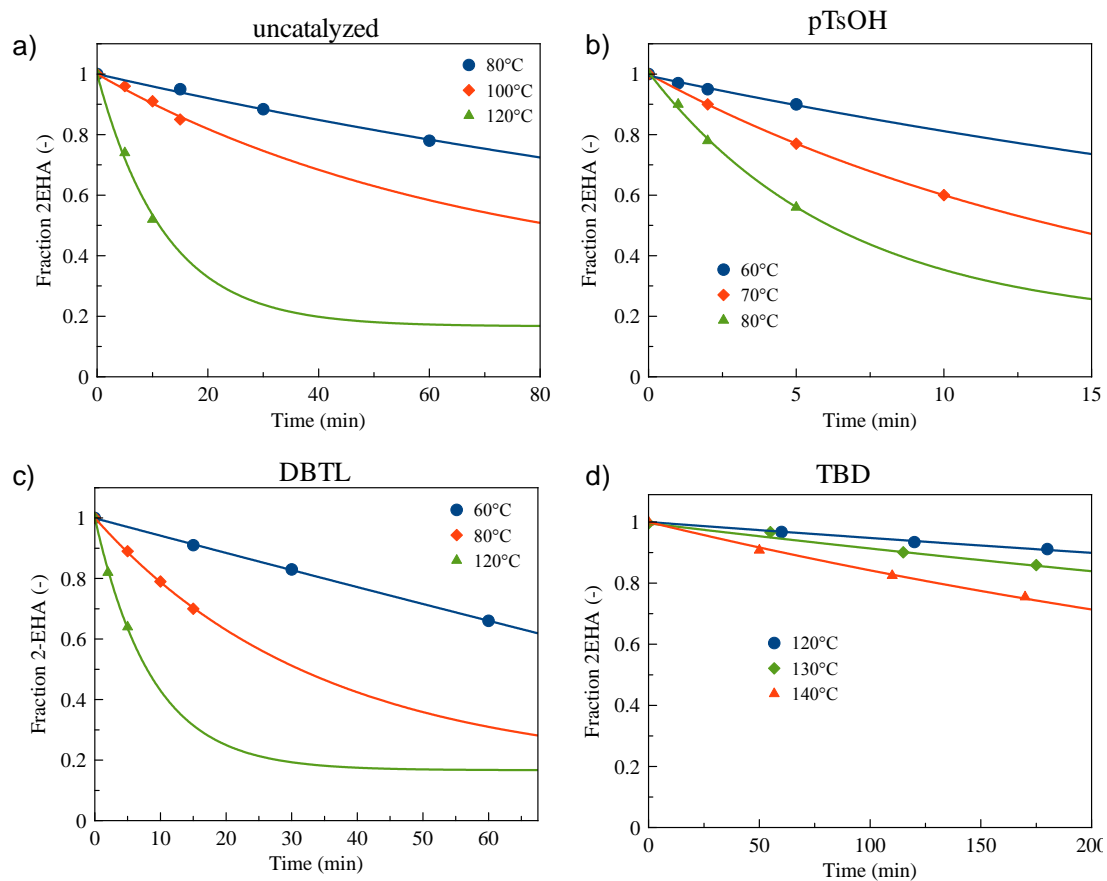
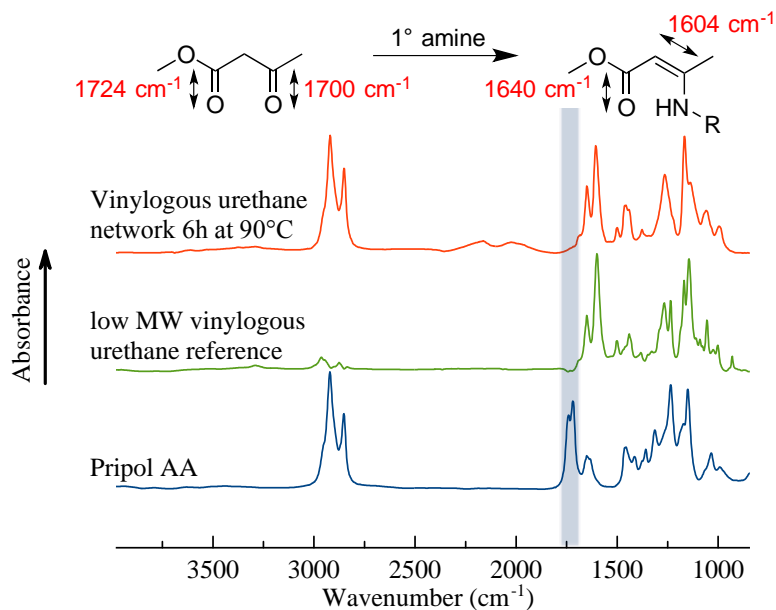


