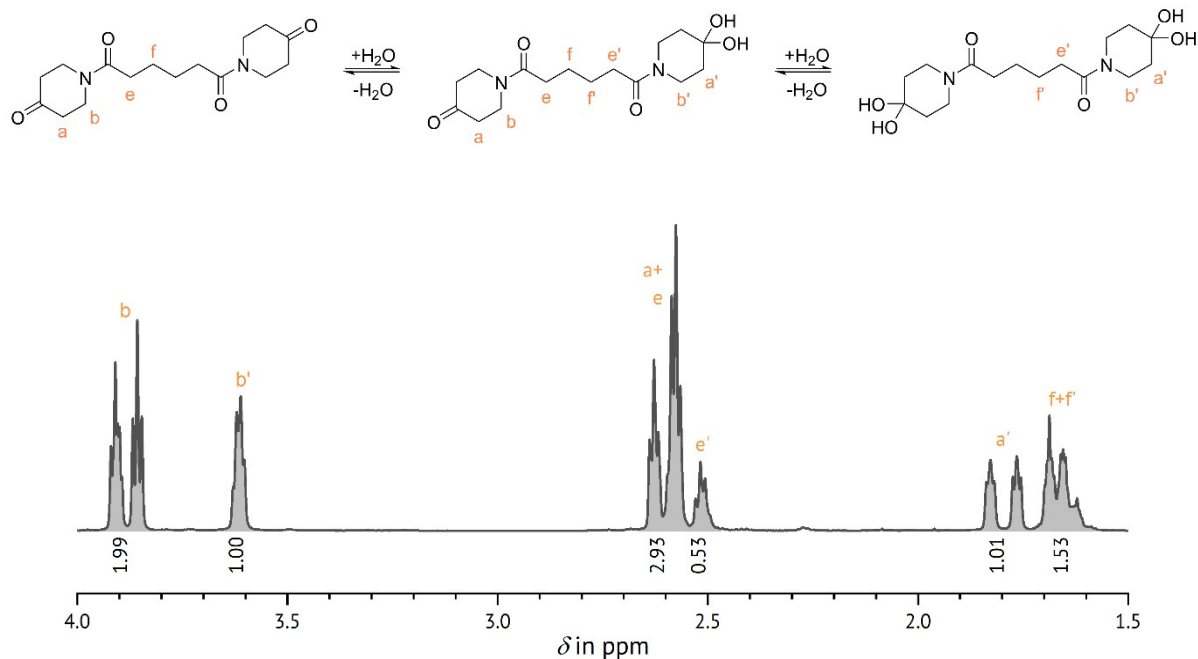


Figure S12: ¹H NMR spectrum of ABP in D₂O to determine diol content by integration of proton signals as measure for electrophilicity

It was found that the integral assigned to protons $b = 1.99$ and the integral assigned to protons $b' = 1.00$.

$$p_{diol} = \frac{b'}{b' + b} \quad (3)$$

$$p_{diol} = \frac{1.00}{1.00 + 1.99}$$

$$p_{diol} = 33\%$$

A diol content of 33% was found.

