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Supporting Information

# Vinylogous Urea—Urethane Vitrimers: Accelerating and Inhibiting Network Dynamics through Hydrogen Bonding

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**Supporting information**

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# Experimental section

## Materials

Benzylamine (99%), tert-butyl acetoacetate (98%), ethylene glycol (≥99%), ethylenediamine-n,n'-bis(acetoacetamide), 2-ethyl hexanol (≥99%), 2-ethylhexyl amine (98%), trimethylolpropane tris [poly(propylene glycol),amine terminated] ether and 2,2,6-Trimethyl-4H-1,3-dioxin-4-one (95%) were purchased from Sigma Aldrich. Butylamine (≥99%) and ethyl acetoacetate (>98%) were purchased from TCI Chemicals. Dimethylformamide was purchased from Fisher. All reactants were used as received.

## Instrumentation

*Nuclear Magnetic Resonance (NMR).* NMR spectroscopy was performed using a 400 MHz Bruker Avance III HD; 9.4 Tesla.

*Thermogravimetric Analysis (TGA).* Thermogravimetric analysis was performed using a TA Instruments Discovery Thermogravimetric Analyzer in the Soft Matter Characterization Facility at the University of Chicago. Tests were conducted by an heating for 1h at 100°C followed by a ramp at a rate of 10 °C/min starting from operating temperature (ca. 30 °C) to 600 °C.

*Differential Scanning Calorimetry (DSC).* DSC was performed using a TA Instruments Discovery 2500 Differential Scanning Calorimeter in the Soft Matter Characterization Facility at the University of Chicago. Samples were prepared in aluminum hermetic pans purchased from TA instruments. Dynamic networks underwent a heat-cool-heat cycle (150°C/-50°C/150°C) run at 10 °C/min.

*Fourier Transform Infrared Spectroscopy (FTIR).* FTIR was performed on Shimadzu IRTracer-100 Fourier transform infrared spectrophotometer in the Soft Matter Characterization Facility at the University of Chicago with GladiATR (diamond prism) single bounce attenuated total reflection (ATR) attachment.

*Mass Spectrometry (MS).* Electrospray ionization mass spectrometry (ESI-MS) and liquid chromatography mass spectrometry (LC-MS) were performed on an Agilent 1100 series LC/MSD system equipped with a diode array detector and single quad MS detector (VL), equipped with an electrospray source (ESI-MS). UV detection allowed to detect eluting compounds ($\lambda$ = 214 nm).

*Rheological experiments.* – Rheology was performed using a TA Instruments ARES-G2 shear rheometer with Forced Convection Oven (20 °C – 500 °C) attached to an Air Chiller System (-120 °C – 20 °C) or using a TA Instruments Discovery HR-30 shear rheometer in the Soft Matter Characterization Facility at the University of Chicago. An 8 mm parallel plate was used for all tests. Temperature sweep experiments were performed from 0 °C to 150 °C with a heating rate of 3°C/min, 1Hz and an applied strain of 0.01%. Stress relaxation experiments were performed at various temperatures within its rubbery plateau region (150-100 °C). The sample was loaded in the same way as described in the temperature sweep experiment. Conditioning options were set to 1 N axial compression force and strain adjustments were disabled. A 1% strain was then applied, and the stress was monitored for each temperature. Creep measurements were taken from 50 – 110°C. Samples were loaded onto the rheometer at 90 °C and then cooled after 1 hour to their testing temperature. Axial compression force was set to 1 N and 4000 Pa of shear stress was applied to the sample for 7200 seconds.

*Tensile testing.* Tensile analysis was performed using a Zwick-Roell zwickiLine Z0.5 Materials Testing Instrument with a 500 N load cell in the Soft Matter Characterization Facility at the University of Chicago. Samples were cut into rectangular strips (length x width x thickness = 30 mm x 5 mm x 0.3 mm) and pulled uniaxially at a strain rate of 10 mm/min. Specimens were clamped using silicon rubber clamps to prevent tearing of the material.

*Wide-Angle X-Ray Scattering (WAXS).* WAXS was performed on a SAXSLAB (XENOCS)'s GANESHA 300XL at the University of Chicago. A Cu Kα source ($\lambda = 0.154$ nm) at a power of 40 mA and a voltage of 40 kV was used. Film samples were mounted on the holder using Kapton tape and shot directly for 3 mins at q = 0.05 – 0.25. For the high temperature measurement a temperature stage was used of 3°C/min and the sample was left at 150°C for 5 minutes.

## Synthetic procedures

### *Synthesis of 2-ethylhexyl acetoacetamide*

2-Ethylhexylamine (35.17 mmol) was brought together with 2,2,6-trimethyl-4H-1,3-dioxin-4-one (35.17 mmol) and 10mL DMF in a round bottomed flask. The flask was immersed in an oil bath at 140°C and was left to stir for 30 minutes. The flask was cooled and the content was poored in 400 mL water and was extracted with DCM (100mL). The organic layer was further extracted with 1M HCl (2x 200 mL), 10% CuSO4 solution (2x 100 mL) to remove the remaining 2-ethylhexylamine. The solvent was evaporated and the mixture was further purified by column chromatography (pentane/EtOAc 6/4). A yellow oil as pure product was obtained. LC-MS (214 nm, m/z, ES+, $[M+H]^+ = 214.2$, $C_{12}H_{23}NO_2$) Yield = 23%. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 6.95 (s, 1NH), 3.36 (s, 2H), 3.16 (t, 2H), 2.21 (s, 3H), 1.39 (m, 1H), 1.32-1.08 (m, 8H), 0.83 (t, 6H).

### *Synthesis of 2-ethylhexyl acetoacetate*

2-Ethylhexanol (34.93 mmol) was mixed together with ethyl acetoacetate ( 38.42 mmol) in a distillation setup. The mixture was then heated to 125 °C at 800 mbar for 4 h to remove the formed ethanol.

Afterward, the temperature was lowered to 80°C and the pressure was reduced gradually to 1 mbar. Finally, to remove the final traces of 2-ethylhexanol and ethyl acetoacetate, the mixture was left for another 1h at 1 mbar. No further purification was performed. LC-MS (214 nm, m/z, ES+, $[M+H]^+$= 215.2, $C_{12}H_{22}O_3$) Yield = 83%. $^1$H NMR (400 MHz, $CDCl_3$, δ): 4.00 (d, 2H), 3.38 (s, 2H), 2.21 (s, 3H), 1.5 (m, 1H), 1.35-1.15 (m, 8H), 0.82 (t, 6H).

*Synthesis of model compound* ***3-(butylamino)-N-(2-ethylhexyl)but-2-enamide (1)***

In a vial, butylamine (2.11 mmol) was added to N-(2-ethylhexyl)-3-oxobutanamide (1.41 mmol) in chloroform (3 mL) together with a small spoon of $MgSO_4$. The mixture was filtered to remove the $MgSO_4$ and was placed in the vacuum oven to remove the excess of butylamine. Don't filter over silica, the reverse reaction back to the starting product happens because of the acidity of silica. LC-MS (214 nm, m/z, ES+, $[M+H]^+$= 269.2, $C_{16}H_{32}N_2O$) Yield = 50%. $^1$H NMR (400 MHz, $C_6D_6$, δ): 9.64 (s, 1NH), 4.43 (s, 1NH), 4.18 (s, 1H), 3.25 (m, 2H), 2.73 (q, 2H), 1.57 (s, 3H), 1.36-1.10 (m, 13), 0.86 (m, 6), 0.71 (t, 3H).

*Synthesis of model compound* ***2-ethylhexyl-3-(butylamino)but-2-enoate (1')***

In a vial, butylamine (4.67 mmol) was added to 2-ethylhexyl acetoacetate (7 mmol) in chloroform (5 mL). The mixture was left to stir at room temperature overnight. Afterward, a spoon of $MgSO_4$ was added and the mixture was filtered over silica to remove the excess of amines. LC-MS (214 nm, m/z, ES+, $[M+H]^+$= 270.2, $C_{16}H_{31}NO_2$) Yield = 89%. $^1$H NMR(400 MHz, $C_6D_6$, δ): 8.96 (s, 1NH), 4.77 (s, 1H), 4.23 (m, 2H), 2.61 (q, 2H), 1.65 (m, 1H), 1.43 (s, 3H), 1.42-1.02 (m, 12H), 0.92-0.80 (m, 6H), 0.68 (t, 3H).

*Transamination exchange*

Benzylamine (0.356 mmol) was added to a solution of the N-butyl vinylogous urea or N-butyl vinylogous urethane (0.071 mmol) model compound in benzene-$d_6$ (0.65 mL). Five equivalents of benzylamine relative to the VU groups were used to obtain a pseudo-first-order reaction at low conversions. The mixture was kept at 30 °C or 50 °C in an NMR tube, and spectra were taken online at different time intervals. The reaction was followed by integration of the $CH_3$ signal at 1.57 and 1.51 ppm for **1** and **3** respectively or CH signal at 4.75 and 4.80 ppm for **1'** and **3'** respectively.

*Synthesis of ethylene glycol bis(acetoacetate)*

The synthesis was adopted from Spiesschaert et al.[1]. Ethylene glycol was mixed together with tert-butyl acetoacetate (in a molar ratio of 1:2.3) in a distillation setup. The mixture was then heated to 125 °C at 800 mbar for 3 h to remove the formed tert-butanol. Afterward, the pressure was reduced gradually to 5 mbar in the timespan of 1 h. Finally, to remove the final traces of tert-butanol and tert-butylacetoacetate, the mixture was left for another 1 h at 5 mbar. No further purification was performed. Yield = 95%. $^1$H

NMR (400 MHz, $CDCl_3$, δ): 11.87 (s, 2H, enol), 4.99 (s, 2H, enol), 4.35 (s, 4H), 3.47 (s, 4H), 2.25 (s, 6H), 1.95 (s, 6H, enol).

