Supporting Information

Fast processing of highly crosslinked low-viscosity vitrimers

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Experimental part

Material

Polypropylene glycol (PPG, M_n = 400 and 2000 g.mol^{-1}), Jeffamine D-400 (M_n = 400 g.mol^{-1}), *tert*-butylacetoacetate (TBAA, >98 %), and tris(2-aminoethyl)amine (TREN, 96%) were purchased from Sigma Aldrich and used without further purification. Tetrahydrofuran (THF) was purchased from Acros Organics. Para-toluene sulfonic acid monohydrate (pTsOH*H_20, 98%) and acetone were purchased from TCI.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance Ultrashield 300 MHz spectrometer. Deuterated DMSO was used as the solvent in each sample. Coupling constants and chemical shifts are given in hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording NMR spectra were as followed: 1D ^{1}H: flip angle, 30°; acquisition time, 4.1 s; pulse delay, 7.75 µs; number of scans, 16; spectral window, 8 kHz. 1D ^{13}C: jmod pulse program was used with acquisition time of 1.36 s and 3072 number of scans. 2D COSY ^{1}H-^{1}H: The cosygpppqf pulse sequence from Bruker catalogue was used without modification; acquisition time, F1 0.01 s and F2 0.17 s; spectra window, 6 kHz for both F1 and F2 dimensions; number of scans, 8. 2D HSQC ^{1}H-^{13}C: The hsqcedetgp pulse sequence from Bruker catalogue was used without modification; acquisition time, F1 7.68 ms and F2 0.16 s; spectra window, 6.4 kHz for F2 and 16.6 kHz for F1; number of scans, 8. Diffusion ordered NMR spectroscopy (DOSY) experiments were performed at 25 °C with 16 scans and 64 planes in F1 dimension.

Infrared (ATR-FTIR) spectra were measured using a Perkin–Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe.

Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/ SDTA851e instrument under nitrogen atmosphere at a heating rate of 10 K·min^{-1} from 25 °C to 800 °C for the dynamic mode or at 100 °C and 150 °C during 120 min for the isothermal mode.

Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating rate of 10 K ·min^{-1}.

Dynamic mechanical analysis (DMA) was performed on a SDTA861e DMA from Mettler Toledo utilizing rectangular sample (*ca.* 2.1 mm (T), 2.0 mm (W) and 8.0 mm (L)) and using tension clamp. The axial force was adjusted to 1 N and a temperature ramp was then performed from -40 °C to 100 °C at a rate of 3 K·min^{-1} with an oscillating force of 1 N, a displacement amplitude of 10 µm and a regular frequency of 1 Hz.

Rheology experiments were performed on an Anton Paar MCR 302. The experiments were performed in parallel plate geometry using 8 mm sample disks. Unless specified, the experiments were performed using a normal force of 1 N, an oscillating frequency of 1 rad.s^{-1} and a strain of 1 %. For all rheology experiments, the applied stress was comprised in the linear viscoelastic region at the measured temperatures. For amplitude sweep experiments, the strain was varied from 0.01 to 100 %. For temperature sweep experiments, a normal force of 0.2 N, a strain of 1% and a frequency of 1 rad.s^{-1} was applied and G' and G'' was followed. For frequency sweep experiments, a normal force of 0.2 N, a strain of 1% and a frequency from 100 to 0.1 rad.s^{-1} was applied at a constant temperature and G' and G'' was followed. For stress relaxation experiments, a strain of 1 % was applied to the material and the relaxation modulus (G(t)) was followed over time at a constant temperature.

Reprocessability. To reprocess the network, the polymer was broken into pieces and placed into a rectangular mold (A: 70 mm x 40 mm x 2 mm; B: 30 mm x 15 mm x 2 mm) for compression molding. This assembly was placed in a 130°C - 150 °C preheated compression press for 1-2 min under 0.5 metric tons of pressure. Then the pressure was increased to 2 tons and kept constant for an additional 2-13 min. After 4 to 15 min of pressing in total, the mold was cooled down for 30 min and the sample was removed from the metal sheet with a razor blade. The temperature and pressing time have been adjusted according to the amine and acid content, where a higher content of pending amines and pTsOH were used, the material was pressed at lower temperatures for shorter periods of time and vice versa. For instance: PPG$_{400}$-based vitrimers with 5 mol.% excess amine moieties were processed for 15min in total at 150°C, whereas networks with 20 mol.% excess amine moieties and 6 mol.% of pTsOH were processed for 3 min at 130°C.

Solubility. Solubility tests were carried out with samples of 6 mm diameter and 1.5 to 2 mm thickness with a weight of around 40 to 60 mg and 3 mL of THF. Those tests were performed for 24 h at room temperature. Then, the solvent was removed, and the samples were dried under vacuum for two days at 40°C. The soluble fraction was calculated using equation (1), while the swelling ratio was calculated using equation (2).

$$Soluble\ fraction\ (\%) = \frac{m_i - m_d}{m_i} \quad (1)$$

$$Swelling\ ratio\ (\%) = \frac{m_s - m_i}{m_i} \quad (2)$$

with m_i, m_s and m_d being the initial, swollen and dry mass, respectively.

As a control experiment, Soxhlet extraction was also carried out in refluxing THF for 24 h. Typically, 1 g of sample was placed in an extraction unit of known weight and subsequently immersed in dried THF as solvent. Next, the sample was dried at 40 °C under vacuum for 48 h. The remaining dried sample was weighted, and the soluble fraction was calculated using equation (1).

Synthetic Procedures

Bis-polypropylene$_{400}$ glycol acetoacetate (PPG$_{400}$-AA): Polypropylene glycol (PPG$_{400}$, M_n ≈ 400 g.mol^{-1}, 120 g, 3.0x10^{-1} mol) and *tert*-butyl acetoacetate (100 g, 6.32x10^{-1} mol) were added in two steps in a 250 mL bottom flask. The viscous mixture was heated for 60 min at 130 °C, and *tert*-butanol product was continuously removed by vacuum distillation throughout the reaction. When the temperature of the still head dropped to 40 °C and *tert*-butanol condensation stopped, the unreacted tert-butyl acetoacetate was removed by distillation at 130 °C under 2 mbar vacuum. Yield = 95 %.

^{1}H NMR (300 MHz, DMSO-d$_6$, *δ ppm*): 0.98-1.11 (-CH$_2$-CH(**CH$_3$**)-), 1.12-1. (-CH$_2$-CH(**CH$_3$**)-O(C=O)-), 2.14-2.22 (-CH$_2$-(C=O)-**CH$_3$**), 3.20-3.70 (-**CH$_2$**-**CH**(CH$_3$)-, -**CH$_2$**-CH(CH$_3$)-O-(C=O)- and (-**CH$_2$**-(C=O)-CH$_3$), 4.83-5.03 (-CH$_2$-**CH**(CH$_3$)-O-(C=O)-).