PBP

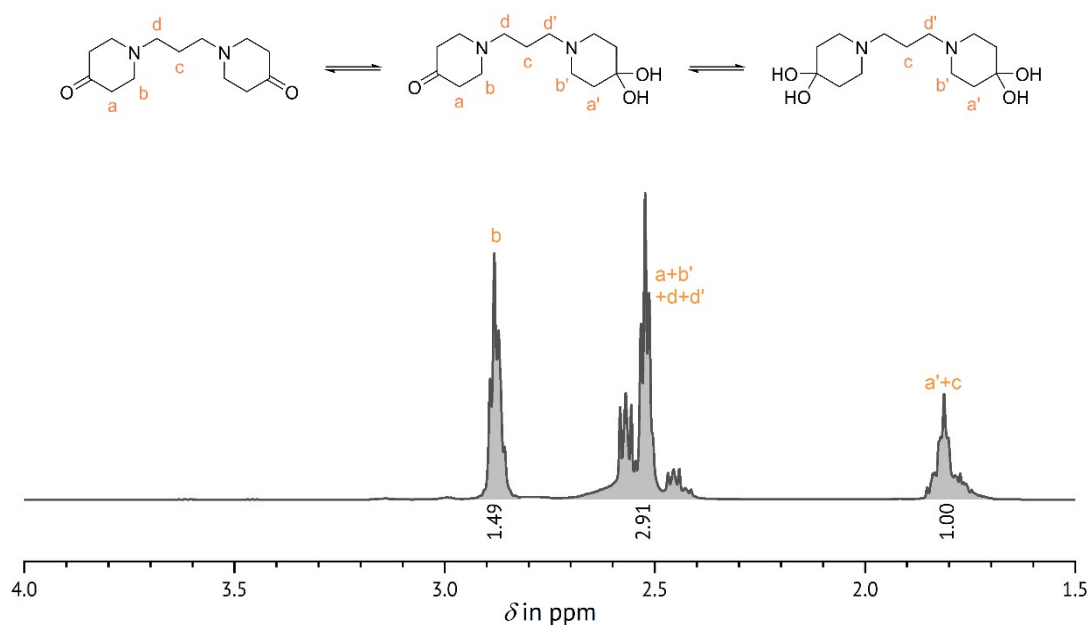


Figure S13: ^1H NMR spectrum of PBP in D_2O to determine diol content by integration of proton signals as measure for electrophilicity.

In contrast to ABP and OBP determination of diol content p_{diol} requires determination of $a' = b'$ first, as no distinct signals show up in NMR spectrum.

It was found that the integral assigned to protons $b = 1.49$ and the integral assigned to protons $a' + c = 1.00$.

In one molecule of PBP in D_2O signals $a + a'$ equals 8 protons whilst signal c equals 2 protons, leading to equation (4).

$$a + a' = 4c \quad (4)$$

$$b + a' = 4c$$

$$a' = 4c - b$$

$$a' = 4c - 1.49 \quad (4a)$$

with

$$a' + c = 1.00 \quad (5)$$

$$c = 1.00 - a' \quad (5a)$$

combining equations (4a) and (5a)

$$a' = 4 \cdot (1.00 - a') - 1.49 \quad (4b)$$

$$a' = 4.00 - 4a' - 1.49$$

$$a' = \frac{4.00 - 1.49}{5}$$

$$a' = 0.50$$

It was found that the integral assigned to protons $b = a = 1.49$ and the integral assigned to protons $a' = 0.50$.

$$p_{diol} = \frac{a'}{a' + a} \quad (2)$$

$$p_{diol} = \frac{0.50}{0.50 + 1.49}$$

$$p_{diol} = 25\%$$

A diol content of 25% was found.