*Synthesis of polymer networks*

A 25 mg/ml DMF stock solution was prepared for ethylenediamine-n,n'-bis(acetoacetamide), as well as for ethylene glycol bis(acetoacetate). To a precisely weighed amount of trifunctional amine, the acetoacetamide and acetoacetate were added. Once mixed, the solvent mixture was poored into a Teflon cup and was left to dry. The drying process was as follows, 2 days on a heated plate at 50 °C, 2 days in a vacuum oven at 50 °C and 4 hours at 120°C in a vacuum oven to ensure full curing.

*Network compositions*

**Table S1.** Material compositions for 0.5g or 3.40909 mol of triamine crosslinker.

| **Material** | **ED-bis(acetoacetamide) (mmol)** | **EG-Bis(acetoacetate) (mmol)** |
|---|---|---|
| **VU-$O_{100}$** | | 3.239 |
| **VU-N50O50** | 1.619 | 1.619 |
| **VU-N60O40** | 1.943 | 1.295 |
| **VU-N70O30** | 2.267 | 0.972 |
| **VU-N80O20** | 2.591 | 0.648 |
| **VU-N90O10** | 2.915 | 0.324 |
| **VU-$N_{100}$** | 3.239 | |

# Kinetic Study

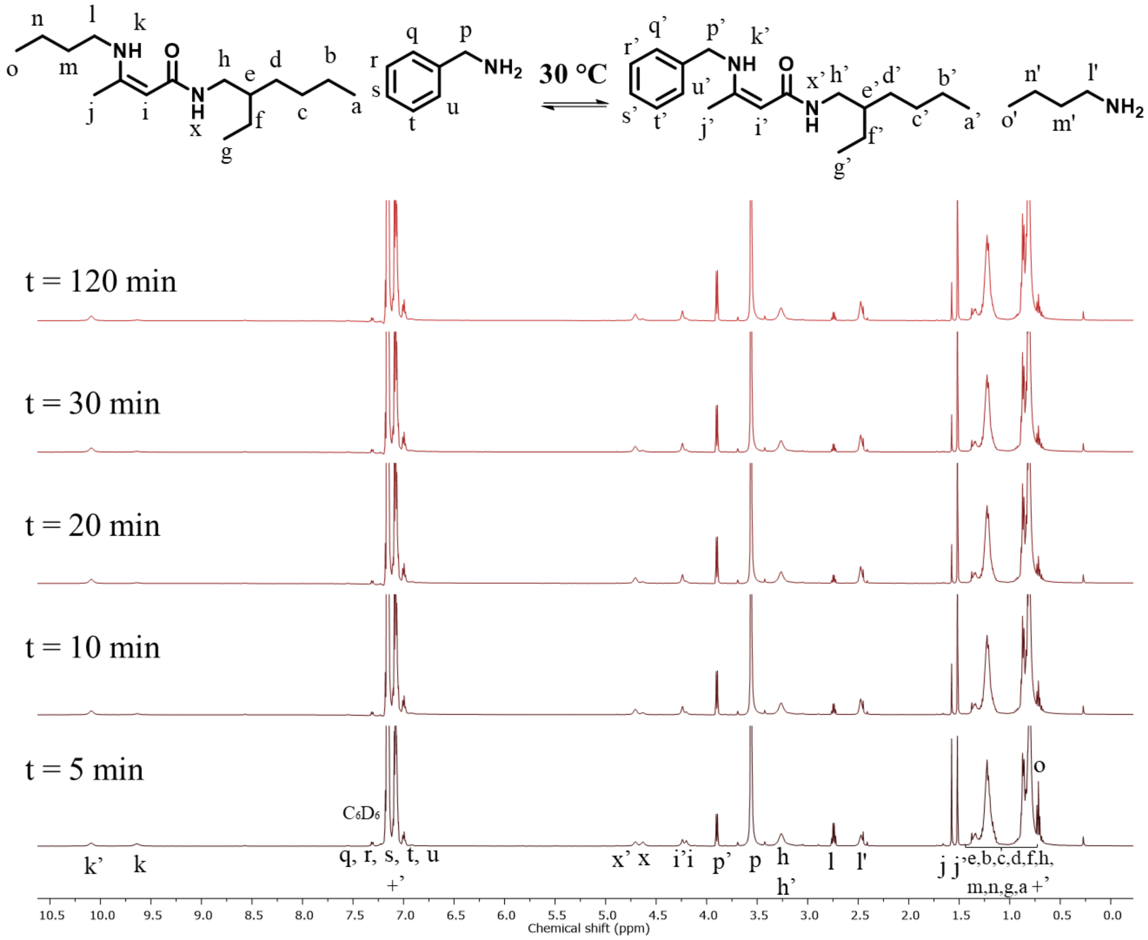

**Figure S1**. $^1$H NMR spectrum of transamination of ***3-(butylamino)-N-(2-ethylhexyl)but-2-enamide*** (**1**) to (**3**) measured at 30°C in benzene-d$_6$.

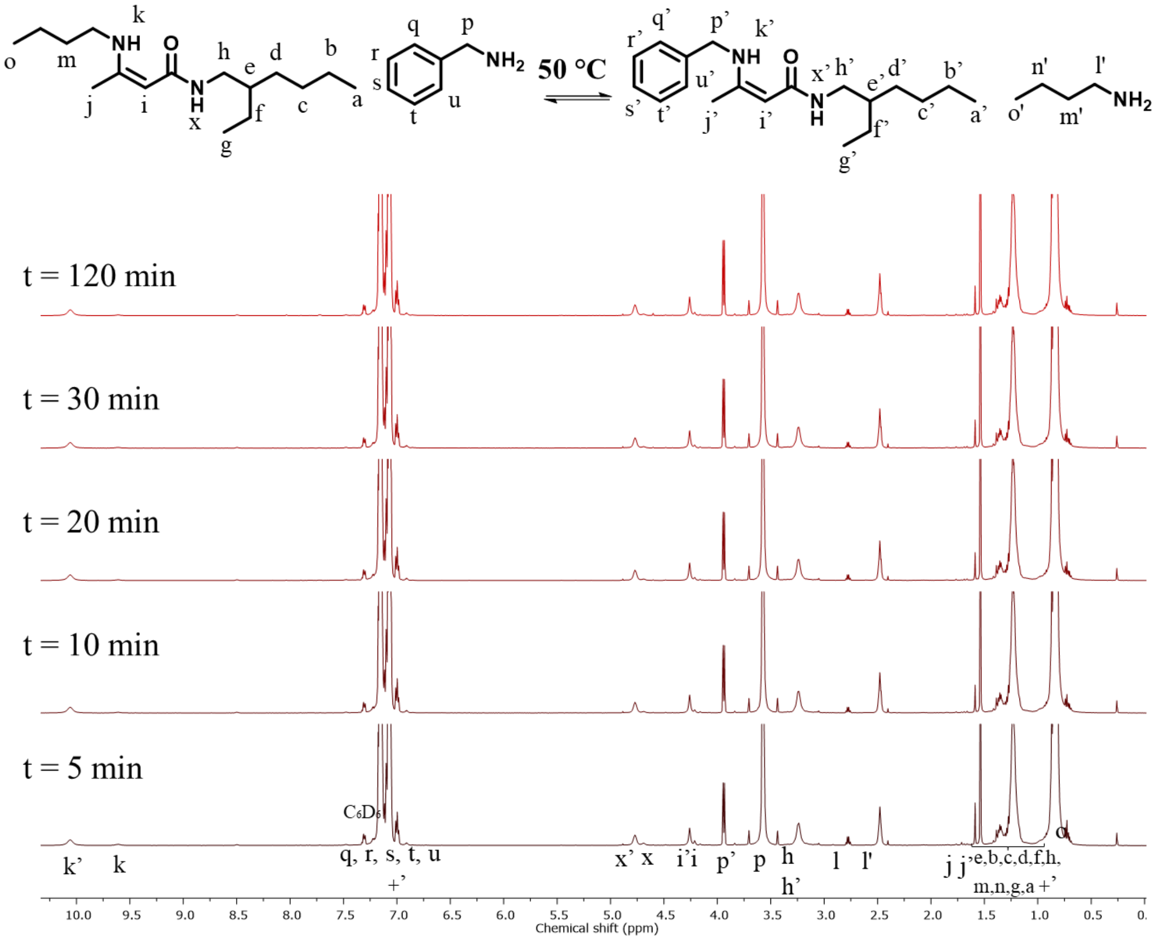

**Figure S2**. $^1$H NMR spectrum of transamination of ***3-(butylamino)-N-(2-ethylhexyl)but-2-enamide*** (**1**) to (**3**) measured at 50°C in benzene-d$_6$.

