Electronic Supplementary Material (ESI) for Polymer Chemistry.

Polydimethylsiloxane quenchable vitrimers

Tyler Stukenbroeker,[a] Wendi Wang,[a] Johan Winne,[b] Filip E. Du Prez,[b] Renaud Nicolaÿ*[a] and Ludwik Leibler*[a]

[a] Matière Molle et Chimie, École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI Paris)–CNRS, UMR-7167, Paris Sciences et Lettres (PSL) Research University, 10 rue Vauquelin, 75005 Paris, France.
[b] Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group and Laboratory for Organic Synthesis, Ghent University, Krijgslaan 281 S4-bis, B-9000 Ghent, Belgium.
Corresponding author emails: renaud.nicolay@espci.fr ; ludwik.leibler@espci.fr

Supporting Information

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1. Materials: 6–7%-(Aminopropylmethylsiloxane)-dimethylsiloxane copolymer, 1,800-2,200 cSt was purchased from GELEST and used without further purification. ^1H NMR analysis of the material showed 6.06% of the silicon centers were functionalized with propylamine groups (integration of $–CH_2$-N relative to CH_3-Si peak). 1-Butylamine was purchased from Alfa Aesar. *tert*-Butyl acetoacetate, cyclohexanedimethanol, methyl acetoacetate, and Poly(ethylene glycol) diacrylate were purchased from Sigma Aldrich. ^1H and ^{13}C NMR spectra were recorded at 297 K on a Bruker AVANCE 400 spectrometer at 400 and 100 MHz, respectively, and referenced to the residual solvent peaks (^1H, δ 7.26 for $CDCl_3$; ^{13}C, δ 77.16 for $CDCl_3$). ESI-HRMS experiments were carried out using a LTQ-Orbitrap XL from Thermo Scientific and operated in positive ionization mode.

2. Model experiment: *tert*-Butyl acetoacetate (5 mL), butyl amine (4.48 mL), 10 mL chloroform and anhydrous magnesium sulfate (1.52 g) were added in a bottom flask. The mixture was heated at 50 °C for 3 h under stirring and then cooled to ambient temperature. The mixture was filtered to remove water absorbed magnesium sulfate, eliminated solvent and redundant butyl amine by rotary evaporation under reduced pressure. Yellow liquid product was obtained with a yield of 84 % (compound **1**).[1] ^1H NMR (400 MHz, $CDCl_3$): δ ppm: 0.91 (t, 3H, CH_3), 1.36 (m, 2H, CH_2), 1.44 (S, 9H, $C(CH_3)_3$), 1.53 (m, 2H, CH_2), 1.86 (s, 3H), 3.16 (m, 2H, CH_2-N), 4.34 (s, 1H), 8.44 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm: 13.9, 19.4, 20.2, 28.8, 32.8, 42.9, 77.8, 83.5, 161.3, 170.9.

To demonstrate the capacity of incorporating vinylogous amide functions via exchange, we conducted transamidation reaction between the synthesized mono-functional vinylogous urethane (0.8435 g, 3.95 mM, 60 eq) and amine functionalized PDMS (3.2949 g, 0.066 mM). The reaction was conducted under stirring in THF for 5 h at 100 °C. After that, the THF was evaporated. NMR ^1H spectra indicated the *tert*-butyl acetoacetate groups were grafted onto PDMS chain (Figure S1).