1,4-Cyclohexanedione

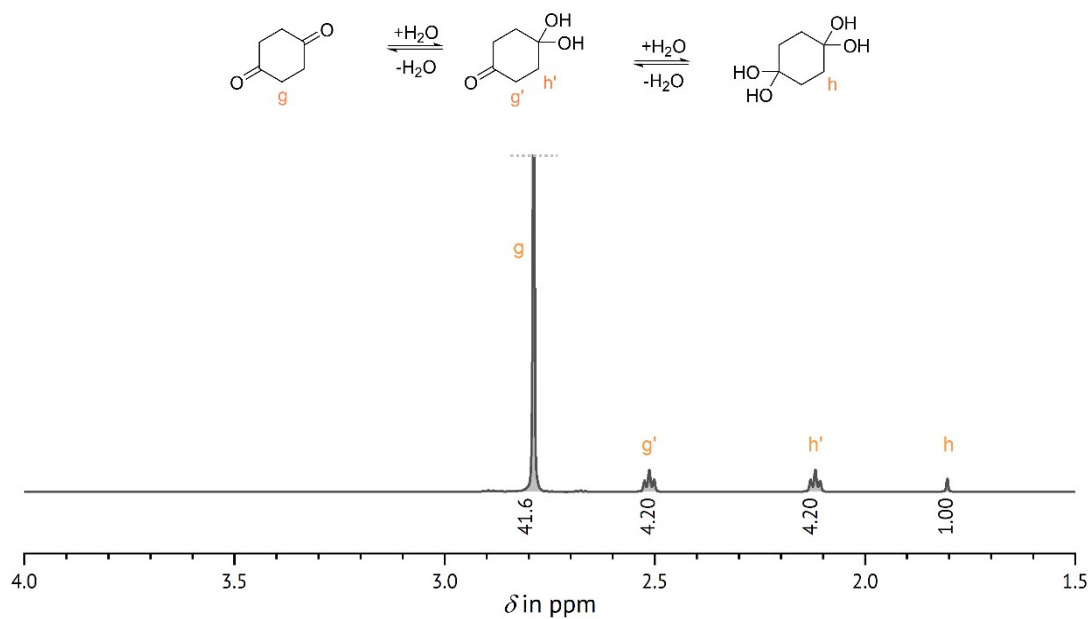


Figure S14: ¹H NMR spectrum of 1,4-cyclohexanedione in D₂O to determine diol content by integration of proton signals as measure for electrophilicity.

It was found that the integrals assigned to protons $g = 41.6$, $g' = 4.20$, $h' = 4.20$ and the integral assigned to protons $h = 1.00$.

$$p_{diol} = \frac{h' + h}{h' + h + g' + g} \quad (6)$$

$$p_{diol} = \frac{1.00 + 4.20}{1.00 + 4.20 + 4.20 + 41.6}$$

$$p_{diol} = 10\%$$

A diol content of 10% was found.

4. NMR spectra of model compounds NAP-I and NAP-E

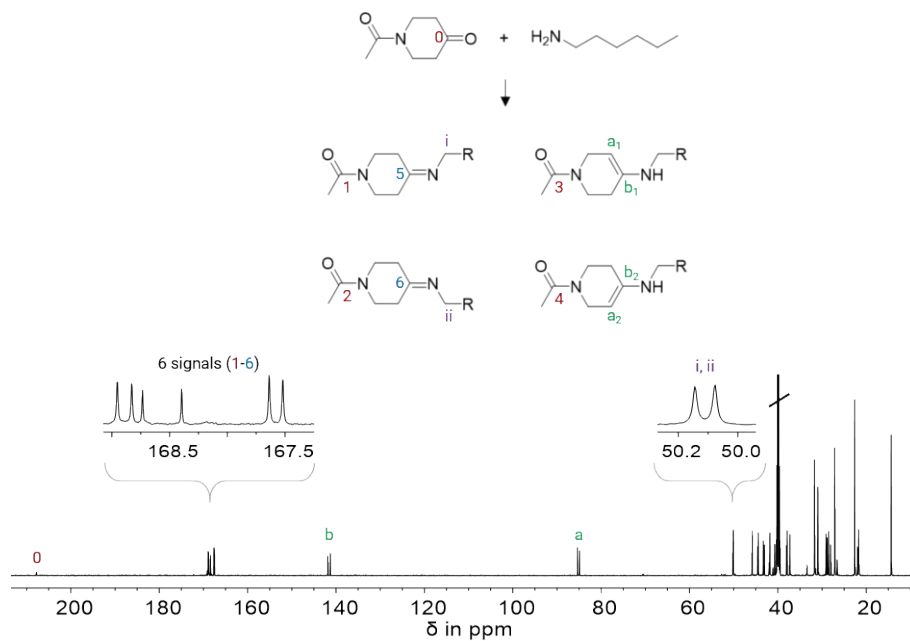


Figure S15: ^{13}C $\{^1\text{H}\}$ NMR spectrum of reaction product of NAP and hexylamine showing both, NAP-I and NAP-E were formed. Hindered rotation of the C-N-bond leads to multiple carbon signals, which were assigned to the respective product structures.