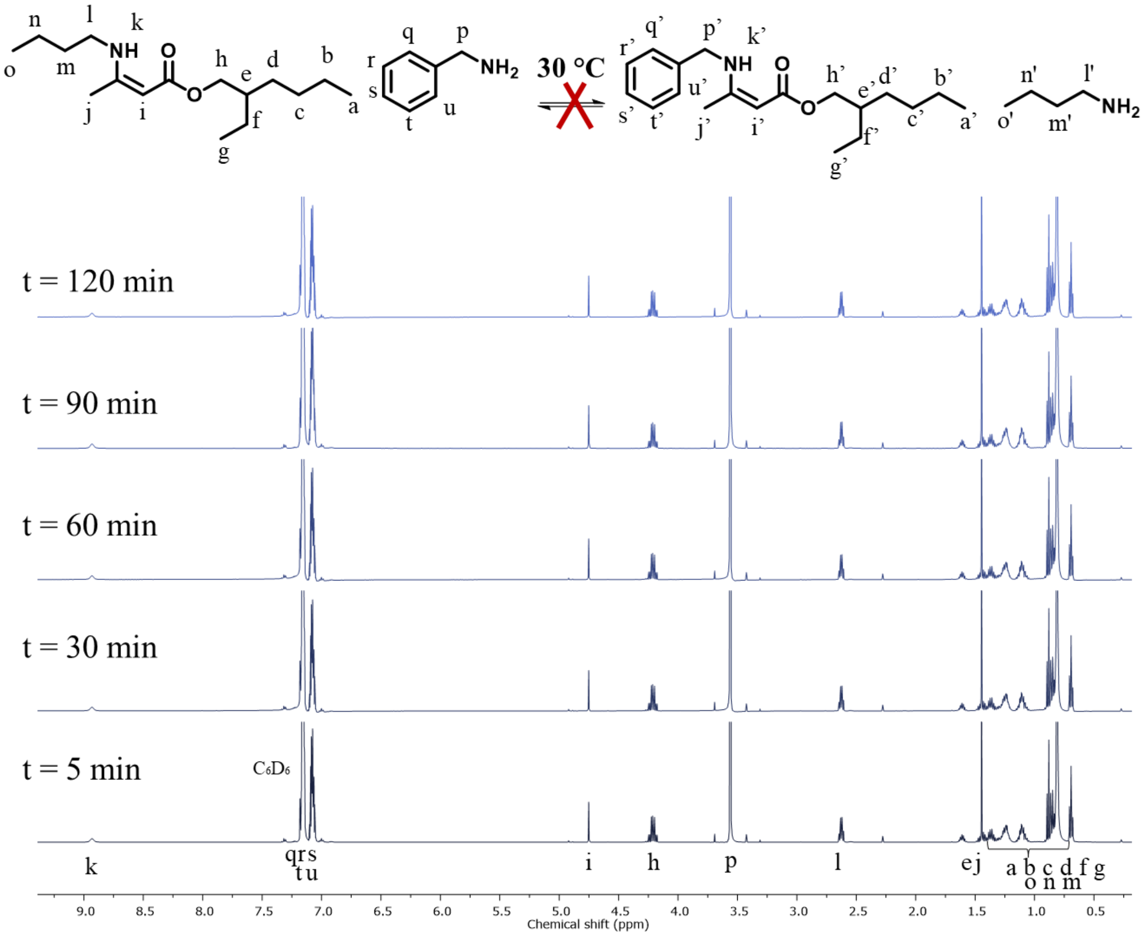

**Figure S3**. $^1$H NMR spectrum of transamination of ***2-ethylhexyl-3-(butylamino)but-2-enoate*** **(1')** to **(3')** measured at 30°C in benzene-d$_6$. There is no transamination at 30 °C and thus no product formation of **(3')** is evidenced.

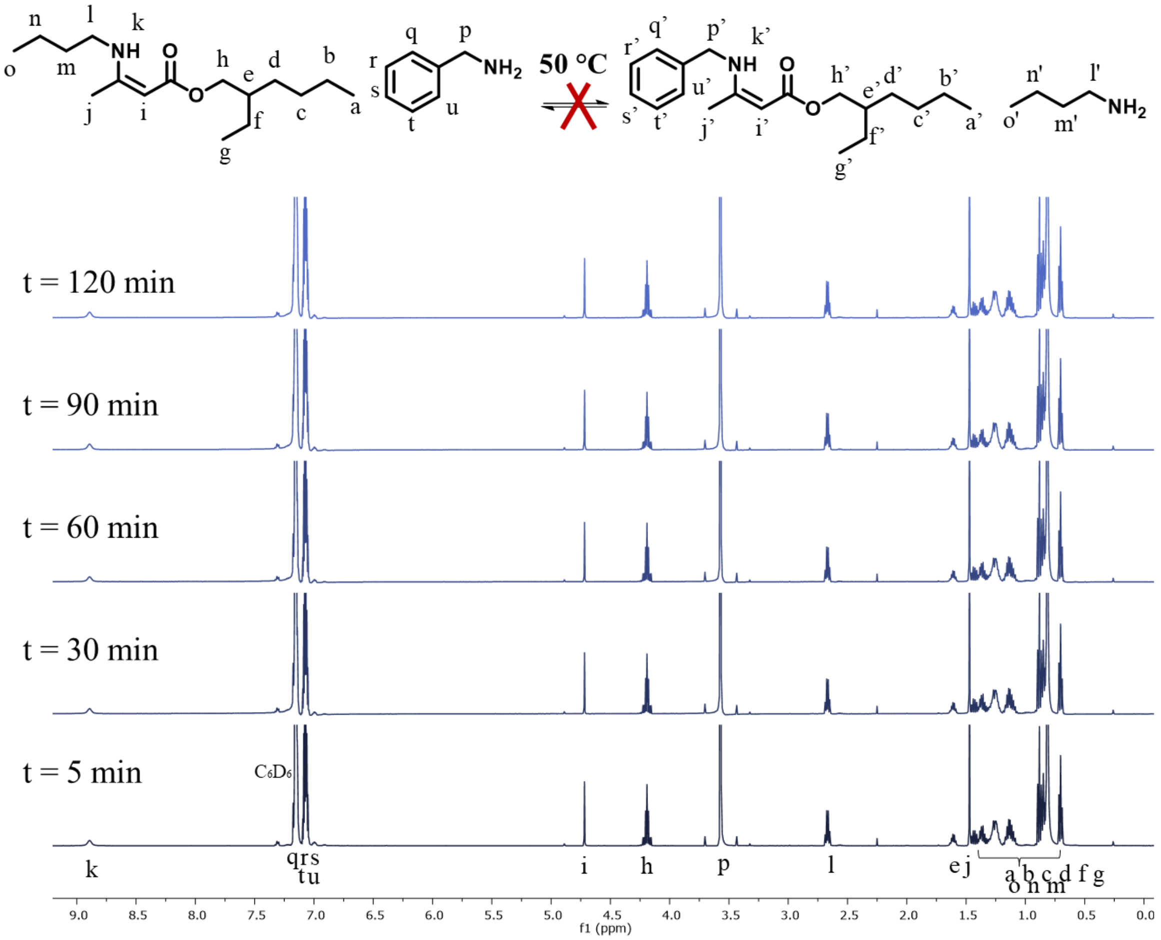

**Figure S4**. $^1$H NMR spectrum of transamination of ***2-ethylhexyl-3-(butylamino)but-2-enoate*** **(1')** to **(3')** measured at 50°C in benzene-d$_6$. There is almost no transamination at 50 °C (+-1%) and thus almost no product formation of **(3')** is evidenced.

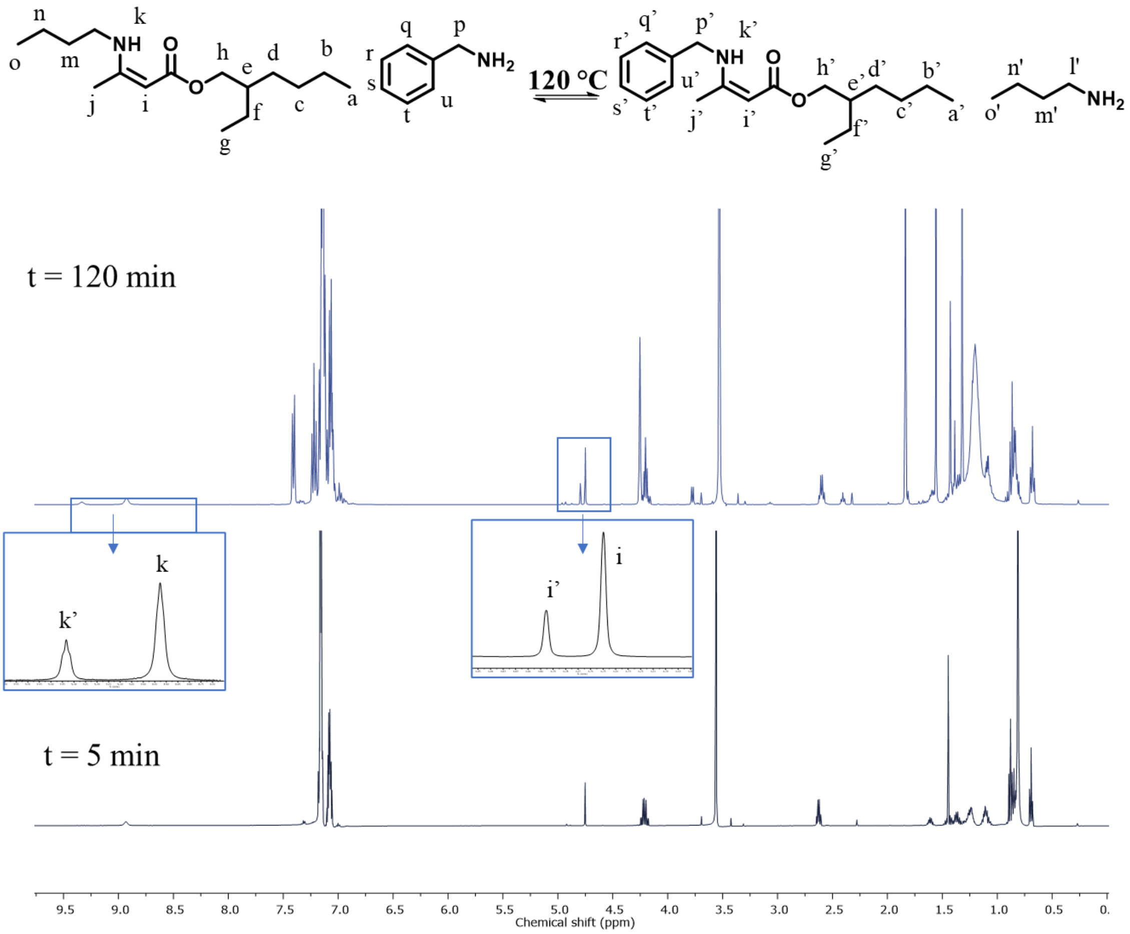

**Figure S5**. $^1$H NMR spectrum of transamination of ***2-ethylhexyl-3-(butylamino)but-2-enoate*** **(1')** to **(3')** measured at 120°C in benzene-d$_6$. Product formation of **(3')** is evidenced.