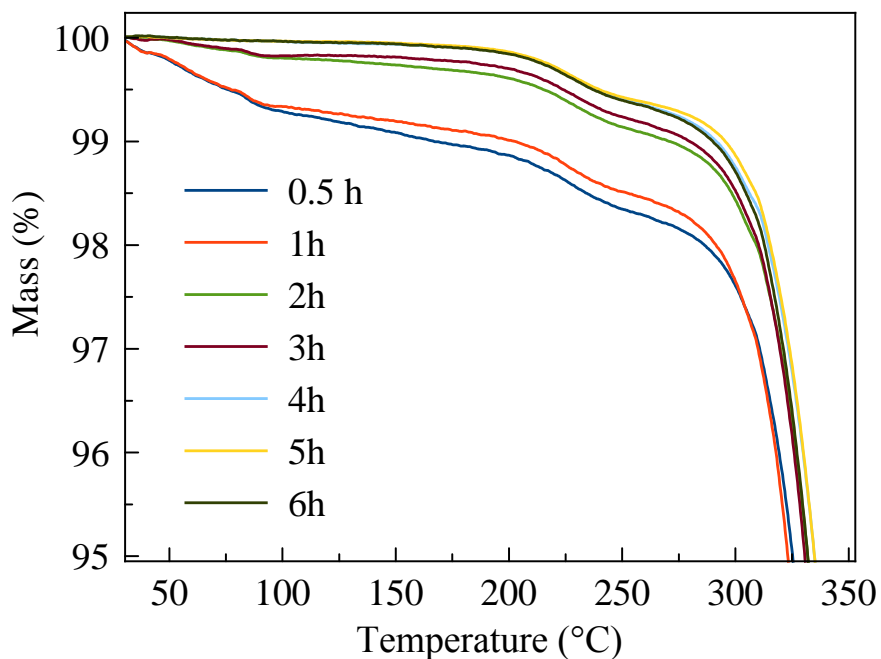
**Supplementary Figure 1:** GC-traces of the uncatalysed exchange reaction at 100°C, showing the appearance of octylamine (3.56 min) and 2-EHamine VU (5.99 min).



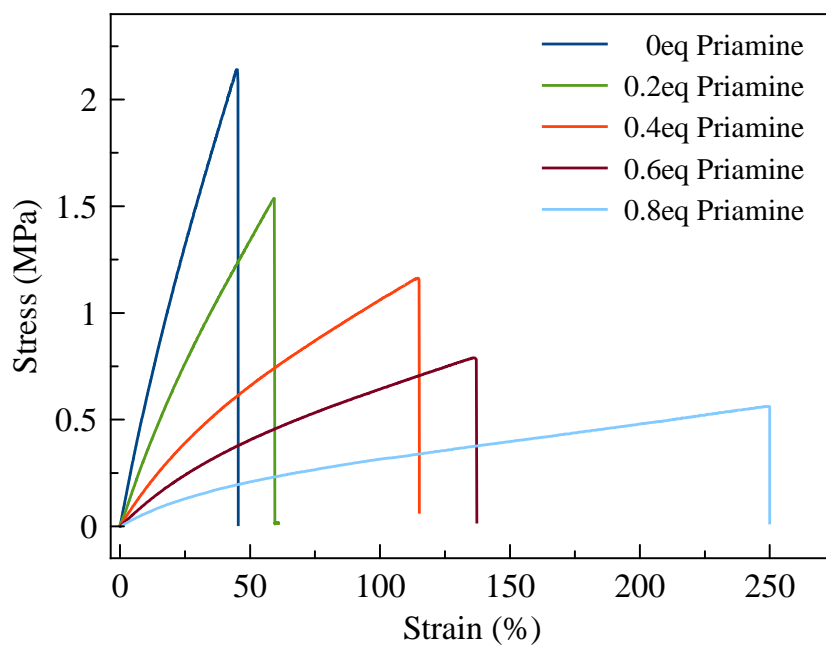
**Supplementary Figure 2:** Decrease of the fraction of 2-EHA as a function of the time at different temperatures a) without catalyst or in presence of b) *p*TsOH, c) DBTL or d) TBD.