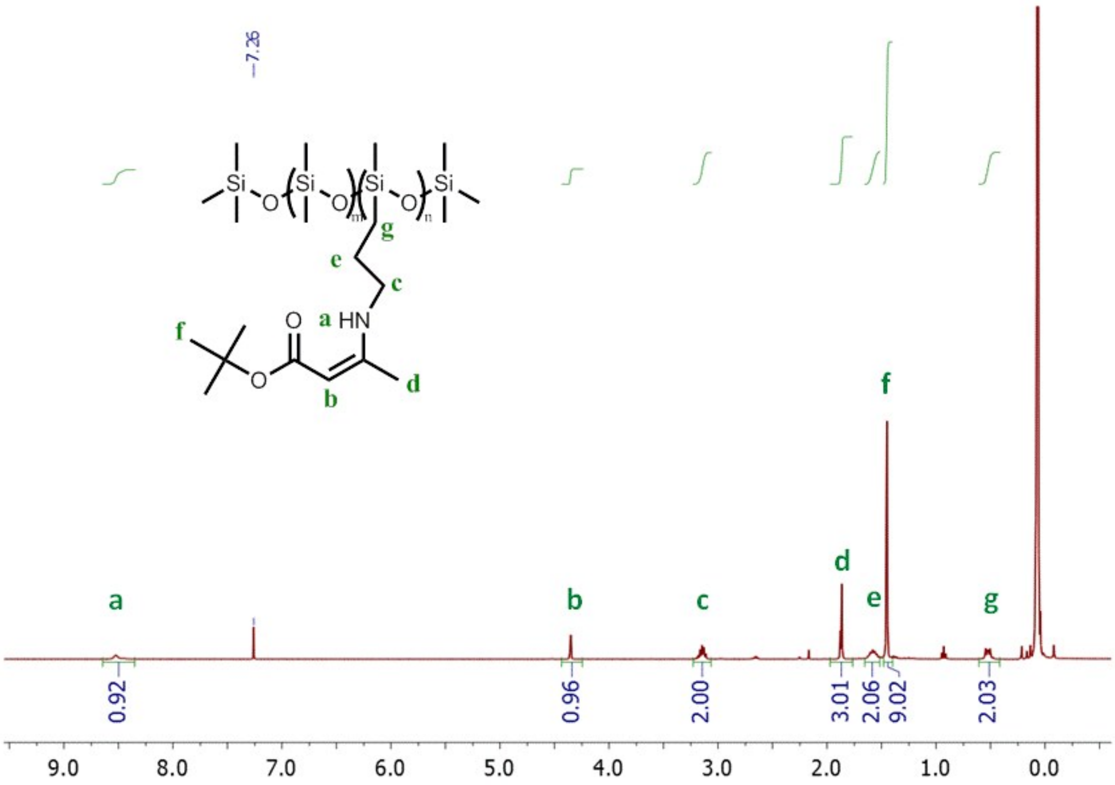
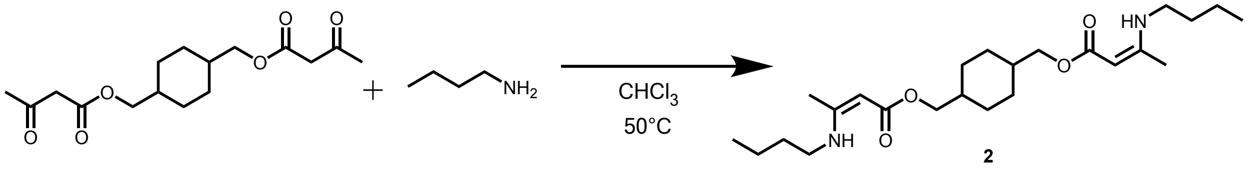


Figure S1. ^{1}H NMR spectrum of PDMS with pendant vinylogous urethane groups in $CDCl_3$

3. Synthesis of the bis-vinylogous urethane crosslinker 2: Cyclohexane dimethanol bis-acetoacetate was prepared as described in the literature.[2] 6 g of this compound (19.2 mmoles) and 5.7 mL butyl amine (57.6 mmoles) were dissolved in 50 mL of chloroform in a flask. Excess magnesium sulfate was added. The mixture was heated at 50 °C for 3 h under stirring and then cooled to ambient temperature. The mixture was gravity filtered to remove solids. Solvent and residual butyl amine were removed by rotary evaporation under reduced pressure. White powder product was obtained with a yield of 89% (compound **2**). ^{1}H NMR ($CDCl_3$): δ ppm: 0.92 (t, 6H, CH_3), 1.39 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 3.18 (m, 4H, CH_2-N), 3.83 (d, 4H, -CH2-O), 4.42 (s, 2H, CH(=C)-C), 8.54 (s, 2H, NH), 1.9 (s, 6H, CH_3-C(=C)-N), 1.8, 1.55, 0.98 (m, 10H, cyclohexane). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm: 13.9, 19.5, 20.1, 29.2, 32.6, 37.6, 42.8, 67.7, 81.8, 162.1, 170.9. HRMS (m/z): [M] calculated for $C_{24}H_{42}N_2NaO_4^+$: 445.3037; found: 445.3041.



Scheme S1. Synthesis of the bis-vinylogous urethane crosslinker **2**

4. Network synthesis: Different crosslink densities of network were synthesized. Generally, amine functionalized PDMS (**PDMS-NH$_2$**), 1/3/5/10 equivalents of synthesized crosslinker and approximately 30 vol. % THF (required to reduce viscosity and help disperse the crosslinker homogenously with PDMS) are stirred for 5 minutes and then poured into the desired mold such as glass petri dish. The mixture was heated to 100°C (caution: THF and butylamine fumes) where it gelled after approximately 2 h and was removed after 16 h. The resulting network was clear and odorless.