# Material Characterisation

## Thermal properties

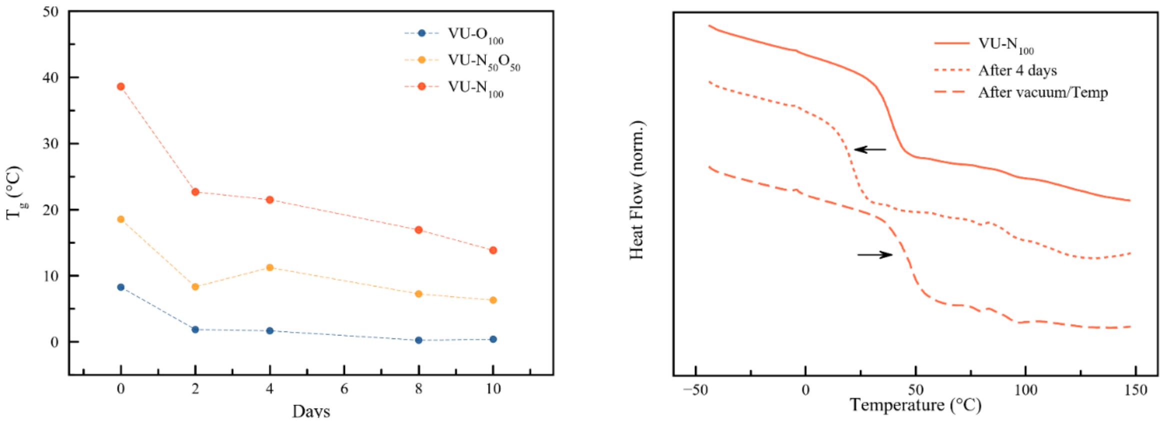

**Figure S6**. Plasticizing effect of water on the VU materials. The hydrogen bonds in the materials can be in competition with polar solvents or molecules such as water. Therefore, the materials presented herein were kept in a dry environment to avoid any plasticizing effect of water, impacting the thermal transitions. Note that a much higher plasticizing effect is observed for VU-$N_{100}$ and VU-$N_{50}O_{50}$ compared to VU-$O_{100}$.

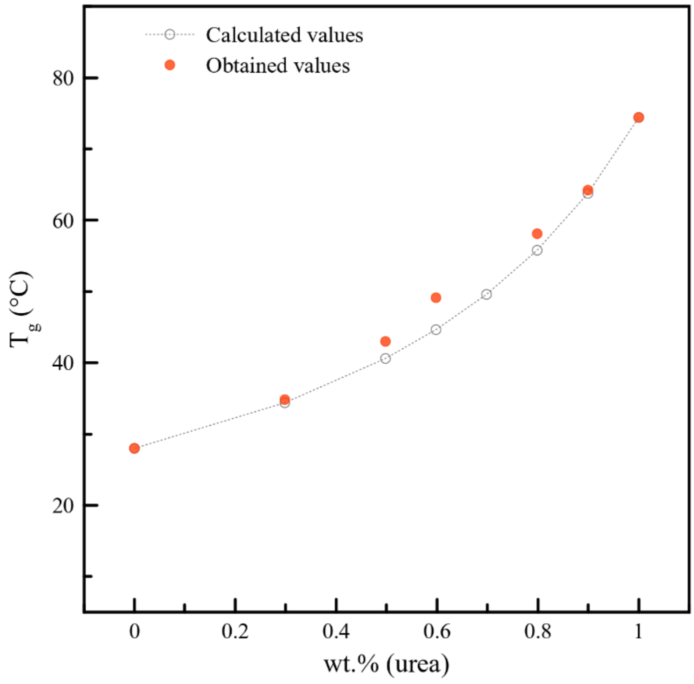

**Figure S7**. Glass transition temperatures of the materials as a function of wt.% urea according to the Fox-Equation. $(\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}})$

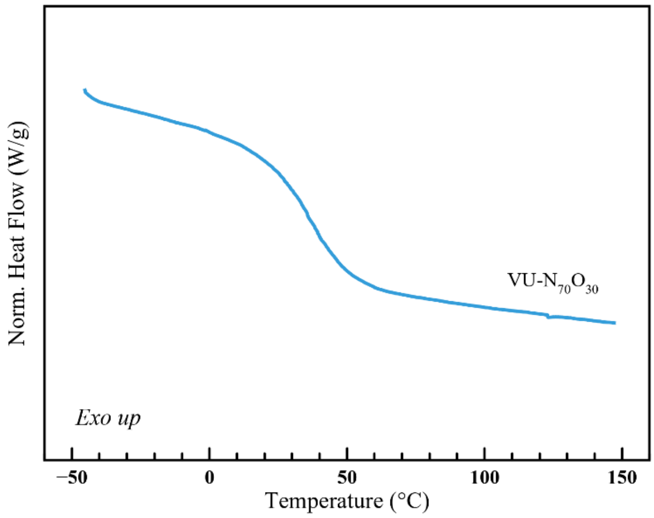

**Figure S8**. DSC thermogram of VU-$N_{70}O_{30}$ at a heating rate of 10°C $min^{-1}$.

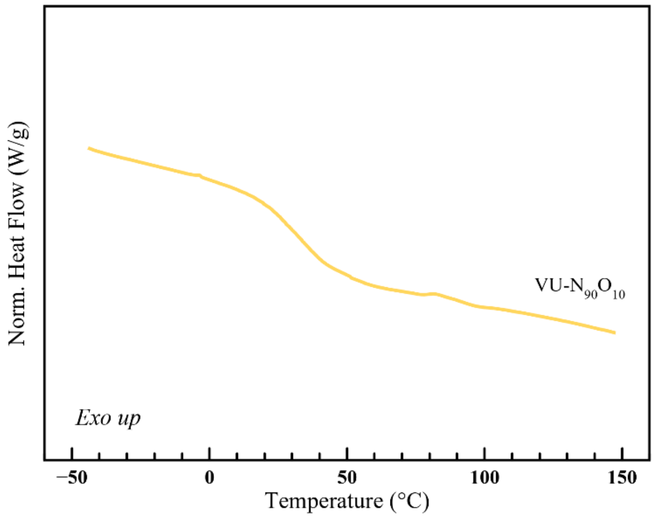

**Figure S9**. DSC thermogram of VU-$N_{90}O_{10}$ at a heating rate of 10°C $min^{-1}$.

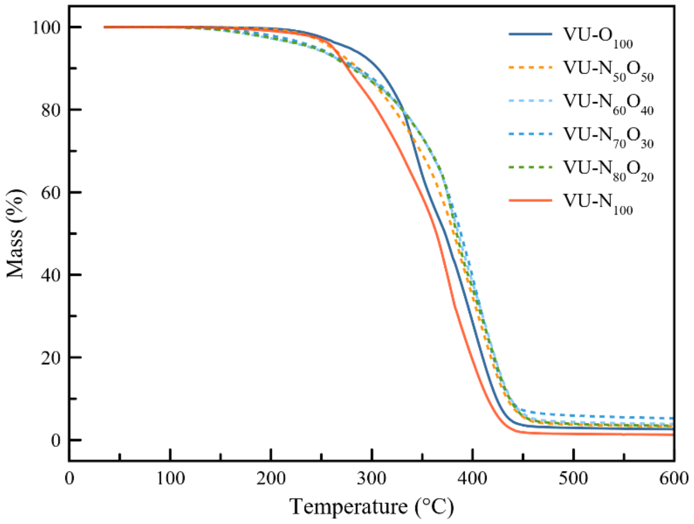

**Figure S10**. TGA thermogram of all materials at a heating rate of 10°C min$^{-1}$.

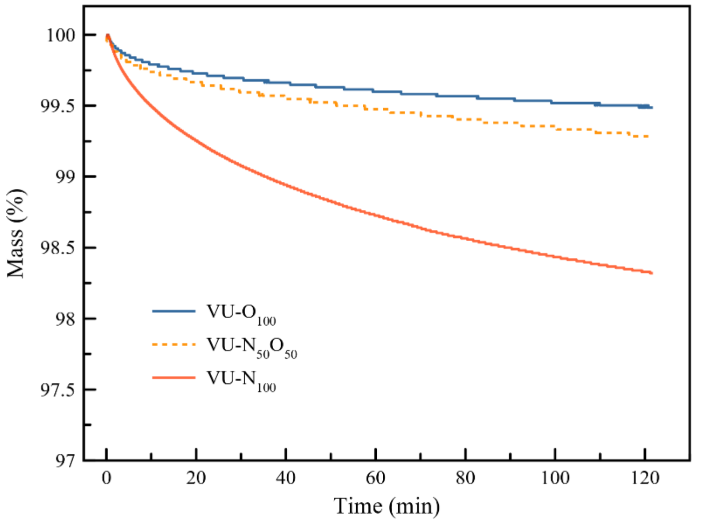

**Figure S11**. Isothermal TGA thermogram of VU-$O_{100}$, VU-$N_{50}O_{50}$ and VU-$N_{100}$ materials at 130 °C as a function of time.