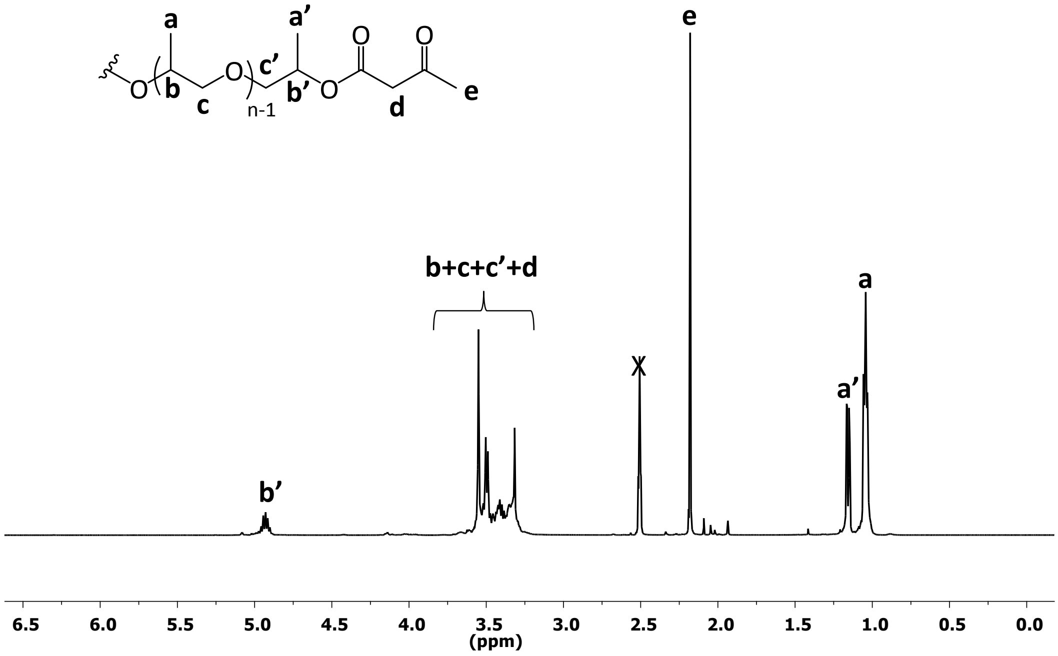


Figure S 1: ^{1}H NMR spectrum of PPG$_{400}$-AA in DMSO-d$_6$ at 25 °C.

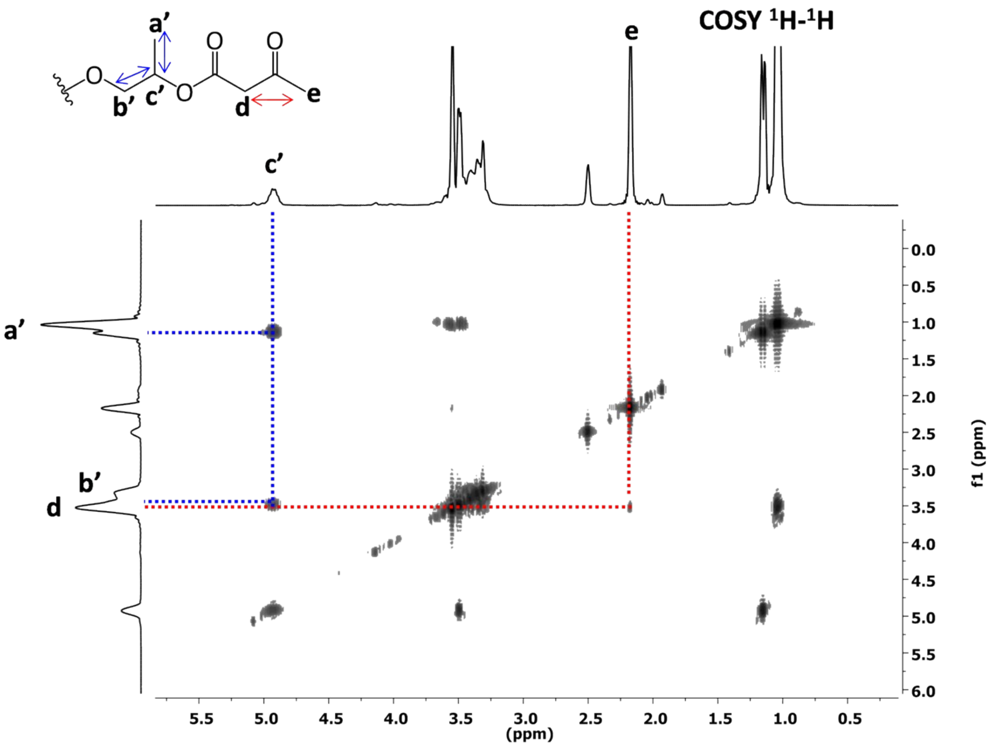


Figure S 2: COSY ^{1}H-^{1}H NMR spectrum of PPG$_{400}$-AA in DMSO-d$_6$ at 25 °C.

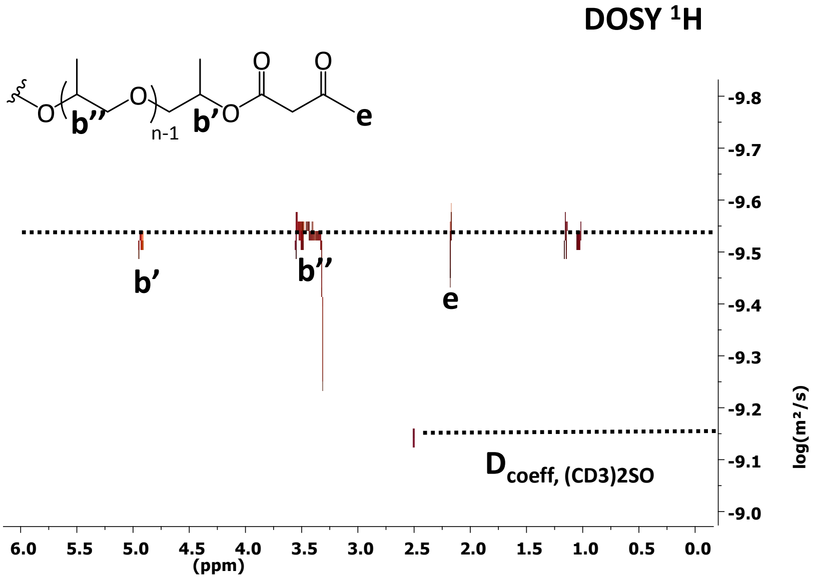


Figure S 3: DOSY ^{1}HNMR spectrum of PPG$_{400}$-AA in DMSO-d$_6$ at 25 °C.