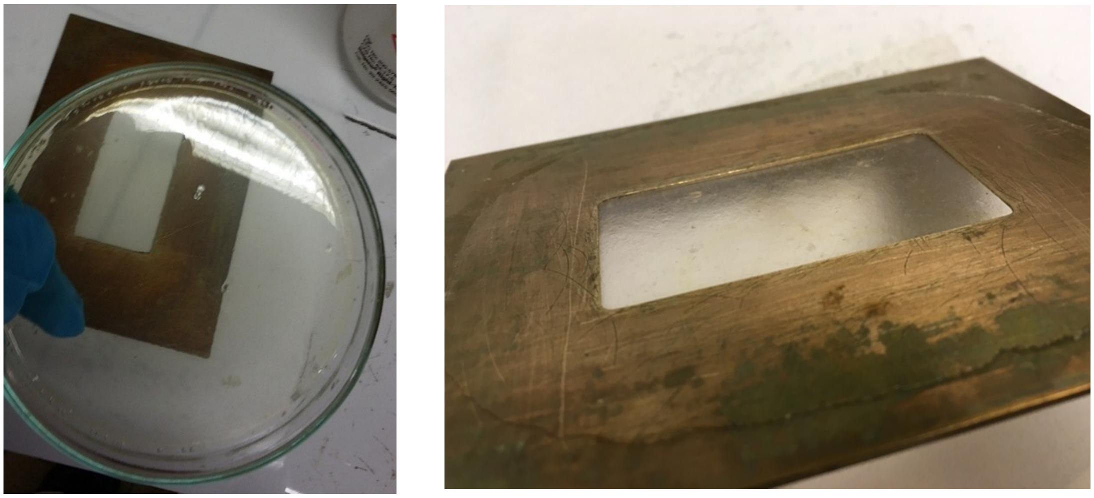


Figure S2. Photograph of 5 eq. network material after solution casting (left) and after subsequent remolding in Carver heated press for 1 h at 100°C with 3 tons of pressure (right) to a thickness of approximately 1.8 mm.

A permanent non-dynamic network was synthesized in an analogous manner using bisacrylate-PEG **3** in place of the bis-vinylogous urethane crosslinker **2**. Figure S2 shows the material obtained after pressing the network containing 5 eq. of bisacrylate-PEG crosslinker **3** in heated press for 1 h at 100°C with 3 tons of pressure. The resulting material is brittle and full of fractures.

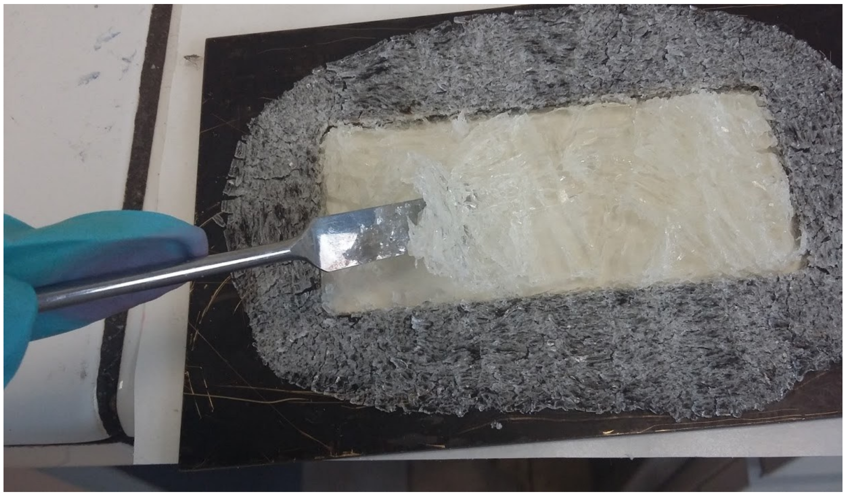


Figure S3. Photograph of the material obtained after pressing the network containing 5 eq. of bisacrylate-PEG crosslinker **3** in heated press for 1 h at 100°C with 3 tons of pressure. The resulting material is brittle and full of fractures.

5. FT-IR. Spectra of the cured material were acquired with Bruker Tensor 37 with Specac ATR. Samples were cut to reveal fresh surface, then pressed against ATR apparatus. Here, the vinylogous portion of the spectra is highlighted for the 3 and 5 eq. vitrimers plus the non-dynamic network formed with 5 eq. of bisacrylate-PEG crosslinker **3**.