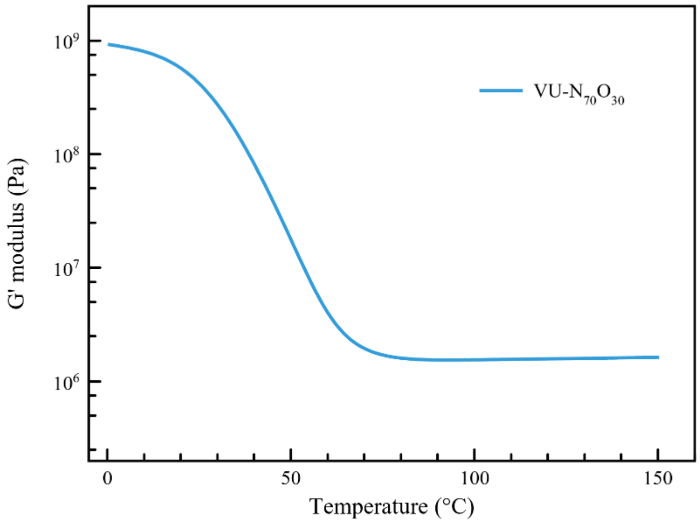

**Figure S12**. Dynamic temperature ramp of VU-$N_{70}O_{30}$ with storage modulus as a function of temperature with a heating rate of 3°C $min^{-1}$.

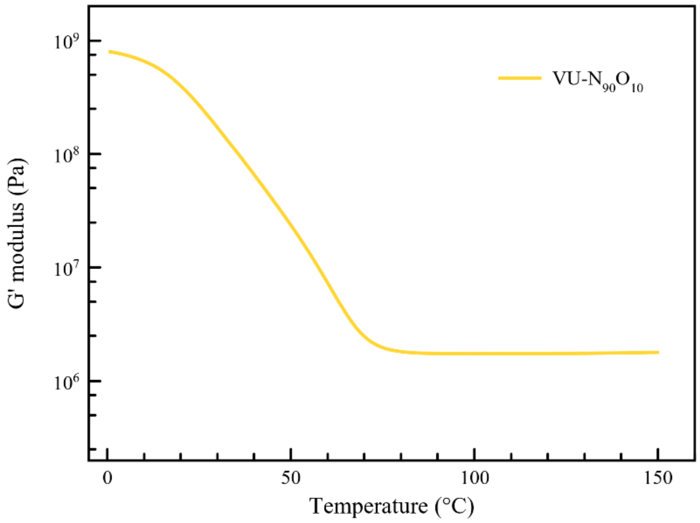

**Figure S13**. Dynamic temperature ramp of VU-$N_{90}O_{10}$ with storage modulus as a function of temperature with a heating rate of 3°C $min^{-1}$.

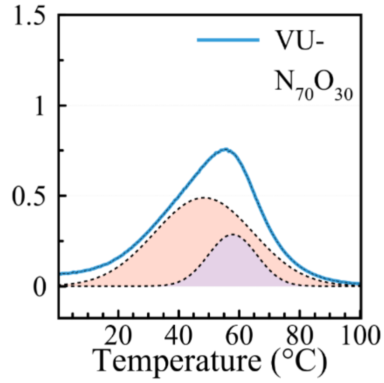

**Figure S14**. Tan delta obtained from dynamic temperature ramp of VU-$N_{70}O_{30}$.

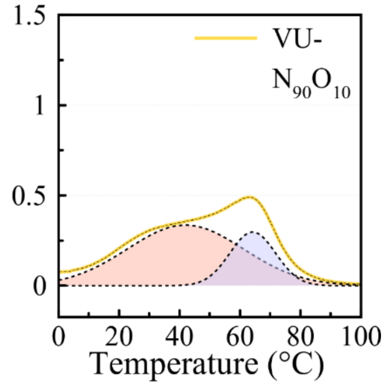

**Figure S15**. Tan delta obtained from dynamic temperature ramp of VU-$N_{90}O_{10}$.

## Tensile tests

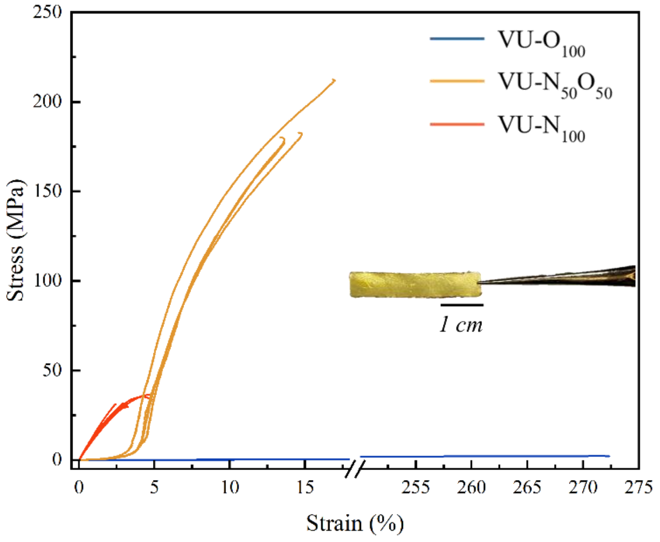

**Figure S16.** Stress as a function of strain for VU-$N_{100}$, VU-$N_{50}O_{50}$ and VU-$O_{100}$ at 25°C.

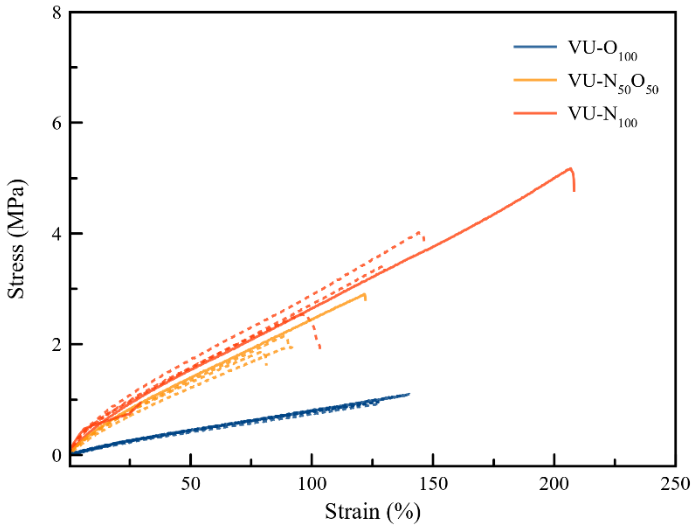

**Figure S17.** Stress as a function of strain for VU-$N_{100}$, VU-$N_{50}O_{50}$ and VU-$O_{100}$ at $T_g$ +30 °C.

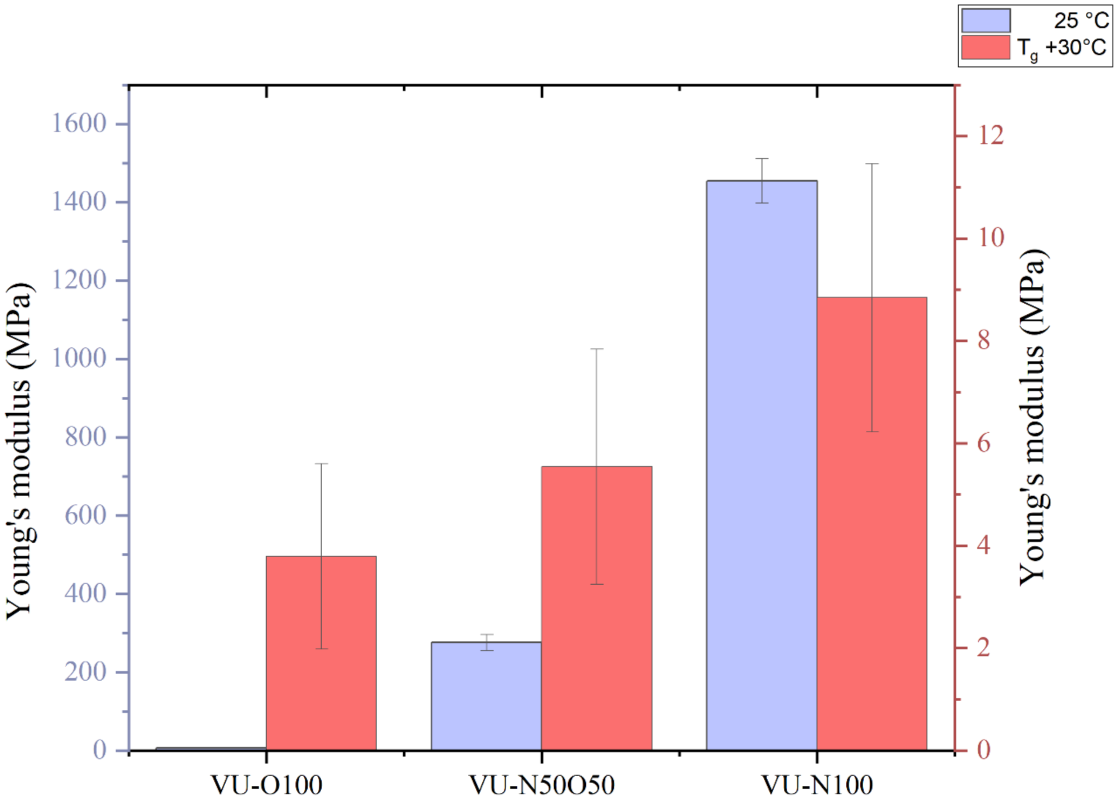

**Figure S18.** Young's modulus for VU-$N_{100}$, VU-$N_{50}O_{50}$ and VU-$O_{100}$ at 25°C (blue) and $T_g$ +30 °C (red).