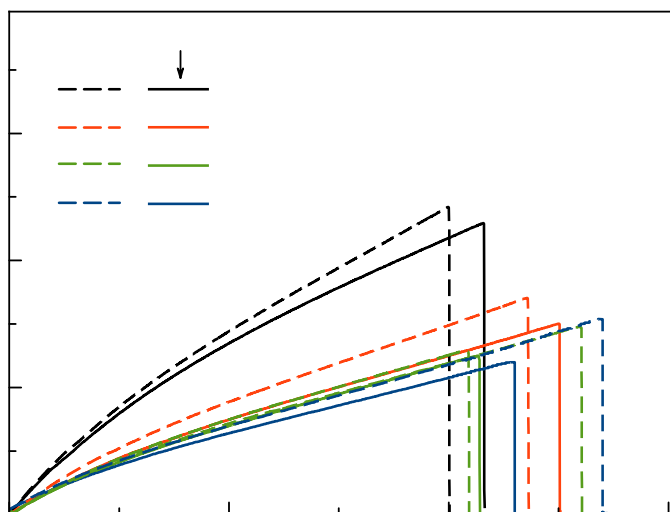
**Supplementary Figure 3:** FT-IR spectra showing the full conversion of the starting compound (acetoacetylated pripol 2044) to the corresponding vinyllogous urethane.



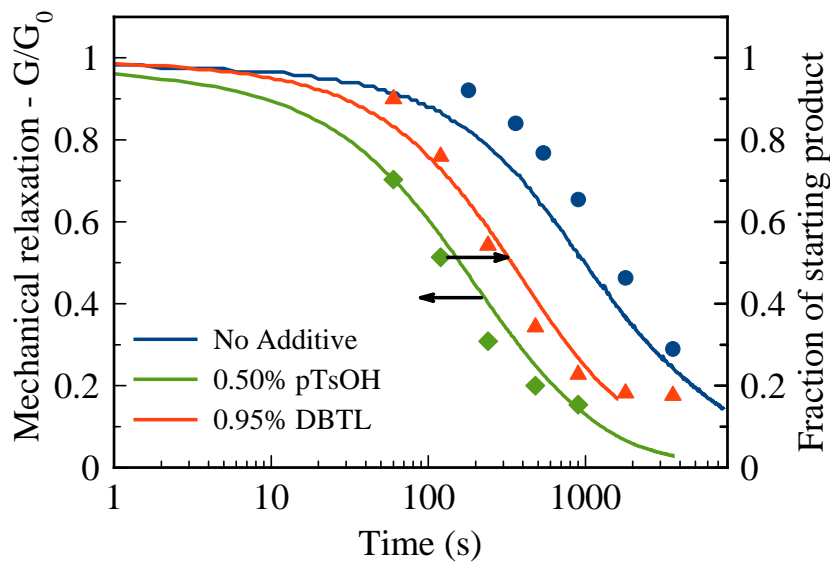
**Supplementary Figure 4:** TGA measurements of the vinyllogous urethane elastomers after different curing times at 90°C. After 4h, no more mass loss is observed before 200°C, indicating the complete evaporation of the water condensate.