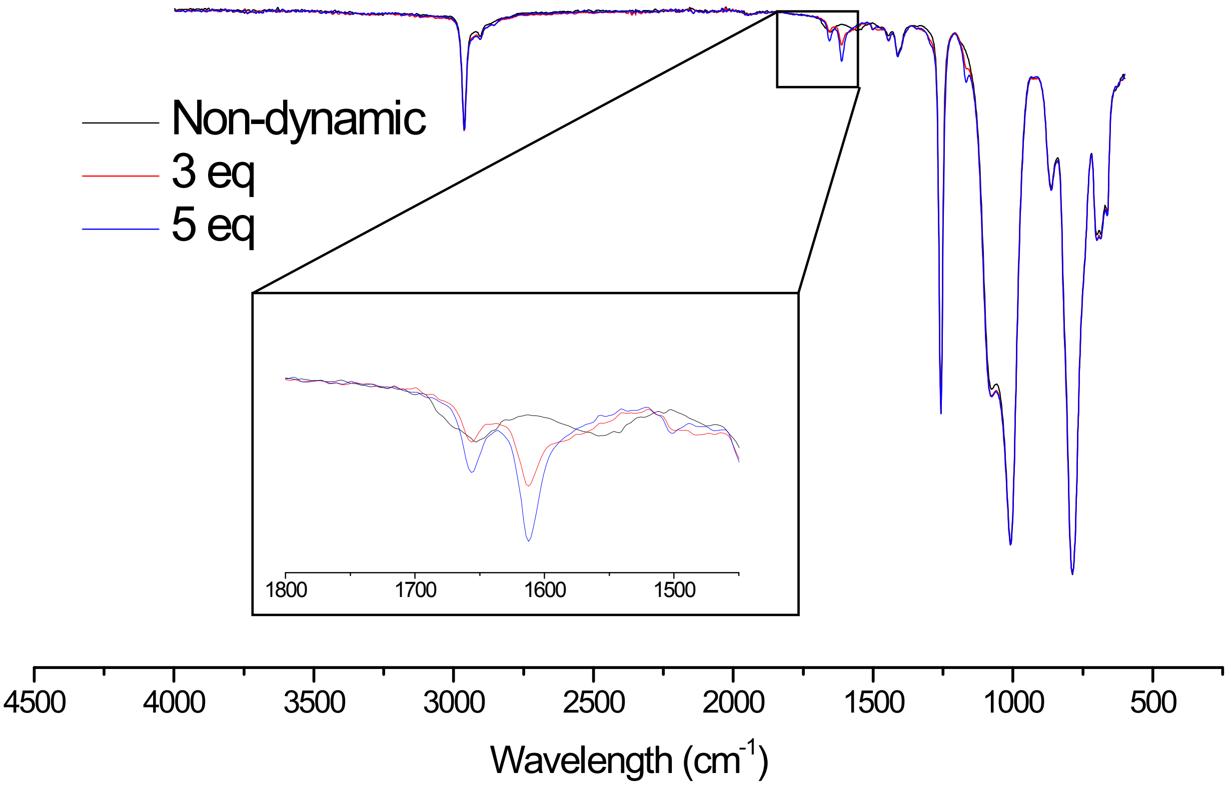


Figure S4. FT-IR spectra of the cured materials obtained from the non-dynamic network and the 3 and 5 eq. vitrimers.

6. Rheology experiments. Measurements were performed with an ARES G2 rheometer. 25 mm diameter circular samples were punched out of the pressed sheets of network and mounted on parallel plate geometry. Temperature was controlled via Peltier plate. Standard stress relaxation (SR) test was comprised of equilibration at 100°C for 1 h followed by the rapid (< 0.03s) application of 2% rotational strain. Data was collected at logarithmic intervals. Normal force of 1 N (compression) maintained throughout experiment resulted in some compression, however this never accounted for more than 2% of initial height.