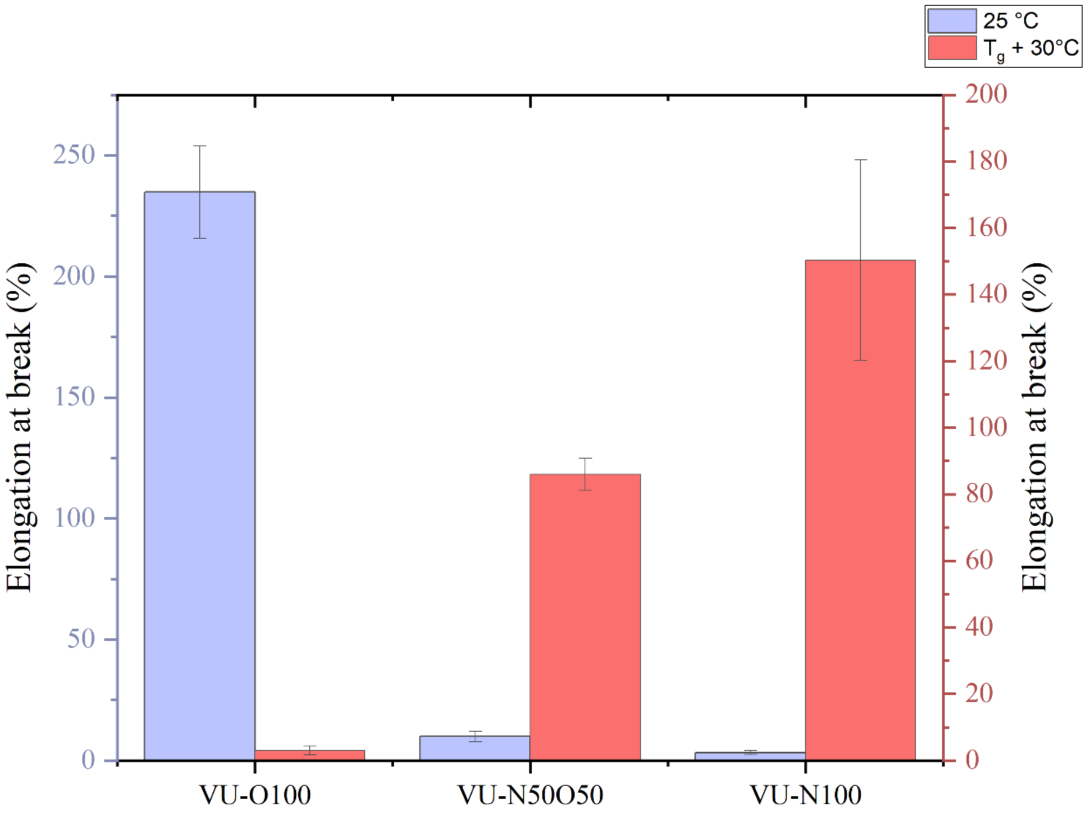

**Figure S19.** Elongation at break for VU-$N_{100}$, VU-$N_{50}O_{50}$ and VU-$O_{100}$ at 25°C (blue) and $T_g$ +30 °C (red).

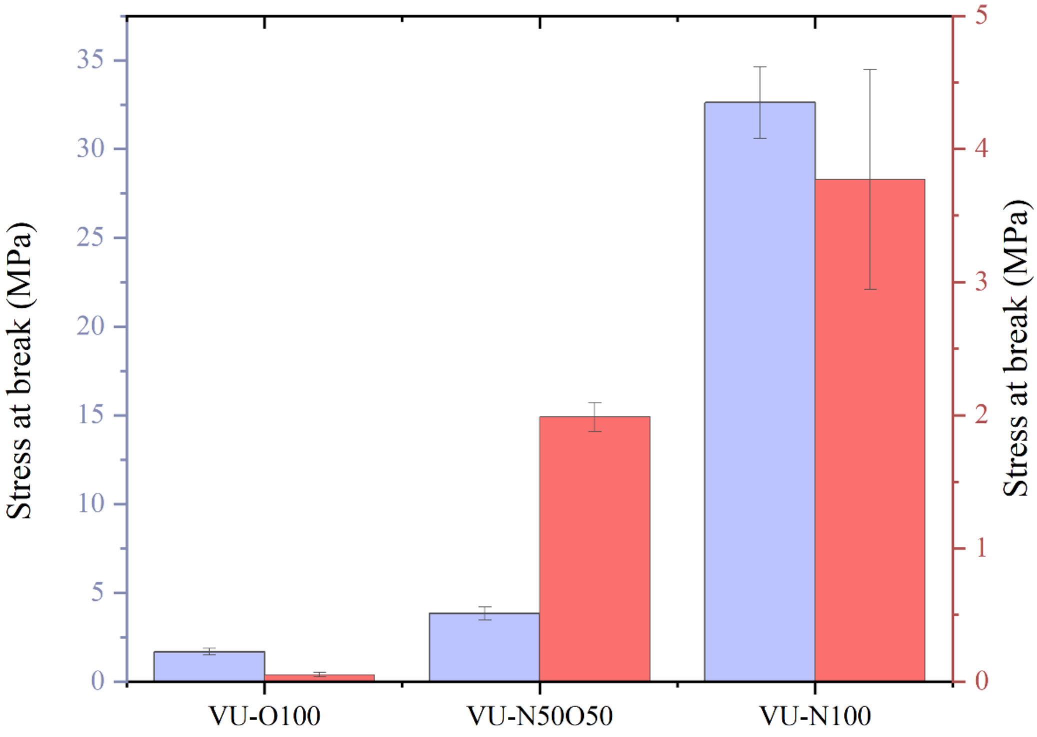

**Figure S20.** Stress at break for VU-$N_{100}$, VU-$N_{50}O_{50}$ and VU-$O_{100}$ at 25°C (blue) and $T_g$ +30 °C (red).