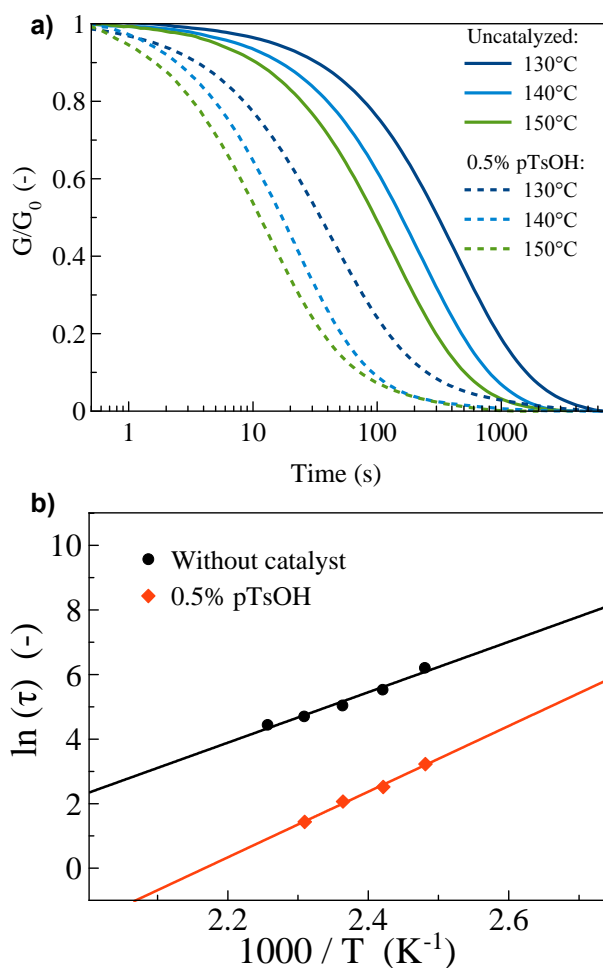
**Supplementary Figure 5:** Tensile tests of vinylgous urethane vitrimers with different compositions.



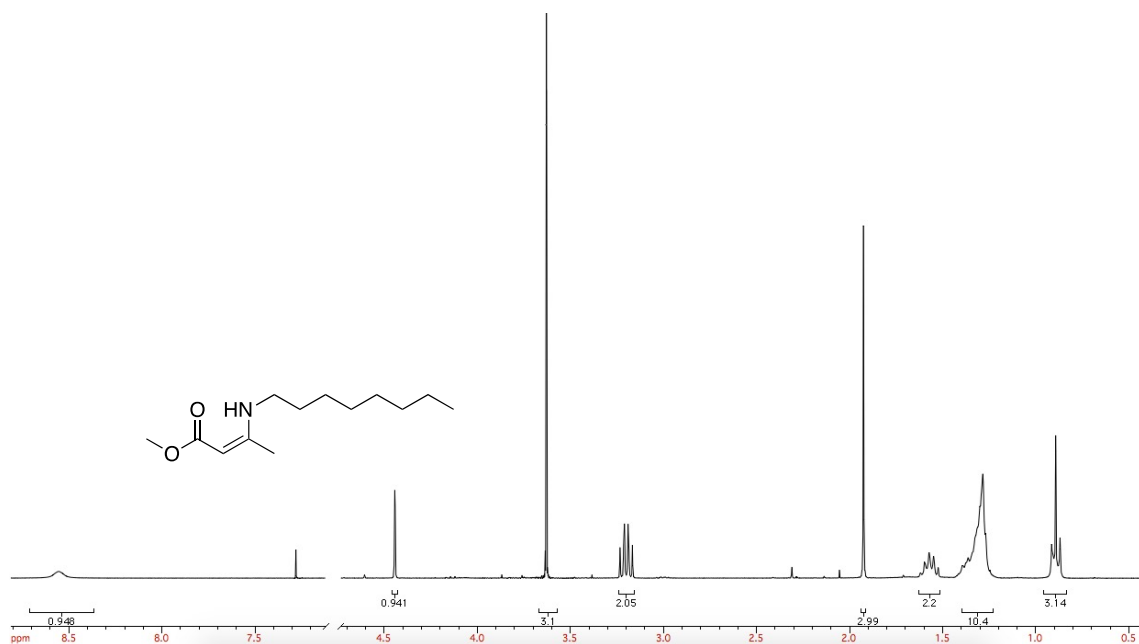
**Supplementary Figure 6:** Tensile test after recycling of the uncatalyzed (full line) and acid catalyzed (dotted line) samples with a stoichiometric ratio of 0.40 : 0.40 : 0.95. Recycling was performed by first grinding the material followed by compression moulding for 30 minutes at 150°C.