5. FT ATIR spectra of polymers

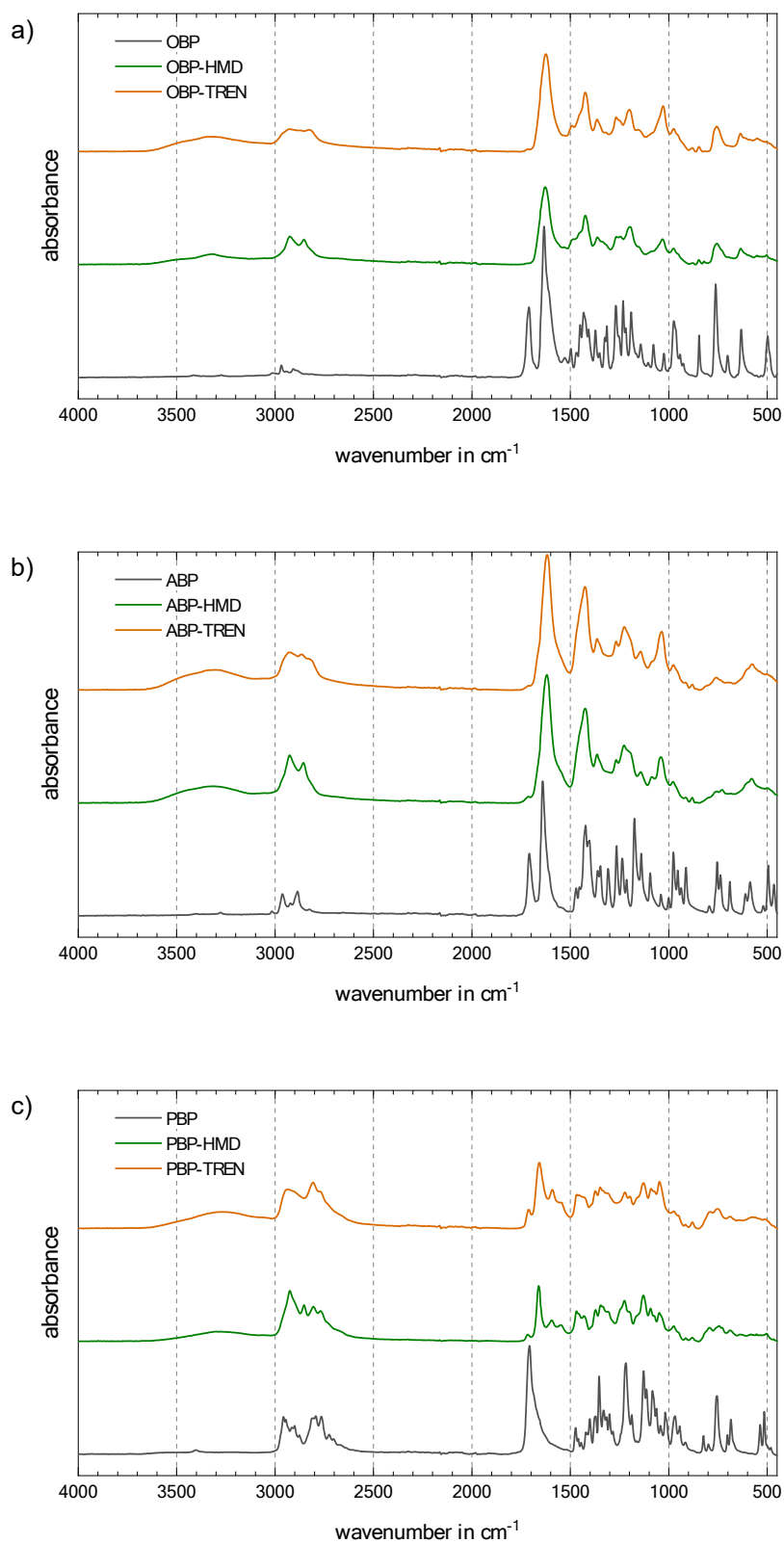


Figure S16: FT-ATIR spectra of a) OBP and the resulting polymers OBP-HMD and OBP-TREN, b) ABP and the resulting polymers ABP-HMD and ABP-TREN, c) PBP and the resulting polymers PBP-HMD and PBP-TREN.