Network synthesis: In order to obtain A$_3$-type networks with 5 mol.% excess of primary amines, *PPG$_{400}$-AA* (M$_n$ ≈ 570 g.mol^{-1}, 5 g, 8.77x10^{-3} mol) and tris(2-aminoethyl)amine (TREN, 898 mg, 6.14x10^{-3} mol) were mixed in a 30 mL polypropylene vial using a DAC 150.1 FVZ speed mixer (typical conditions of mixing: 2 min with a speed of 2500 rpm). Then, the cup was placed in an oven at 80°C for up to 4h to complete the network formation. Hereafter, the polypropylene vial was broken, and the network was cured overnight at 70°C under vacuum. Finally, the sample was cut into pieces of around 1g, and pressed separately in steel molds, following the aforementioned reprocessability procedures. Networks with an increased amount of pending amines were prepared similarly with adjusting the amount of TREN with respect to the targeted excess of 5, 10, 15, 20, and 40mol.% (excess factor “A” (1.05, 1.1, 1.15, 1.2, 1.4)), according to equation (3).

$$n_{TREN} = \frac{n_{PPG} * 2}{3} * A \quad (3)$$

For acid catalyzed networks, *para*-toluene sulfonic acid (pTsOH, $M_{pTsOH*H20}$ = 190.2 g.mol^{-1}, χ_{pTsOH} = 0.3, 1.5, 3.0, 4.5, 6.0 mol.% with respect to vinylogous urethane bonds) was first dissolved in the respective amount of TREN using the speed mixer in the above-mentioned conditions until a clear solution was obtained. Then PPG$_{400}$-AA was added, mixed and followed the described procedure.

B$_3$-type networks containing poly(propylene glycol) bis(2-aminopropyl ether) Jeffamine D-400 (M_n ≈ 400 g.mol^{-1}, 2 g, 5x10^{-3}mol) were prepared using 1,1,1-trimethyl-propane trisacetoacetate (TMPtAA, 1.22 g, 3.17x10^{-3}mol) as trifunctional crosslinker, targeting 5 mol.% excess of amines. Mixing, curing and processing (150°C, 30 min) was performed as described above.

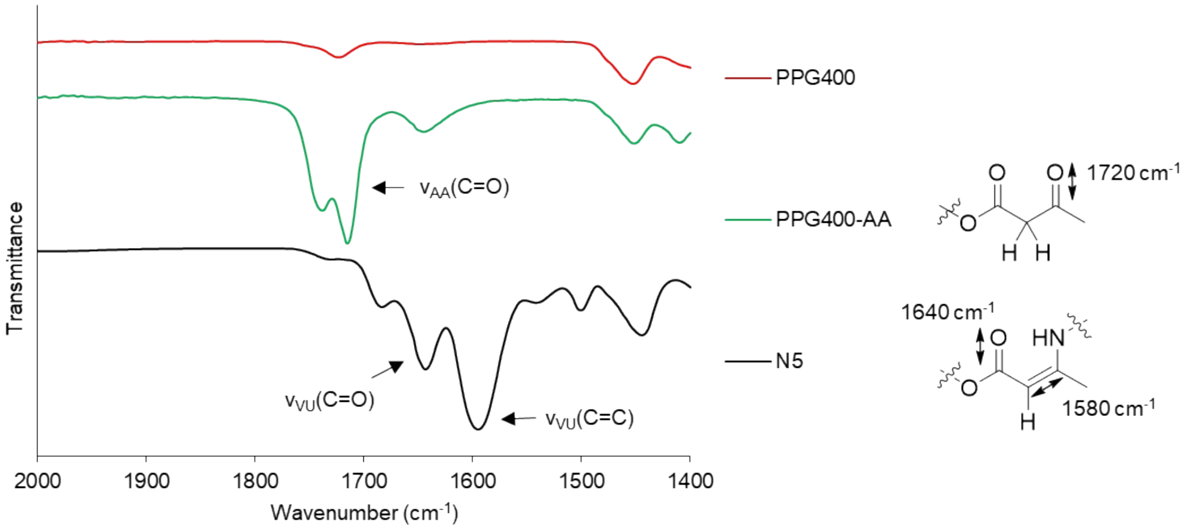


Figure S 4. ATR-FTIR of PPG$_{400}$-AA based vitrimer starting from PPG$_{400}$ (top), PPG$_{400}$-AA and PPG$_{400}$ vitrimer N5 with the characteristic resonance vibration bands at 1720 cm^{-1} (ν$_{AA}$(C=O)), 1640 cm^{-1} (ν$_{VU}$(C=O)), and 1580 cm^{-1} (ν$_{VU}$(C=C)).

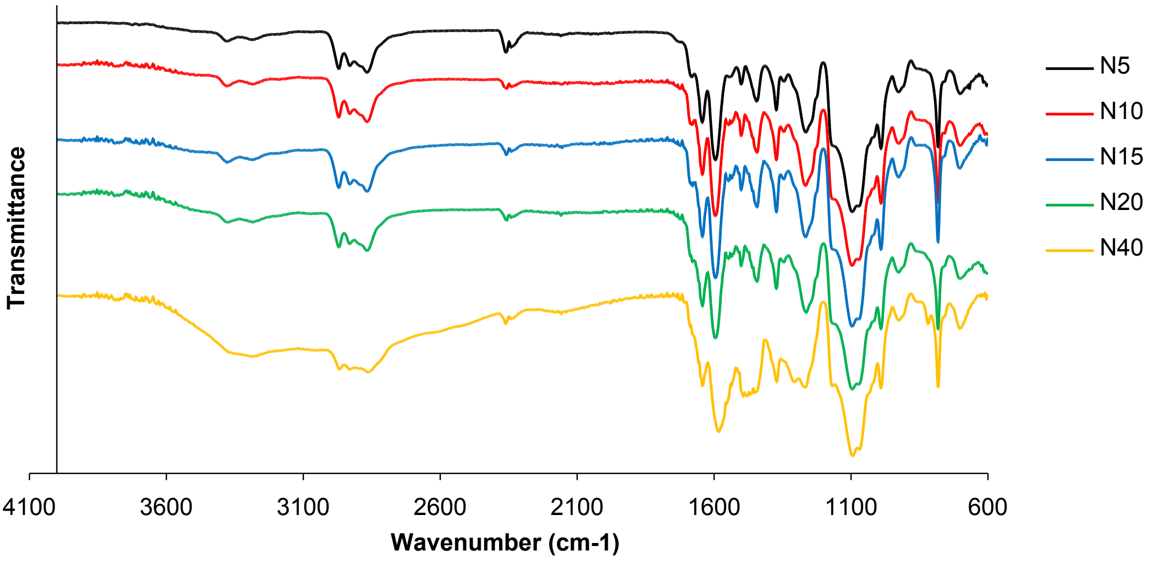


Figure S 5. ATR-FTIR of PPG_{400}-based vitrimers containing 5 mol.% to 40 mol.% excess amines (N5 to N40 respectively). The characteristic vibration bands are present at 1640 cm^{-1} (ν_{VU}(C=O)) and 1580 cm^{-1} (ν_{VU}(C=C)).