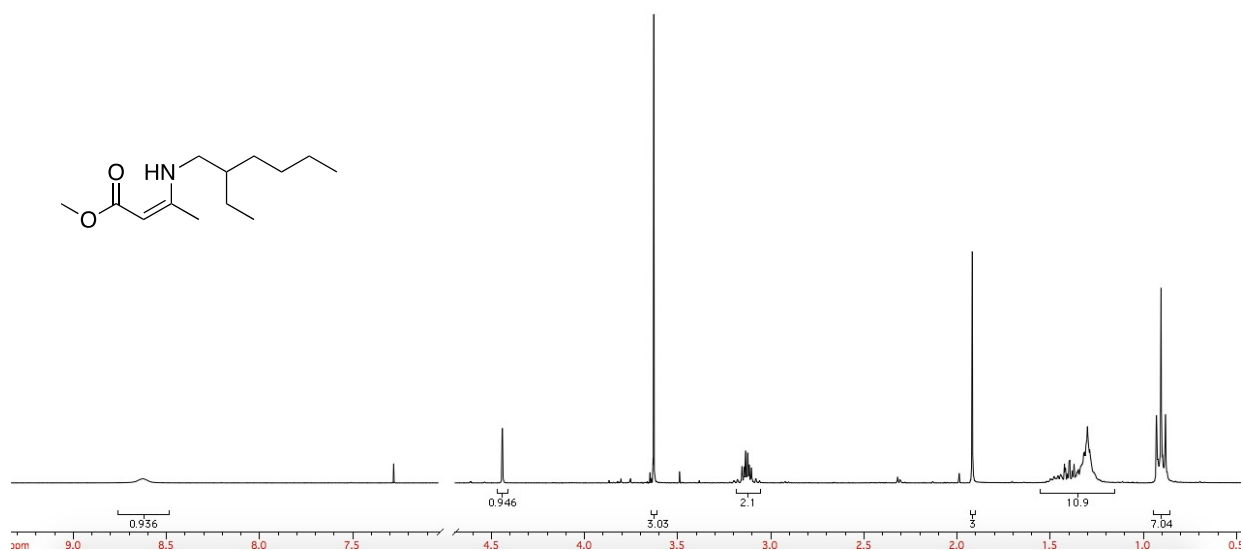
**Supplementary Figure 7:** Comparison of the conversion of the model compound (dots, right axis) with the mechanical stress-relaxation (full line, left axis) caused by the uncatalyzed, *p*TsOH and DBTL catalyzed exchange reactions, both in the case of model reactions and VU vitrimer samples.



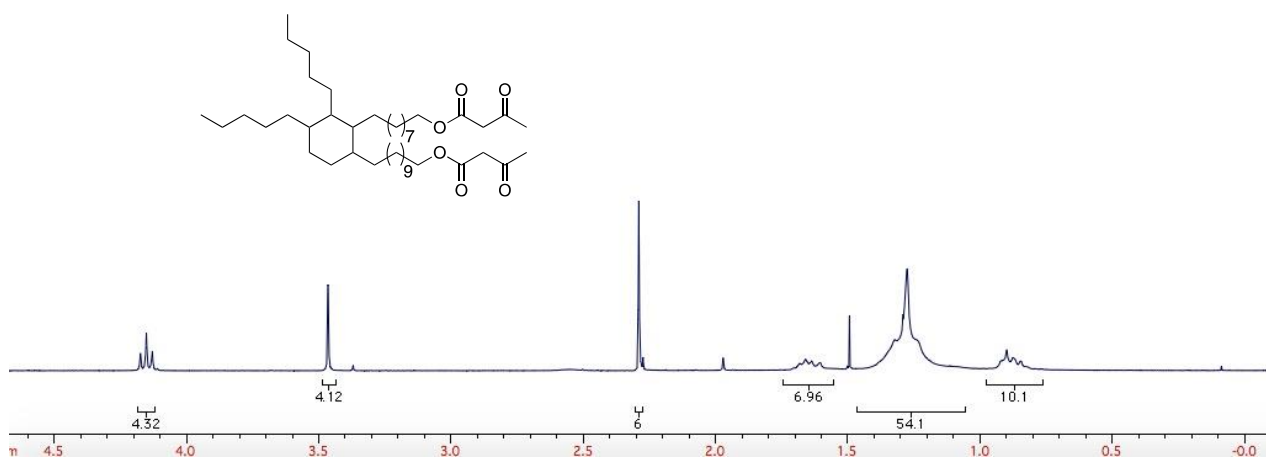
**Supplementary Figure 8:** Stress-relaxation experiments for rigid VU networks. b) Arrhenius plot of the relaxation times of rigid VU networks.