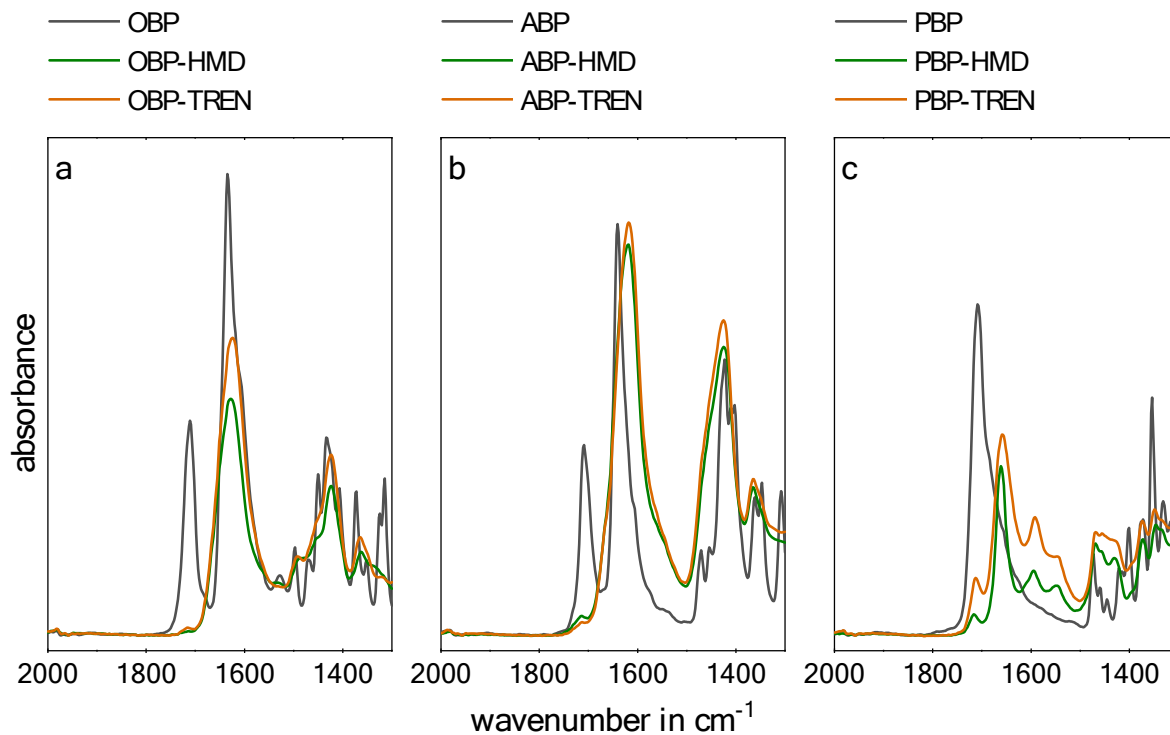


Figure S17: FT-ATIR spectra from 1300 cm^{-1} to 2000 cm^{-1} for comparison of C=O bands in monomers and polymers of a) OBP and the resulting polymers OBP-HMD and OBP-TREN, b) ABP and the resulting polymers ABP-HMD and ABP-TREN, c) PBP and the resulting polymers PBP-HMD and PBP-TREN.