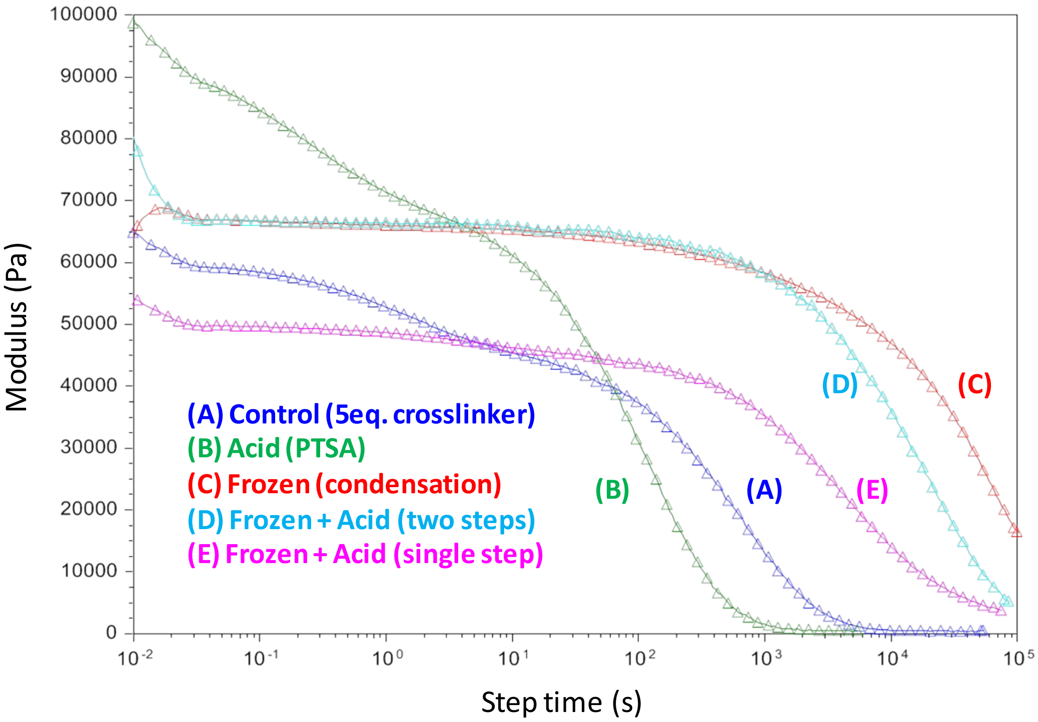


Figure S5. Non-normalized SR curves (2% strain) of the 5eq network and subsequent freezing experiments. See figure 3 in the text for normalized comparison.

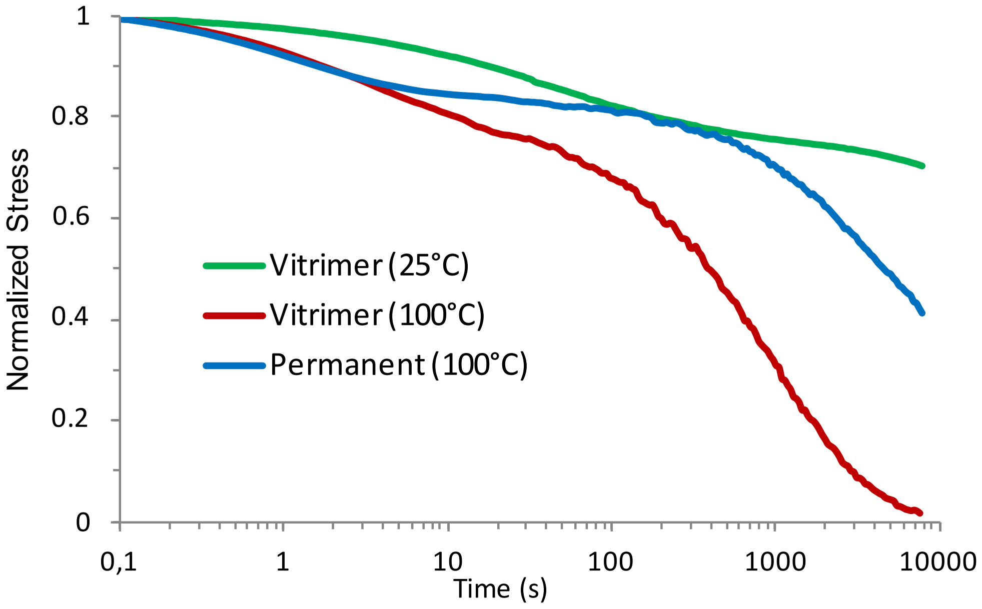


Figure S6. Normalized SR curves (2% strain) of the 5eq network at room temperature and elevated temperature, along with a comparison to permanent network formed with a bis-acrylate crosslinker.

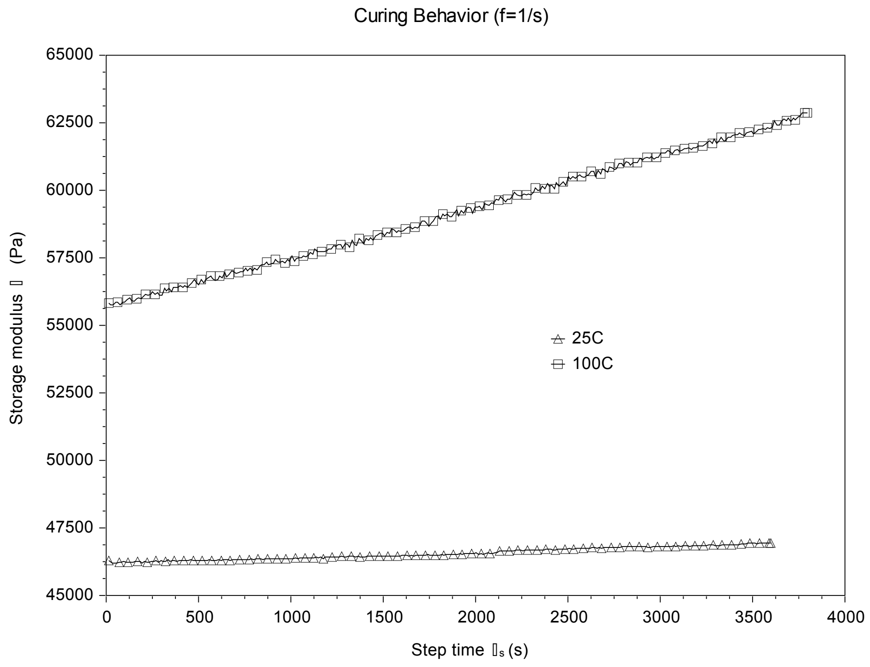


Figure S7. Oscillatory rheometry (f=1 rad/sec, strain=2%) performed at two temperatures shows modulus increase during experiments.