## WAXS

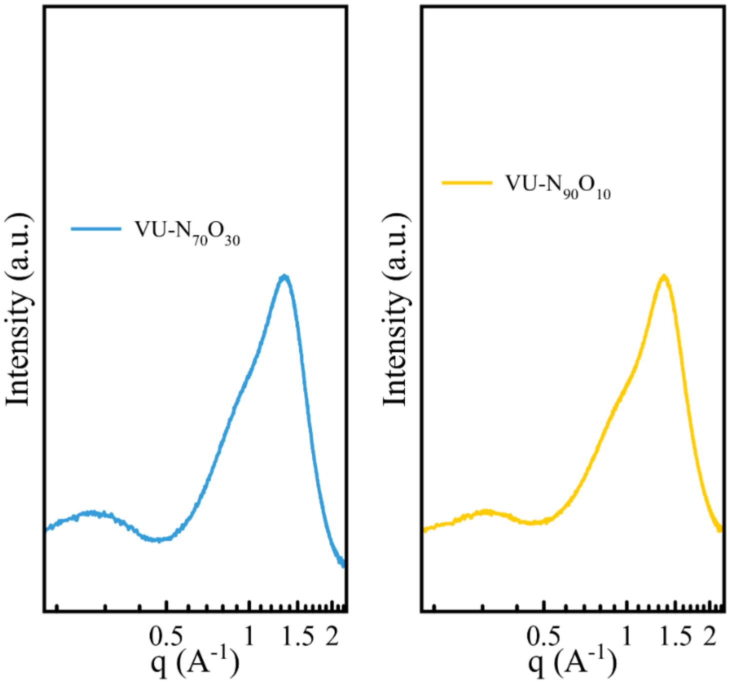

**Figure S21**. 1D-WAXS of VU-$N_{70}O_{30}$ and VU-$N_{90}O_{10}$.

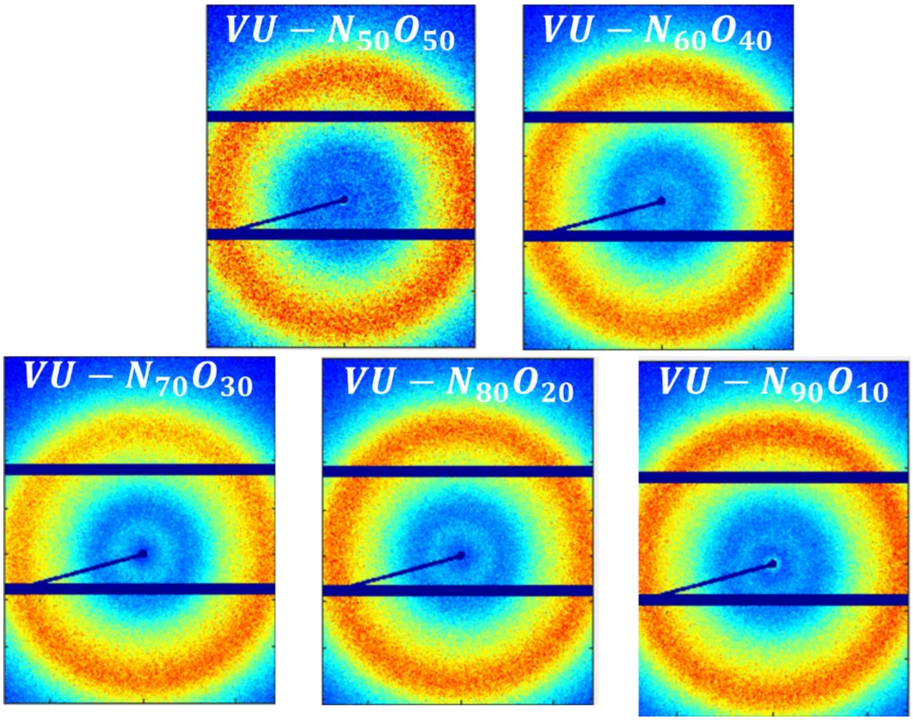

**Figure S22**. 2D-WAXS of all materials.

## FT-IR

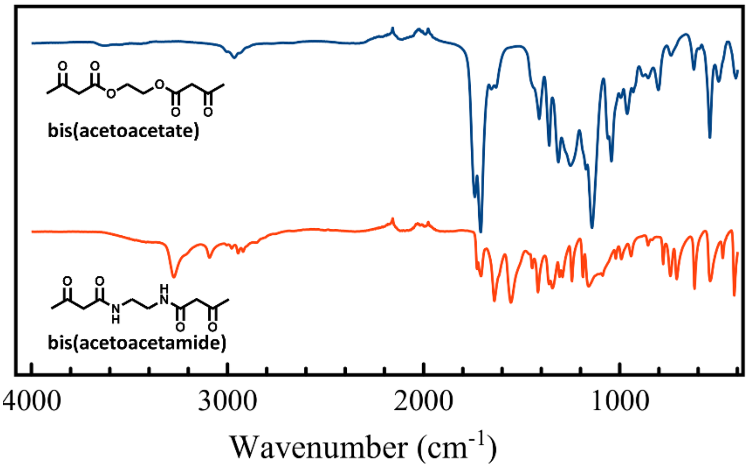

**Figure S23**. FTIR spectroscopy of the starting bis(acetoacetate) in blue and bis(acetoacetamide) in red.

## Stress relaxation measurements

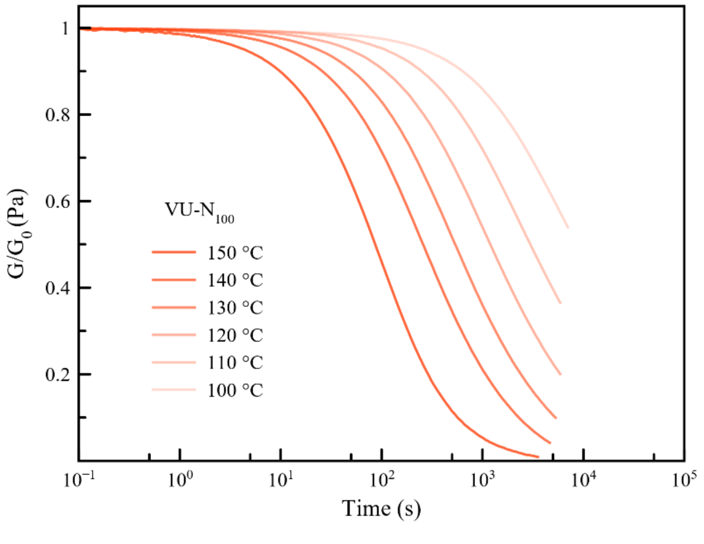

**Figure S24.** Normalized stress-relaxation data of VU-N$_{100}$ with E$_a$ = 122.4 ± 6.1 kJ/mol.

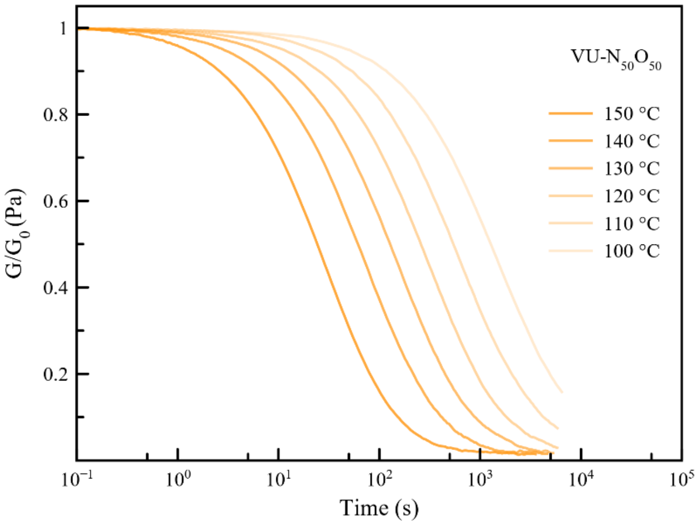

**Figure S25.** Normalized stress-relaxation data of VU-$N_{50}O_{50}$ with $E_a$ = 102.8 ± 3.2 kJ/mol.

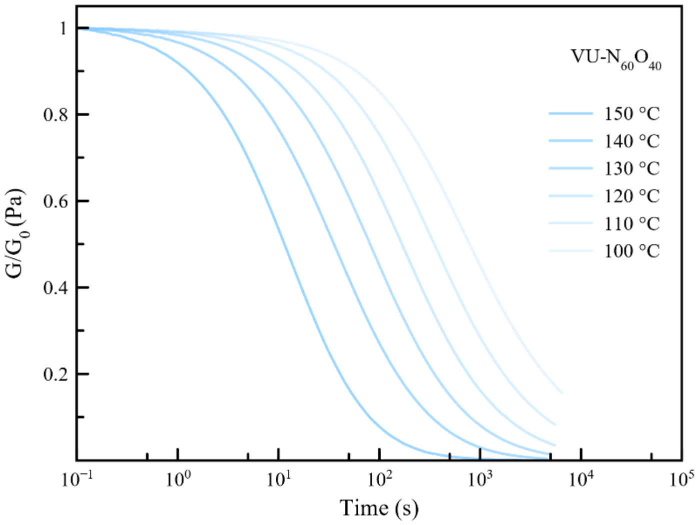

**Figure S26.** Normalized stress-relaxation data of VU-$N_{60}O_{40}$ with $E_a$ = 110.7 ± 6.2 kJ/mol.

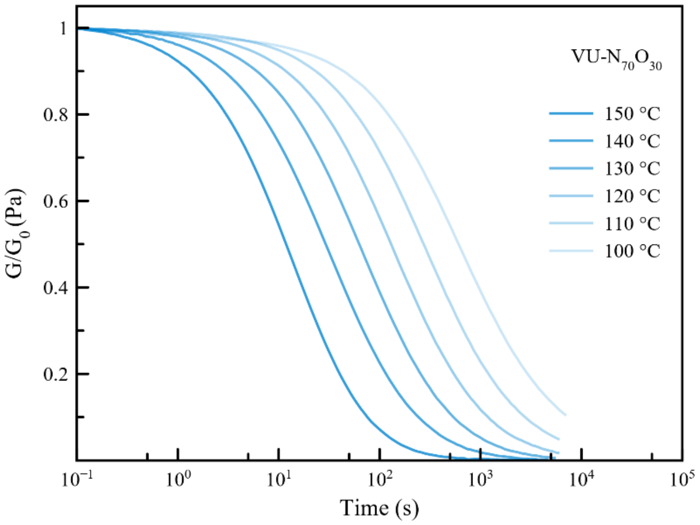

**Figure S27.** Normalized stress-relaxation data of VU-$N_{70}O_{30}$ with $E_a$ = 104.8 ± 4.1 kJ/mol.

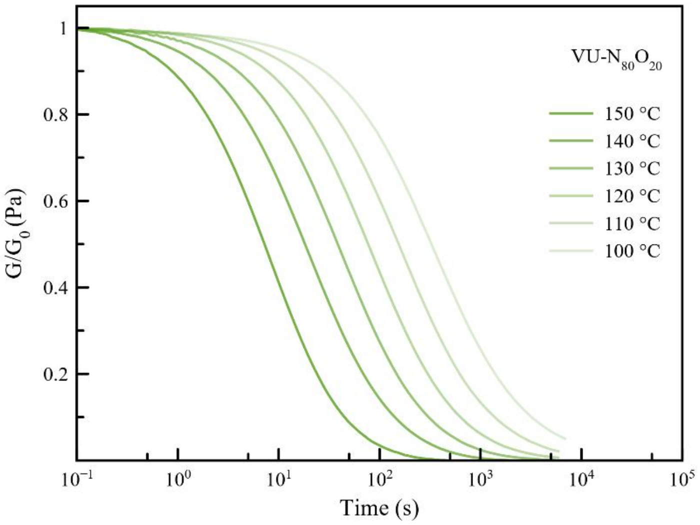

**Figure S28.** Normalized stress-relaxation data of VU-$N_{80}O_{20}$ with $E_a$ = 99.3 ± 4.6 kJ/mol.

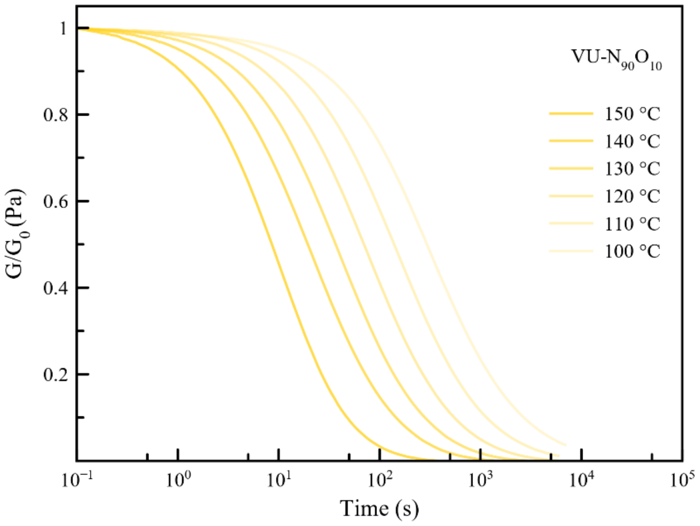