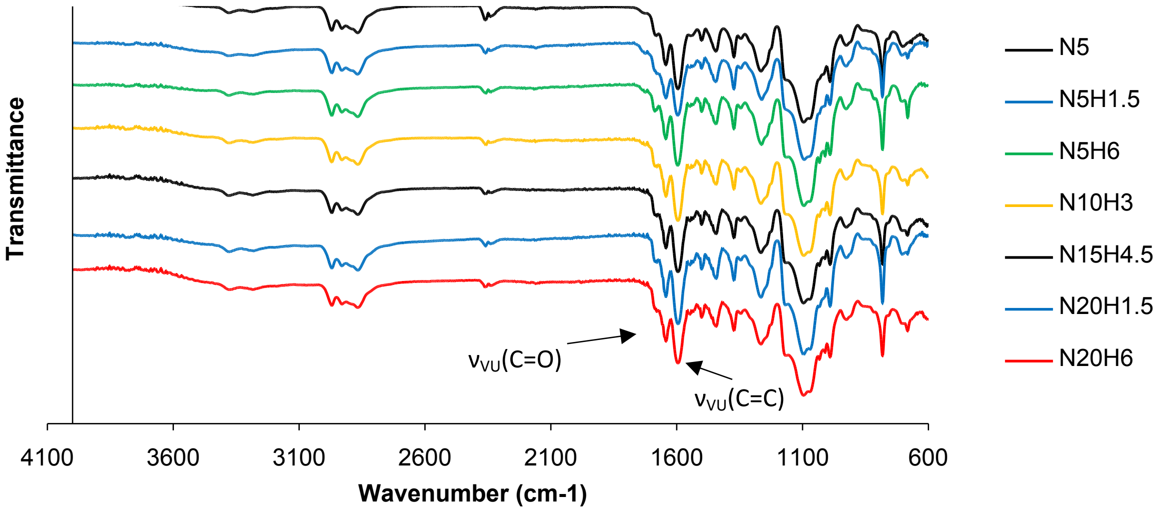
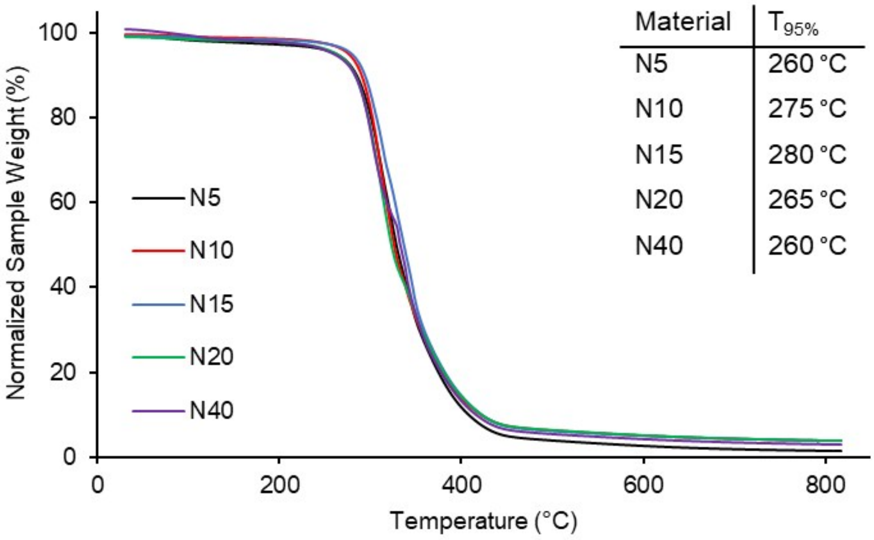


Figure S 6. ATR-FTIR of PPG_{400}-based vitrimers with 5 mol.% to 40 mol.% excess amines (N5 to N40 respectively) and different pTsOH contents. The characteristic vibration bands are present at 1640 cm^{-1} (ν_{VU}(C=O)), and 1580 cm^{-1} (ν_{VU}(C=C)).



Material	$T_{95\%}$
N5	260 °C
N10	275 °C
N15	280 °C
N20	265 °C
N40	260 °C

Figure S 7. TGA thermogram obtained from a temperature ramp at a rate of 10K.min^{-1} under nitrogen. The onset-temperature (5 wt.% loss) was ranging from 260 °C to 280 °C.

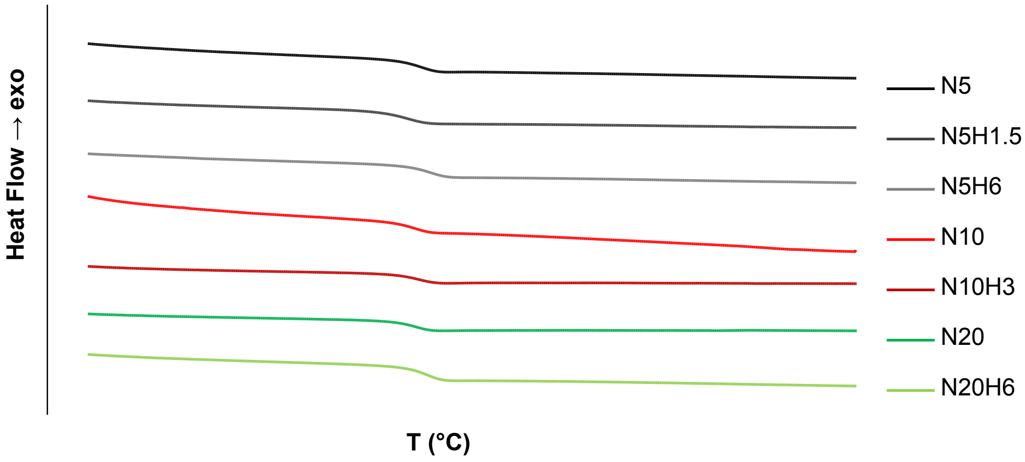


Figure S 8. DSC thermograms of the second heating at 10 K.min^{-1} of PPG$_{400}$-based vitrimer exemplified on N5, N5H1.5, N5H6, N10, N10H3, N20, N20H6 demonstrating a similar T_g (midpoint) ranging from -6 °C to -10 °C.