7. Thermal Analysis. Differential scanning calorimetry (DSC) analyses were performed with a TA instruments Q1000 at a heating rate of 10 °C/min. The vitrimers containing 3eq (top) and 5eq (bottom) of crosslinker **2** have glass transition temperatures near the T_g of pure PDMS ($T_g \approx$ -125°C).

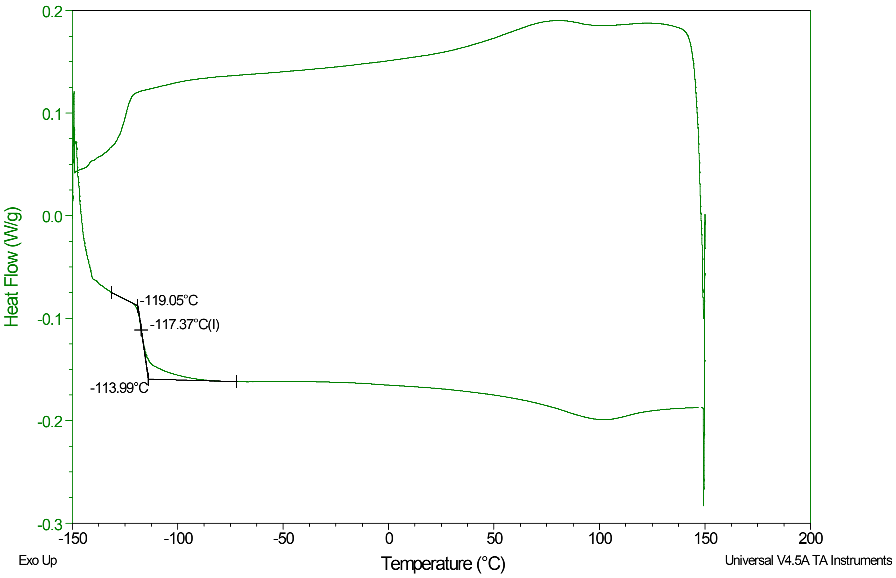


Figure S8. DSC analysis of the vitrimer network prepared with 3 eq. / polymer chain of bis-vinylogous urethane crosslinker **2** at a heating rate of 10 °C/min.

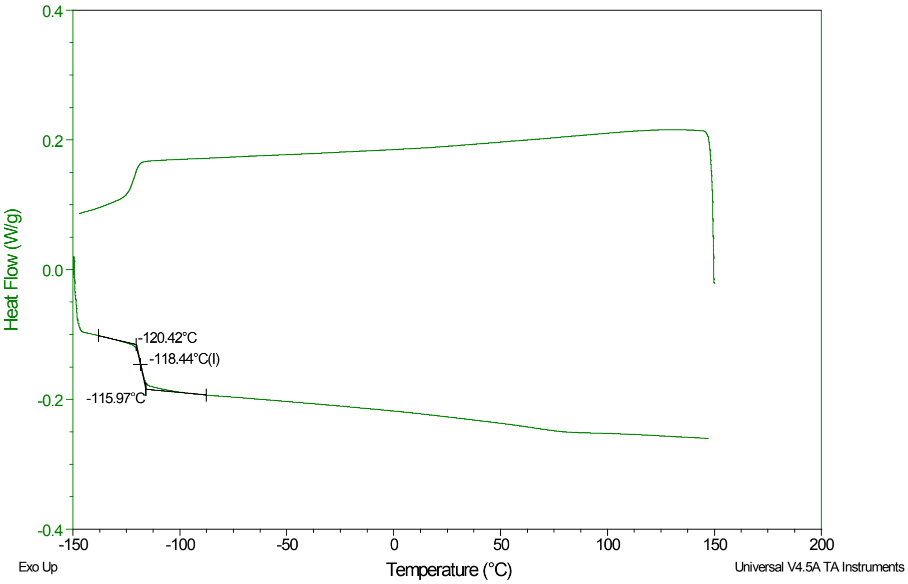


Figure S9. DSC analysis of the vitrimer network prepared with 5 eq. / polymer chain of bis-vinylogous urethane crosslinker **2** at a heating rate of 10 °C/min.