6. TGA data of polymers

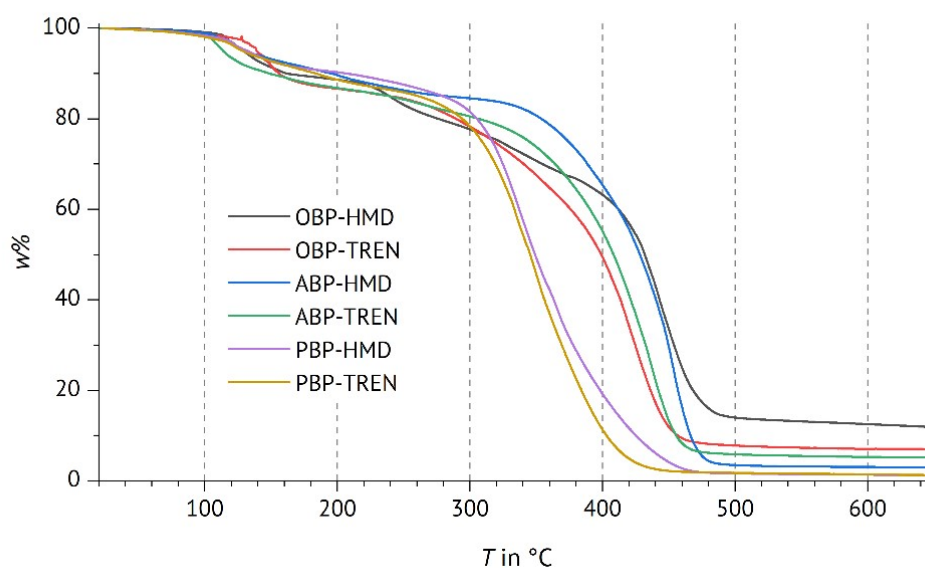


Figure S18: Plots of TGA analysis of all polymers measured under nitrogen atmosphere and at a constant heating rate of 10 K min^{-1} . First decomposition occurs above 100 $^{\circ}\text{C}$.

7. Hydrolysis of Bispiperidone-TREN polymers

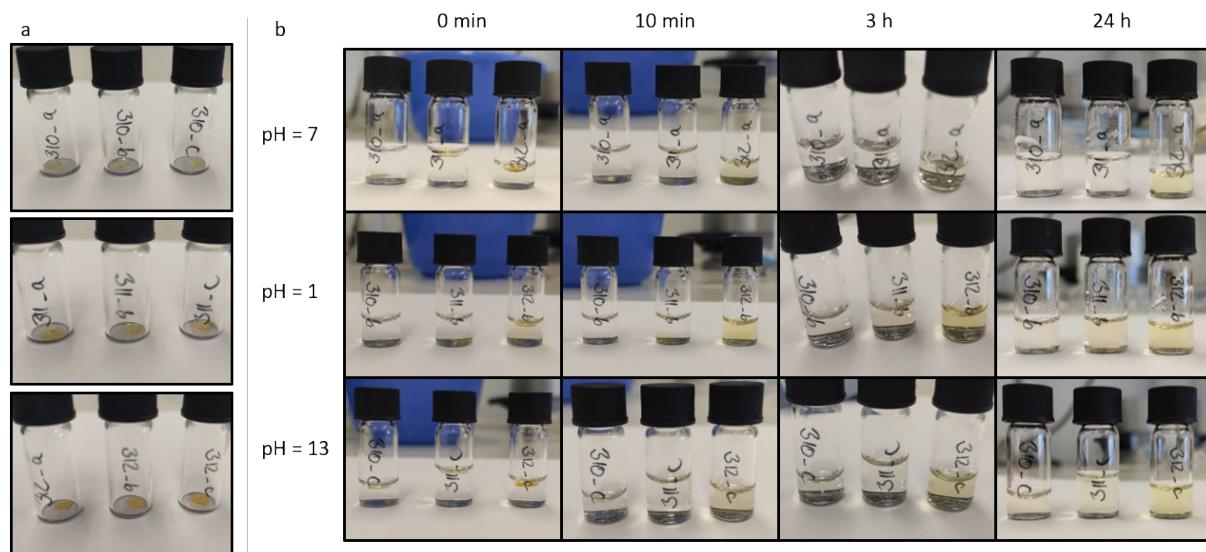


Figure S19: a) Polymers OBP-TREN (top), ABP-TREN (middle) and PBP-TREN (bottom) before hydrolysis, b) Polymers during hydrolysis at pH = 7 (top), 1 (middle) and 13 (bottom) right after addition of aqueous solution (0 min), after 10 min, 3 h and 24 h. Each picture shows from left to right: OBP-TREN, ABP-TREN and PBP-TREN.