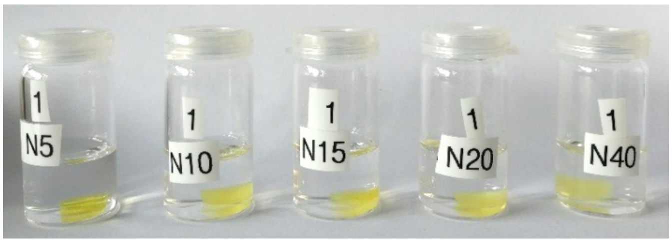


Figure S 9. Soluble fraction samples of N5, N10, N15, N20, and N40 in THF (left to right).

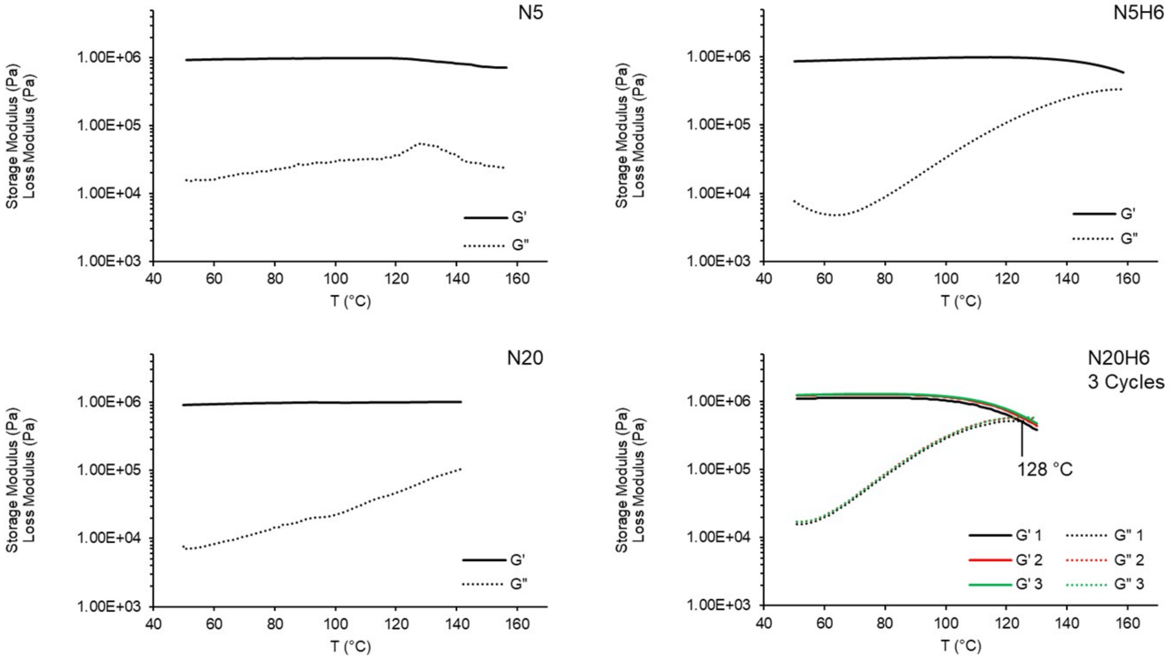


Figure S 10. Temperature sweep experiments displaying storage (G’, full line) and loss modulus (G’’, dotted line) of vitrimers N5, N5H6, N20 and N20H6, obtained with a heating or cooling rate of 5 K.min^{-1} (only heating cycle shown here). Material N20H6 shows a crossover at 128 °C and a fully reversible behavior after 3 cycles (bottom right)