8. Compression creep. Samples for compression experiments were constructed by scraping the newly formed networks from the mold and compressing inside of 20 mL syringe (diameter 2 mm) at 75°C for two hours (pressure applied simply by using lab jack). Cylinders were then cut to heights 15-18 mm. Samples and instrumentation were equilibrated at experiment temperature for 1 hr. Compression of 16.4 N was applied with Instron apparatus for 1 hr and displacement was monitored. Following test, sample height was measured at 5 minute intervals for 20 minutes (test temperature maintained). See figure 2 in the main text for photographs of samples.

9. Tensile experiments. Young's modulus of the 3eq and 5eq materials was measured by preparing a pressed sheet of material in the same manner as the rheology sample preparation. The sample sheets were then cut into the "dumbbell" shape of 10 mm × 2 mm with a thickness of approximately 2 mm. These were mounted on Instron 5564 and elongated 10mm/min until failure. This was repeated with five samples and the average moduli and strain at break were computed. Shown below is the raw data for the 5eq network.

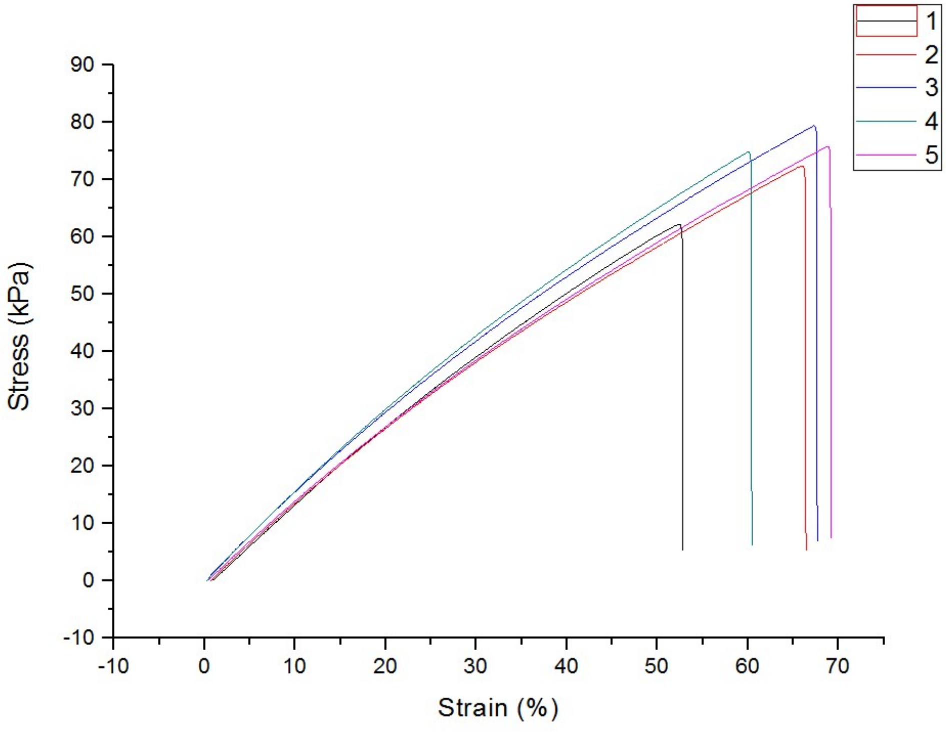


Figure S10. Tensile test (with a crosshead speed of 10mm/min) of the vitrimer network prepared with 5 eq. / polymer chain of bis-vinylogous urethane crosslinker **2**. "Dumbbell" shape specimen of 10 mm × 2 mm with a thickness of approximately 2 mm.