**Supplementary Figure 9:** <sup>1</sup>H-NMR of Methyl-3-(octylamino)but-2-enoate (*i.e.* *N*-octyl vinylogous urethane).



**Supplementary Figure 10:** <sup>1</sup>H-NMR of methyl-3-((2-ethylhexyl)amino)but-2-enoate (*N*-2EH vinylogous urethane).



**Supplementary Figure 11:** <sup>1</sup>H-NMR of acetoacetylated pipol 2044.

**Supplementary Table 1:** k-values obtained from the fitting of the curves of Supplementary Figure 2 and used for the Arrhenius plots.

	Temperature (°C)	k (s <sup>-1</sup> )
Uncatalyzed	80	3,71E-03
	100	9,57E-03
	120	4,80E-02
pTsOH	60	1,93E-02
	70	3,96E-02
	80	8,71E-02
DBTL	60	5,60E-03
	80	2,45E-02
	120	7,11E-02
TBD	120	3,88E-04
	130	8,68E-04
	140	1,75E-03

**Supplementary Table 2:** Properties of soft VU networks with different compositions.

Equivalents of 5 : 6 : 7	$T_g$ (°C)	$E'$ (MPa) <sup>a</sup>	Young modulus E (MPa) <sup>b</sup>	Elongation at failure (%) <sup>b</sup>	Stress at failure (MPa) <sup>b</sup>
0.00 : 0.67 : 0.95	- 9	3.9	3.35 ± 0.01	46 ± 5	2.22 ± 0.25
0.20 : 0.53 : 0.95	- 20	3.3	2.34 ± 0.02	65 ± 7	1.74 ± 0.27
0.40 : 0.40 : 0.95	- 25	2.2	1.99 ± 0.05	119 ± 9	1.20 ± 0.06
0.60 : 0.27 : 0.95	- 30	1.5	1.13 ± 0.02	140 ± 6	0.81 ± 0.05
0.80 : 0.13 : 0.95	- 33	1.1	0.64 ± 0.05	255 ± 35	0.55 ± 0.03

a) Measured *via* DMTA at 50°C. b) Measured *via* tensile testing, average of 4 measurements.

**Supplementary Table 3:** Calculated activation energies from the stress-relaxation experiments and calculated freezing transition temperature.

Catalyst	$E_a$ (KJ mol <sup>-1</sup> )	$T_v$ (°C)
Uncatalyzed	81 ± 3	27
0.50% pTsOH	70 ± 4	-1
0.25% H <sub>2</sub> SO <sub>4</sub>	70 ± 5	10
0.95% DBTL	30 ± 4	-63
1.90% DBTL	31 ± 10	-70
0.50% TBD	122 ± 19	87

## Supplementary Note 1

k-values were obtained using<sup>1</sup>:

$$[Reactant] = 1 - (x_{\infty} - \exp\left(\frac{-kt}{x_{\infty}}\right)) \quad \text{Supplementary Equation 1}$$

With  $x_{\infty}$  = equilibrium concentration of the products =  $\frac{5}{6}$

*Fitted for k = initial rate*

The activation energy was calculated by plotting ln k versus 1000/T.

$$\ln k = -\frac{E_a}{RT} + cte \quad \text{Supplementary Equation 2}$$



# 1 Supplementary Reference

1) Logan, S. R. The kinetics of isotopic exchange reactions. *J. Chem. Educ.* **67**, 371 (1990).