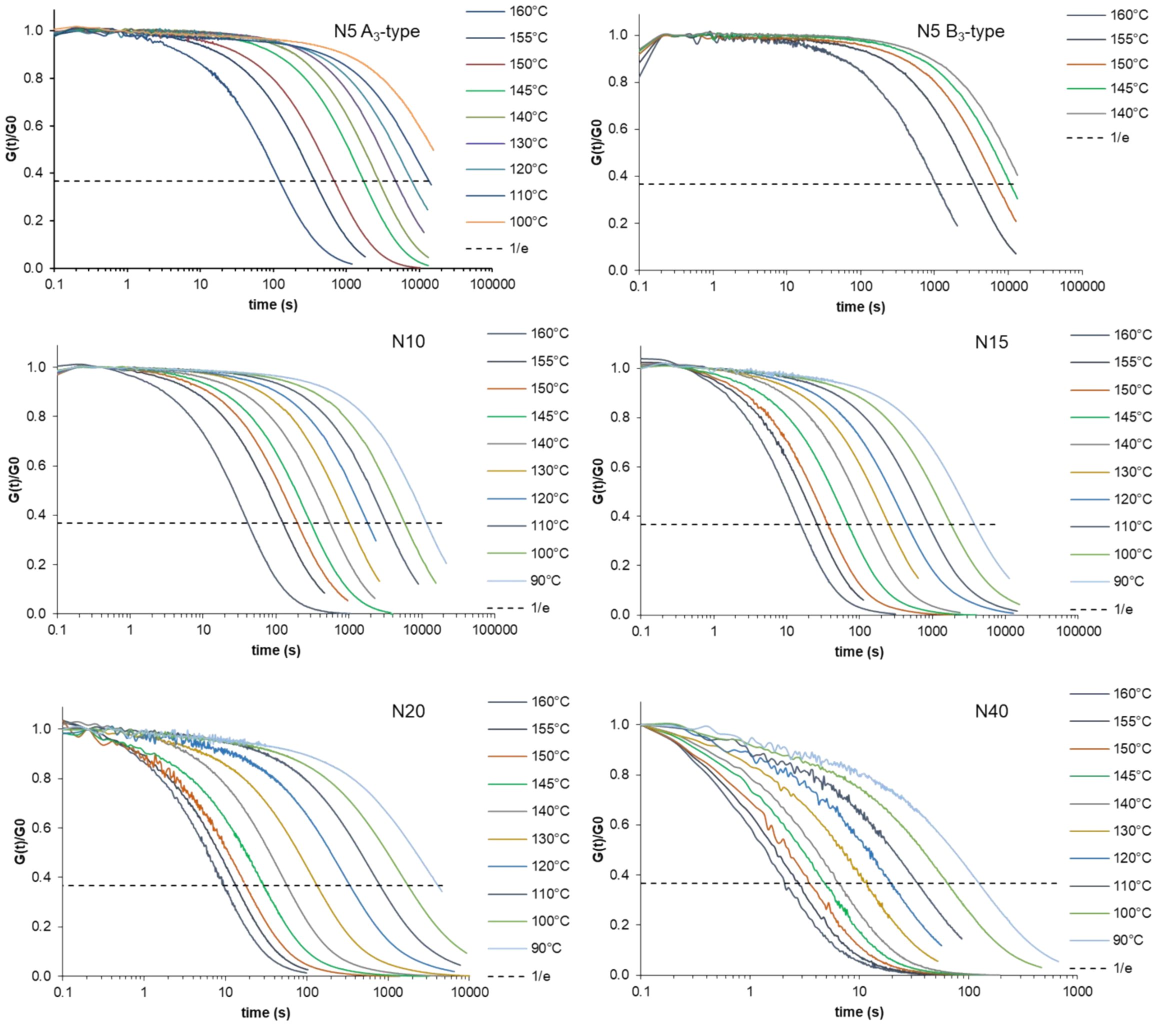


Figure S 11. Stress relaxation graphs from which Arrhenius plots were created by taking the characteristic relaxation time, when the normalized material's stress has been relaxed until 1/e (dotted line). Displayed are the stress relaxation graphs obtained from N5 using A$_3$-type and B$_3$-type architectures (top) followed by the respective A$_3$-type architectures with 10, 15, 20 and 40 mol.% pending amines (N10 to N40, middle to bottom). N5 A$_3$-type measurement point at 100°C has been extrapolated via fitting to a Maxwell-model in order to obtain the characteristic relaxation time.

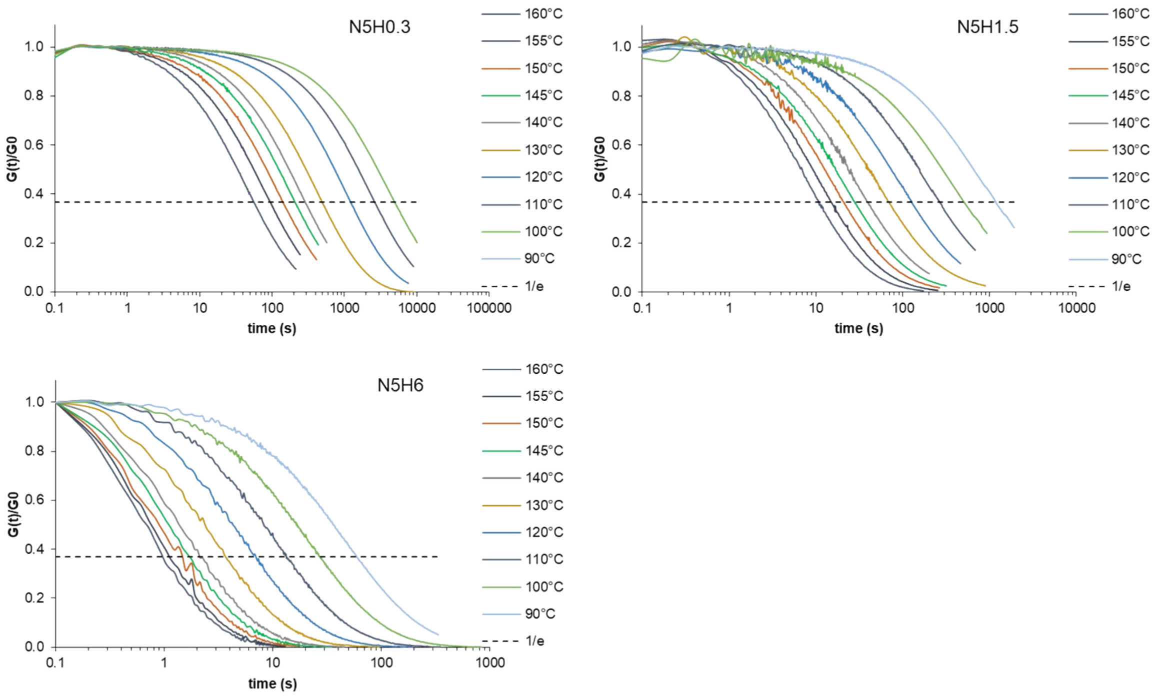


Figure S 12. Stress relaxation graphs from which Arrhenius plots were created (Figure 2 b), main manuscript) by taking the characteristic relaxation time, when the normalized material's stress has been relaxed until 1/e (dotted line). Displayed are the stress relaxation graphs obtained from increasing the amounts of pTsOH from 0.3 mol.%, 1.5 mol.% to 6 mol.% while maintaining 5 mol.% excess of primary amines (N5H0.3, N5H1.5, N5H6).

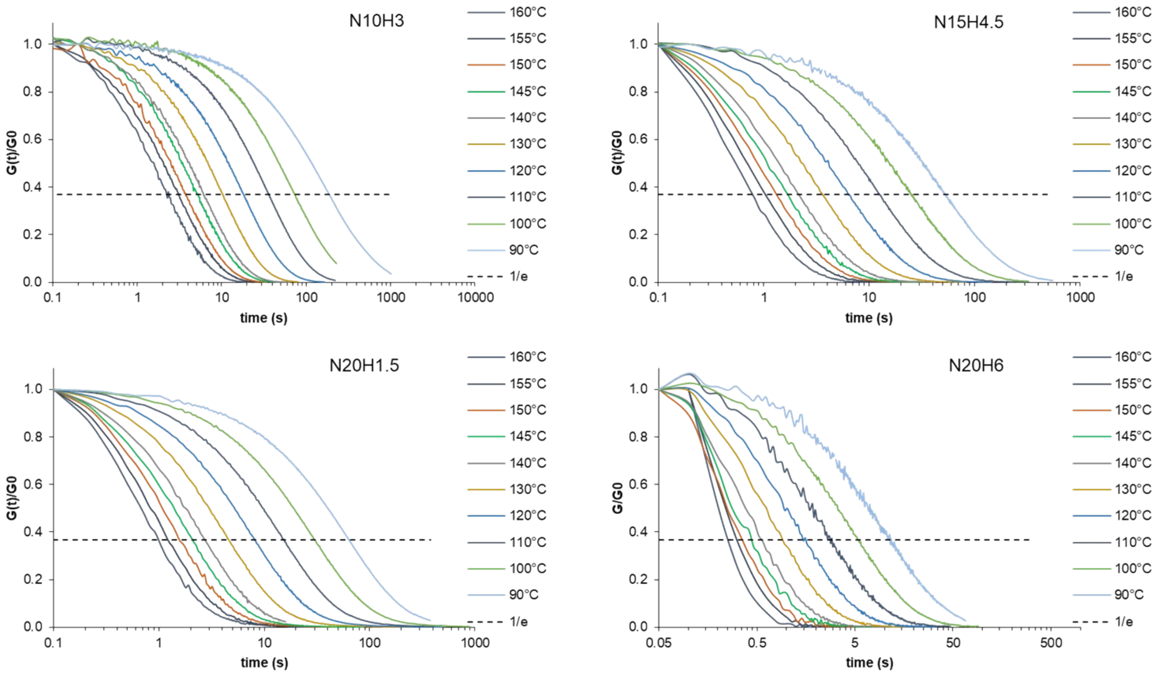


Figure S 13. Stress relaxation graphs from which Arrhenius plots were created (Figure 2 c), main manuscript) by taking the characteristic relaxation time, when the normalized material's stress has been relaxed until 1/e (dotted line). Displayed are the stress relaxation graphs obtained from increasing the amounts of pTsOH and excess of primary amines (N20H1.5, N10H3, N15H4.5, N20H6).