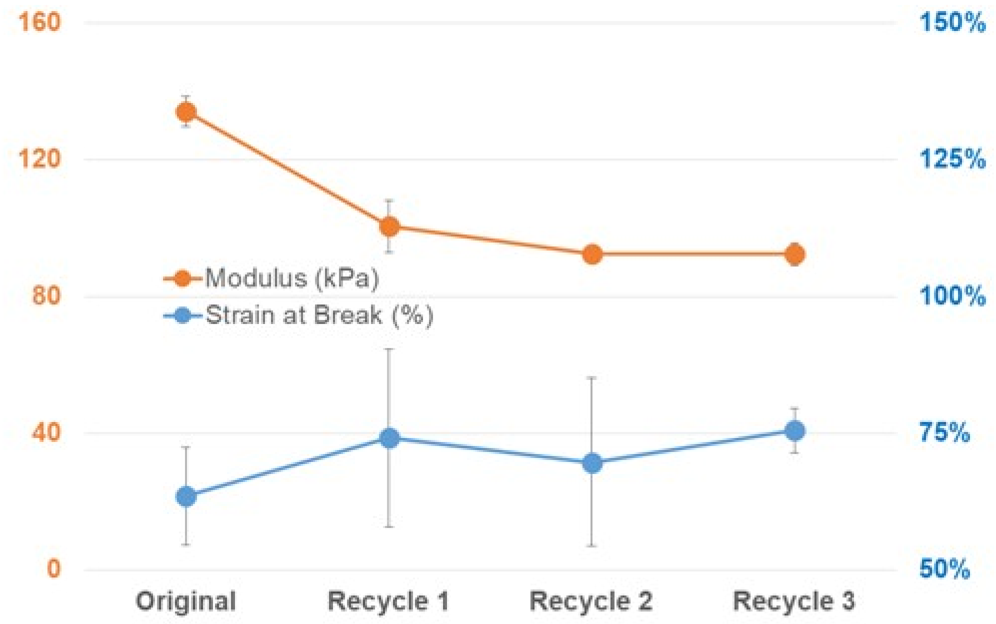


Figure S11. Evolution of the mechanical properties over three remolding cycles of a vitrimer network prepared with 5 eq. / polymer chain of bis-vinylogous urethane crosslinker **2**. Same test parameters as Fig. S10.

10. Solubility and dissolution. The soluble fraction of the networks was measured by submerging a piece of the sample (100-200 mg) in 20 mL of anhydrous THF (a good solvent). This was left on a shaker table for 24 hr and the samples were carefully removed and heated to dryness at 100°C. Soluble fraction = 1-(dry mass/initial mass). Data shown in Table 1 in the text.

To dissolve samples via amine-induced degradation, a sample of the network (100-200 mg) was placed in a round-bottom flask equipped with reflux condenser. 10 mL of 1-butylamine was added and heated until lightly refluxing. After 16 h the products were analyzed by passing the reaction mixture through a paper filter.

11. Condensation procedure. Formed networks were immersed in a bath of 50% (v/v) methylacetoacetate in THF and left at RT for 16 h. They were then rinsed with acetone and dried in vacuum chamber at 50°C for 3h. The resulting material was visually similar to the starting network.

12. One-pot procedure. Network prepared using the crosslinker **2** containing 0.8 wt. % anhydrous *p*-toluenesulfonic acid (1 mol % relative to vinylogous urethane linkages). Formulation ratio was 1 g PDMS-NH2:0.55 mL THF:0.11 mL methylacetoacetate:42 mg acidified crosslinker. Cure procedure was as normal.

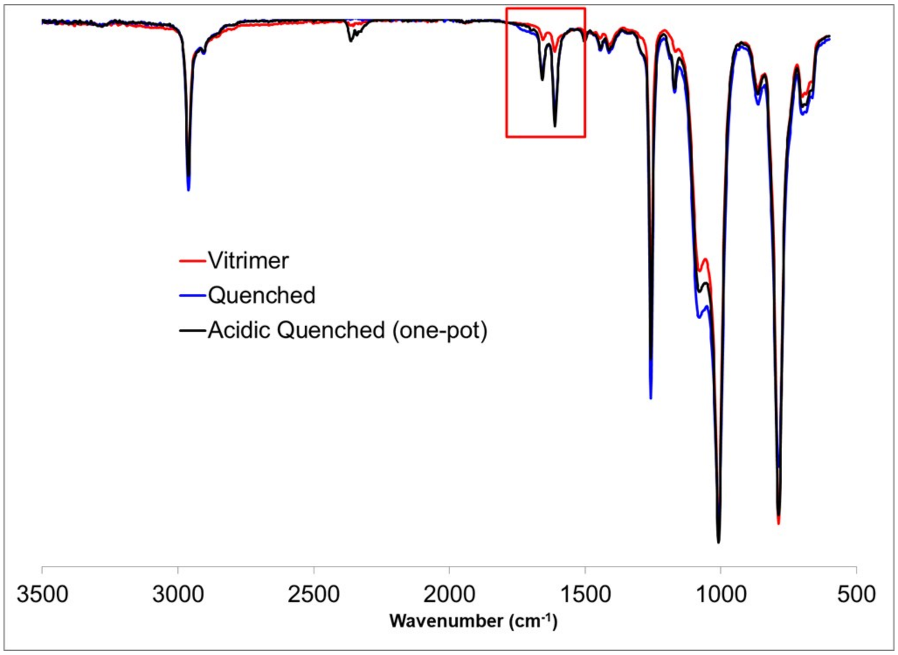


Figure S12. FT-IR spectra of the vitrimer network, the network obtained via the condensation procedure and the network obtained via the one-pot procedure.

13. References

1. H. Hebbache, Z. Hank, S. Boutamine, M. h. Meklati, C. Bruneau and J.-L. Renaud, *C. R. Chim.*, 2008, **11**, 612-619.
2. W. Denissen, G. Rivero, R. Nicolay, L. Leibler, J. M. Winne and F. E. Du Prez, *Adv. Funct. Mater.*, 2015, **25**, 2451-2457.