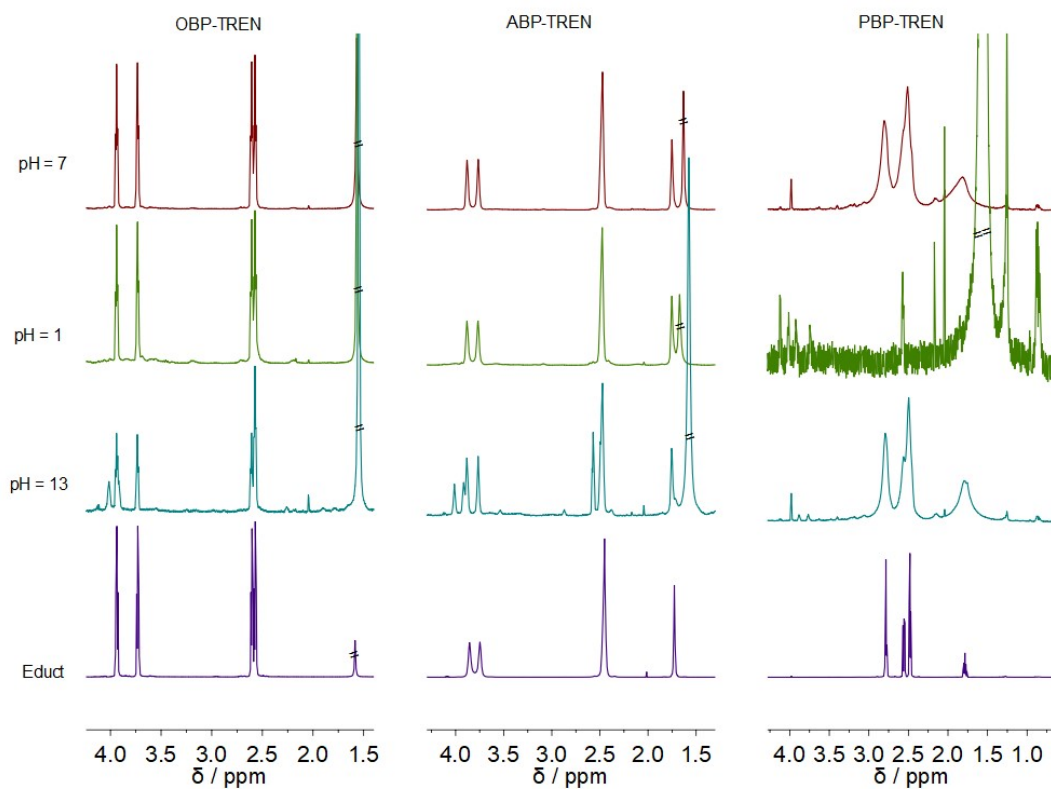


Figure S20: ^1H NMR spectra of the bispiperidones OBP, ABP and PBP as used as educt (bottom) and regained after hydrolysis of OPB-TREN, ABP-TREN and PBP-TREN at pH = 7, 1 and 13.

Additional Signals in proton NMR spectra (Figure S20) of the regained bispiperidones at pH 13 in all three samples show that decomposition in alkalic media occur as well. Therefore, it is not suggested as media for hydrolysis, if monomers should be regained. The spectra of hydrolysed PBP-TREN at pH 1 shows no PBP signals due to protonation of the amines in acidic media. That leads to bad solubility in DCM and the product stays in the aqueous phase during extraction.