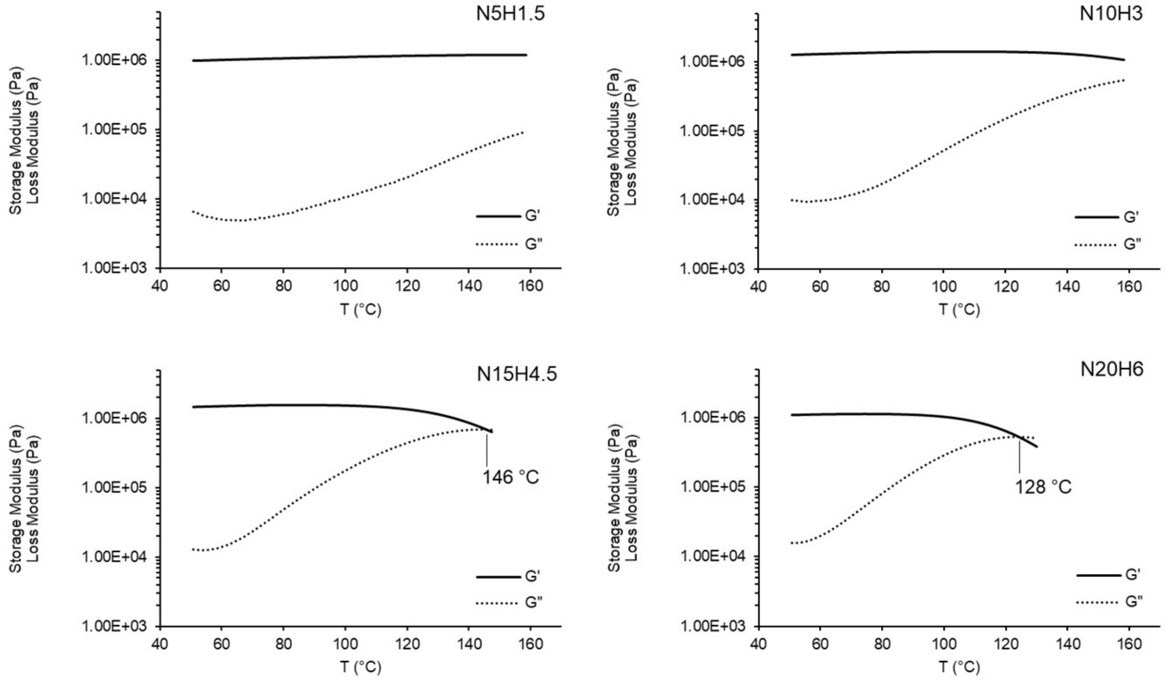
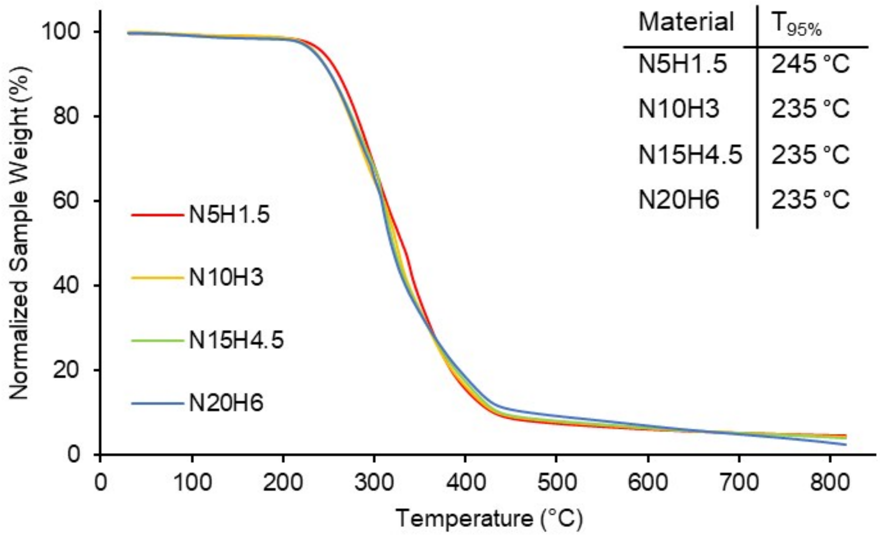


Figure S 14. Storage (G') and loss (G'') moduli monitored as a function of the temperature (heating (up), and cooling (down) at a rate of 5K.min^{-1} for various vitrimer materials. Increasing the exchange rate by adding an acid leads to tunable crossover points of G' and G'' around 146°C (N15H4.5 bottom) and 128°C (N20H6).



Material	$T_{95\%}$
N5H1.5	245 °C
N10H3	235 °C
N15H4.5	235 °C
N20H6	235 °C

Figure S 15. TGA thermogram (10K.min^{-1} in N_2) of vitrimers N5H1.5 (red), N10H3 (yellow), N15H4.5(green), N20H6 (blue) with an onset-temperature after 5% weight loss of 245°C to 235°C respectively.