**Figure S29.** Normalized stress-relaxation data of VU-N$_{90}$O$_{10}$ with $E_a$ = 94.2 ± 2.7 kJ/mol.

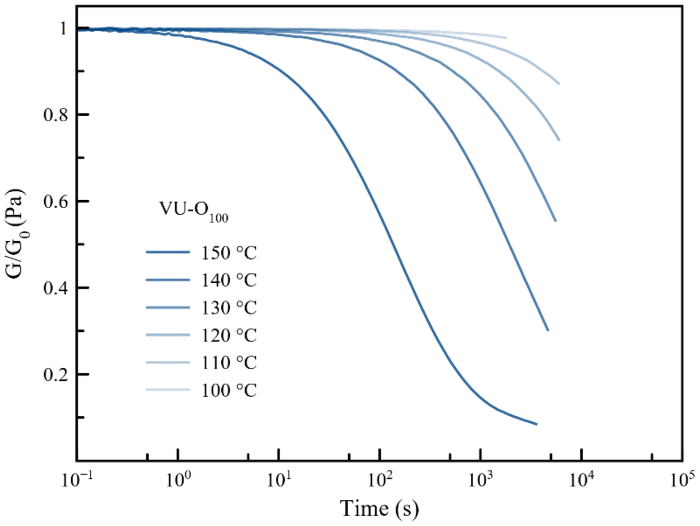

**Figure S30.** Normalized stress-relaxation data of VU-O$_{100}$with $E_a$ = 184.2 ± 23.1 kJ/mol.

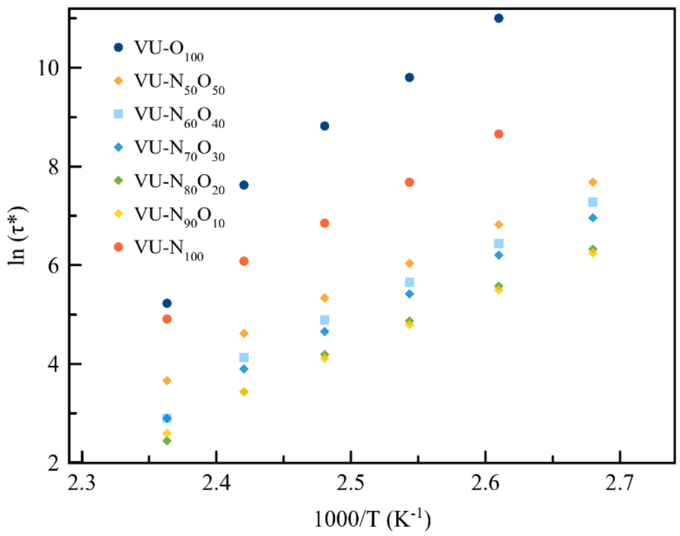

**Figure S31.** Arrhenius plot of all VU materials.

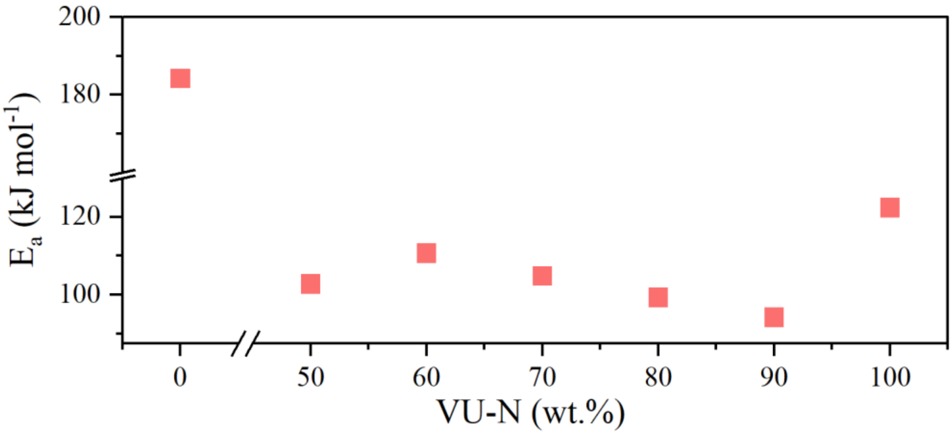

**Figure S32.** Activation energy as a function of VU-N content for the VU-mixtures.

## Creep measurements

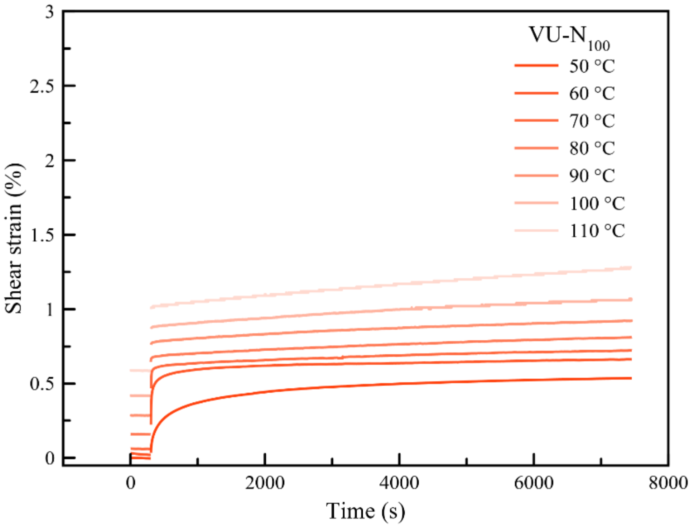

**Figure S33.** Shear strain as a function of time for VU-$N_{100}$.

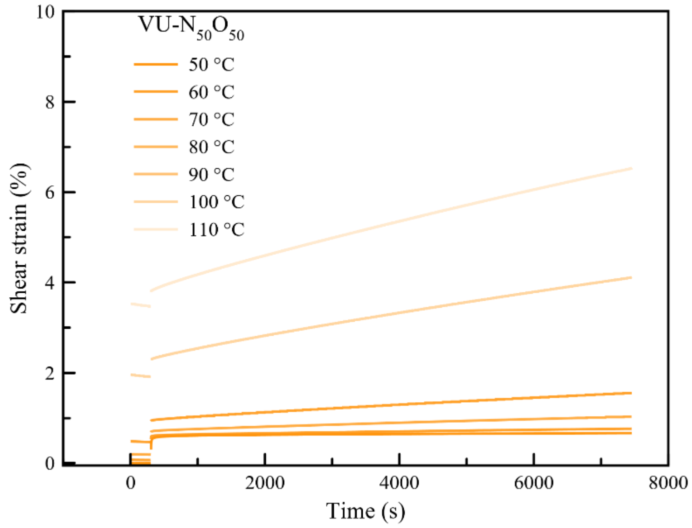

**Figure S34.** Shear strain as a function of time for VU-$N_{50}O_{50}$.

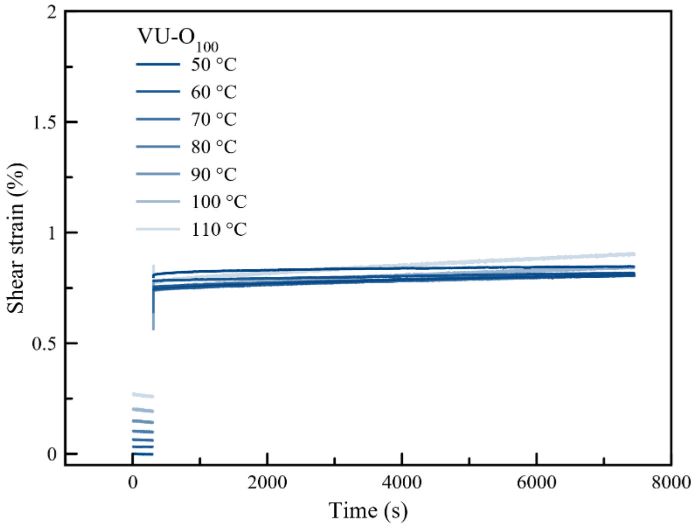

**Figure S35.** Shear strain as a function of time for VU-$O_{100}$.

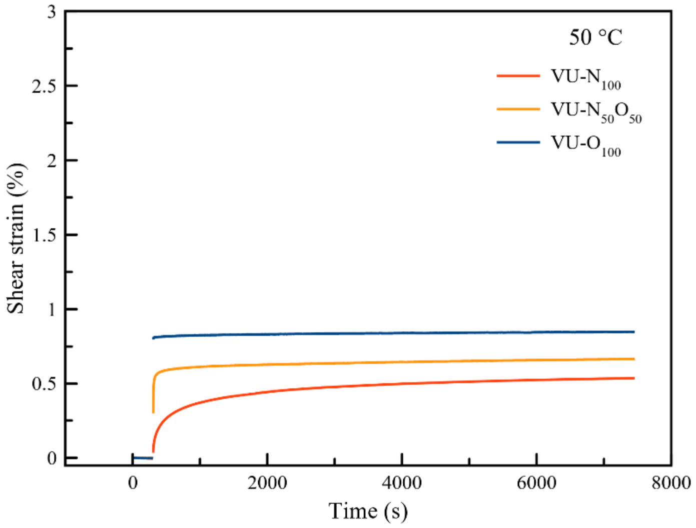

**Figure S36.** Shear strain as a function of time for VU-$N_{100}$, VU-$N_{50}O_{50}$ and VU-$O_{100}$ at 50 °C.

# References

(1) Spiesschaert, Y.; Guerre, M.; De Baere, I.; Van Paepegem, W.; Winne, J. M.; Du Prez, F. E. Dynamic Curing Agents for Amine-Hardened Epoxy Vitrimers with Short (Re)Processing Times. *Macromolecules* **2020**, *53* (7), 2485–2495.