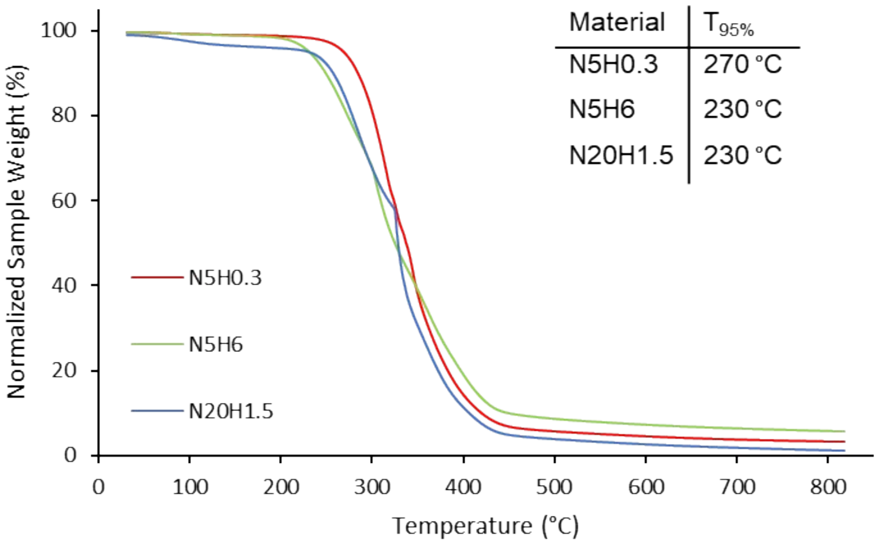


Figure S 16. TGA thermogram (10K.min^{-1} in N_2) of vitrimers N5H0.3 (red), N5H6 (green), N20H1.5 (blue), with an onset-temperature after 5% weight loss of 270°C to 230°C respectively. N20H1.5 shows at the beginning a small decrease, which is ascribed to H_2O.

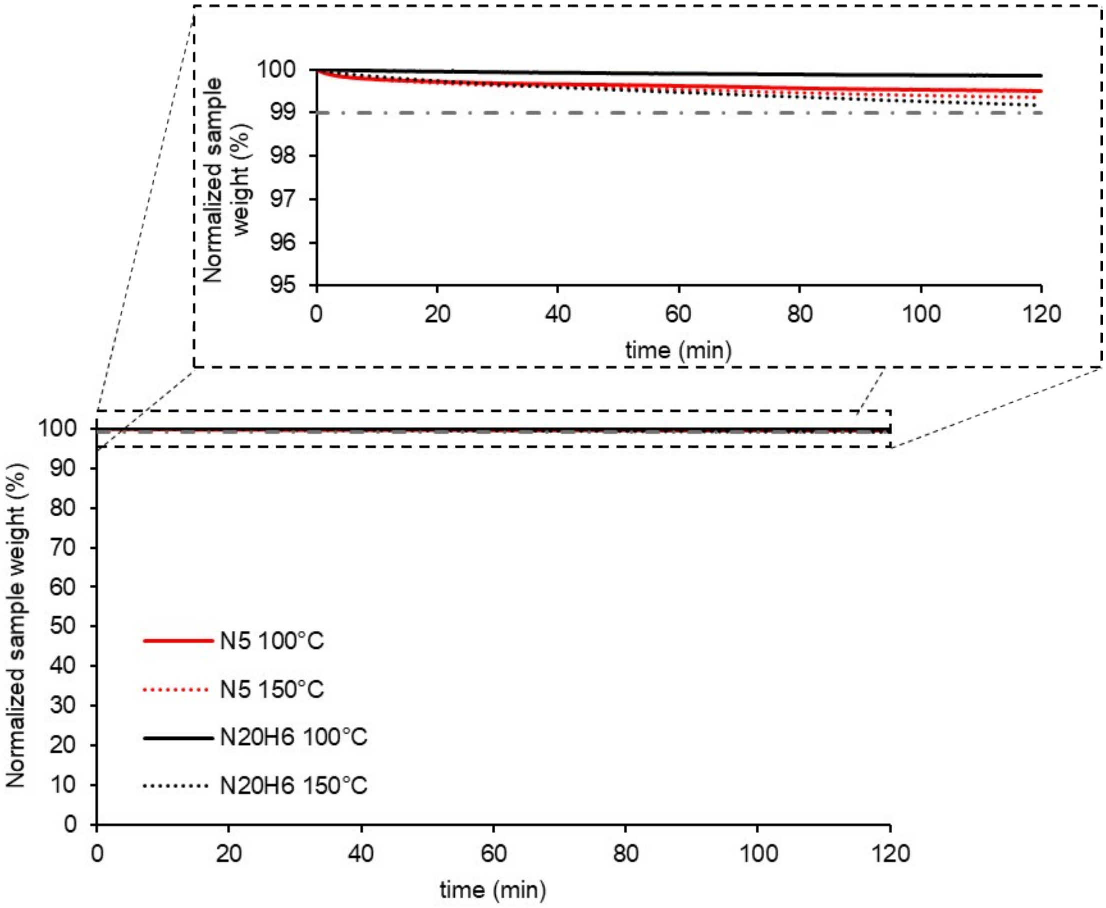


Figure S 17. Isothermal TGA thermogram of N5 and N20H6 in N_2 at 100 °C and 150 °C for 120 min shows minor mass losses, even at 150°C.

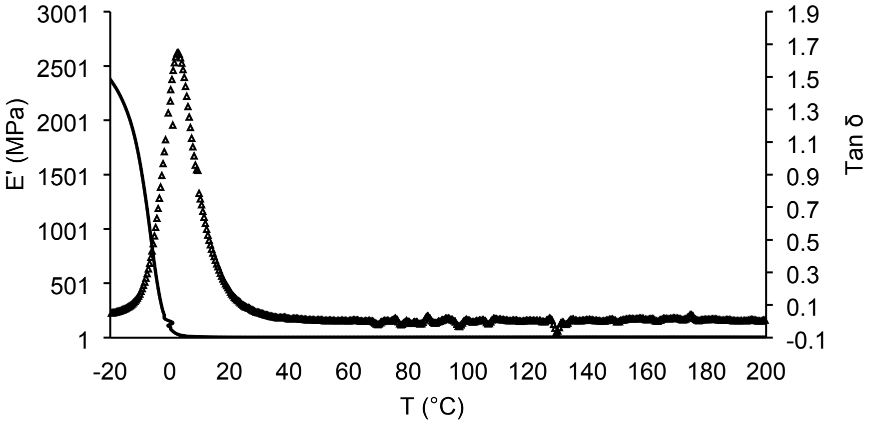


Figure S 18. DMTA measurement of vitrimer N5 in tension mode, showing Young storage modulus (E') as well as tanδ. The graph was obtained with a heating rate of 3 K.min^{-1}, a frequency of 1 Hz and a force amplitude of 1 N.

Crosslinking density $\rho_{crosslink}$ can be calculated from equation (4), using the modulus obtained from the rubbery plateau of the DMTA measurement at 298.15 K, and applying the universal gas constant R (8.314 J.K^{-1}mol^{-1}) to be for N5 610 mol.m^{3}, and 340 mol.m^{3} for vitrimer N20H6.

$$\rho_{crosslink} = \frac{E'}{3 * R * T} \quad (4)$$