Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information:

β-Amino Amide Based Covalent Adaptable Networks with High Dimensional Stability

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Materials

All materials i.e. *N*-Methylbutylamine (98%, Sigma-Aldrich), *N*-isopropylacrylamide (>99%, TCI Chemicals Europe), 2-ethyl-1-hexylamine (98%, Sigma-Aldrich), 1,3-cyclohexanebis(methylamine) (98%, Sigma-Aldrich), 2-ethyl-1-hexylamine (98%, Sigma-Aldrich), methyl acrylate (>99%, TCI Chemicals Europe), acryloyl chloride (96%, stabilized with phenothiazine, ABCR), triethylamine (>99%, Sigma-Aldrich), aminopropyl-terminated polydimethylsiloxanes, DMS A11 (Gelest Inc), methanol (MeOH, >99.8%, Fisher Chemical), tetrahydrofuran (THF, >99.8%, Acros Organics), Jeffamine D400 kindly provided by Huntsman, Priamine 1074 and Pripol 1033, kindly provided by Croda, were used without further purification unless stated otherwise.

Instruments & experiments

*Nuclear magnetic resonance (NMR) s*pectra were recorded on a Bruker Advance Ultrashield 300 MHz spectrometer. Deuterated chloroform ($CDCl_3$) or deuterated DMSO-d_6 was used as solvent. Chemical shifts are given in parts per million (ppm).

*Online infrared (IR) spectroscopy. Were r*ecorded using a MettlerToledo ReactIR 702L with TE MCT detector (Thermoelectrically Cooled Mercury Cadmium Telluride detector). The probe interface was an AgX 6 mm × 1.5 m Fiber (Silver Halide) with a DiComp (Diamond) probe tip. The recorded wavelength range was between 4500 cm^{-1} to 600 cm^{-1}.

Attenuated total reflection Fourier transform infrared spectroscopy (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 air atmosphere at a heating rate of 10 $K \cdot min^{-1}$ from 25 to 800 °C for the dynamic mode or at 200 °C for 2 h for the isothermal measurement.

Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under air atmosphere at a heating rate of 10 $K \cdot min^{-1}$ from −100 to 100 °C.

Rheology experiments were performed on an Anton Paar MCR 302. The experiments were performed in parallel plate geometry using 8 mm sample disks. *Amplitude sweep* experiments were performed using a frequency of 1 Hz, a constant force of 1 N, and a variable shear strain that was

ramped up logarithmically from 0.01% to 10% to observe the linear viscoelastic region. *Stress-relaxation experiments* were performed at different temperatures (200 - 170 °C, with intervals of 10 °C) using a constant shear strain within the linear viscoelastic region of the samples, and a constant force of 1 N. The obtained characteristic relaxation time (τ*) was used to calculate the activation energy.

Creep experiments at different temperatures (50 - 110 °C, with intervals of 10 °C) were performed using a constant force of 1 N. Additionally, in the first 300 s, no shear stress was applied. Subsequently, a 2000 Pa shear stress was applied for 5000 s followed by a recovery period for 3600 s in which the shear strain was monitored. Creep measurements were preceded by a time sweep measurement at 90 °C and a fixed frequency of 1 Hz for 1 h to remove possible thermal history.

A time sweep experiment was performed in parallel plate geometry using 8 mm sample disk with an applied strain of 1% and a frequency of 1 Hz for a duration of 30 min at different temperatures. Storage modulus (G') and loss modulus (G") were recorded over time.

(Re)processability was investigated by cutting the cross-linked material into pieces of about 1 cm, which were then placed into a rectangular mold for compression molding. This assembly was placed in a preheated compression press (180 °C) for 1 min under 0.5 metric tons of pressure. Then the pressure was increased to 3 tons and kept constant for an additional 60 min. After 60 min of pressing, the sample was carefully removed from the mold.

Solubility tests were carried out in vials with samples of 2 mm in diameter, 2 mm in thickness, and a weight of around 15-20 mg, to which 40 mL of THF was added. Those tests were performed for 24 h at 25 °C in THF. The solvent was then removed, and the samples were dried under vacuum overnight at 60 °C. The soluble fraction and swelling ratio were calculated using equation 1 and equation 2, respectively.

$$\text{soluble fraction (\%)} = \frac{m_i - m_d}{m_i} \ (eq.\ 1)$$

$$\text{swelling ratio (\%)} = \frac{m_s - m_i}{m_i} \ (eq. 2)$$

with m_i, m_s, and m_d representing the mass of initial, swollen, and dry samples, respectively.

Hydrolysis tests were conducted by introducing samples of around 20 mg into 20 mL of demineralized water or 1 M HCl or 1 M NaOH solution. A hydrolysis test at elevated temperatures was performed by placing a piece of sample (approximately 70 mg) in a glass vial with 10 mL of demineralized water, which was closed with a silicone septum. Thereafter, the vial was placed in a heated oil bath at 110 °C for the hydrolysis test in boiling water. For all the above-mentioned tests, solvent was removed after the experiment and the samples were dried under vacuum for 24 h at 100 °C until complete dryness. The soluble fraction and swelling ratio were calculated as using equation 1 and equation 2, respectively.

Uniaxial tensile experiments were performed on a Tinius-Olsen H10KT tensile tester, equipped with a 100 N load cell and at a speed of 4 mm/min and a pre-load of 0.02 N. An average of 3 flat dog bone type specimens with an effective gage length of 13 mm, a width of 2 mm and a thickness of around 1-2 mm were used for the tensile tests. The samples were cut out using a Ray-Ran dog bone cutter.

Synthesis of model compound 3-(butyl(methyl)amino)-*N*-isopropylpropanamide (1)*:***

N-isoproprylacrylamide (1 eq.) and *N*-methyl butylamine (1.2 eq.) were mixed and heated at 75°C for 24 h. The residual *N*-methyl butylamine was removed under vacuum resulting in a transparent oil (~ quantitative yield). ^{1}H-NMR spectra (300 MHz, DMSO-d_6) is given in ***Figure S1***. δ ppm 7.77 (d, 1H), 3.81 (m, 1H), 2.50 (m, 2H), 2.26 (t, J = 6 Hz, 2H), 2.15 (t, J = 6 Hz, 2H), 2.11 (s, 3H), 1.45 – 1.17 (m, 4H), 1.03 (d, J =6.6 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H).

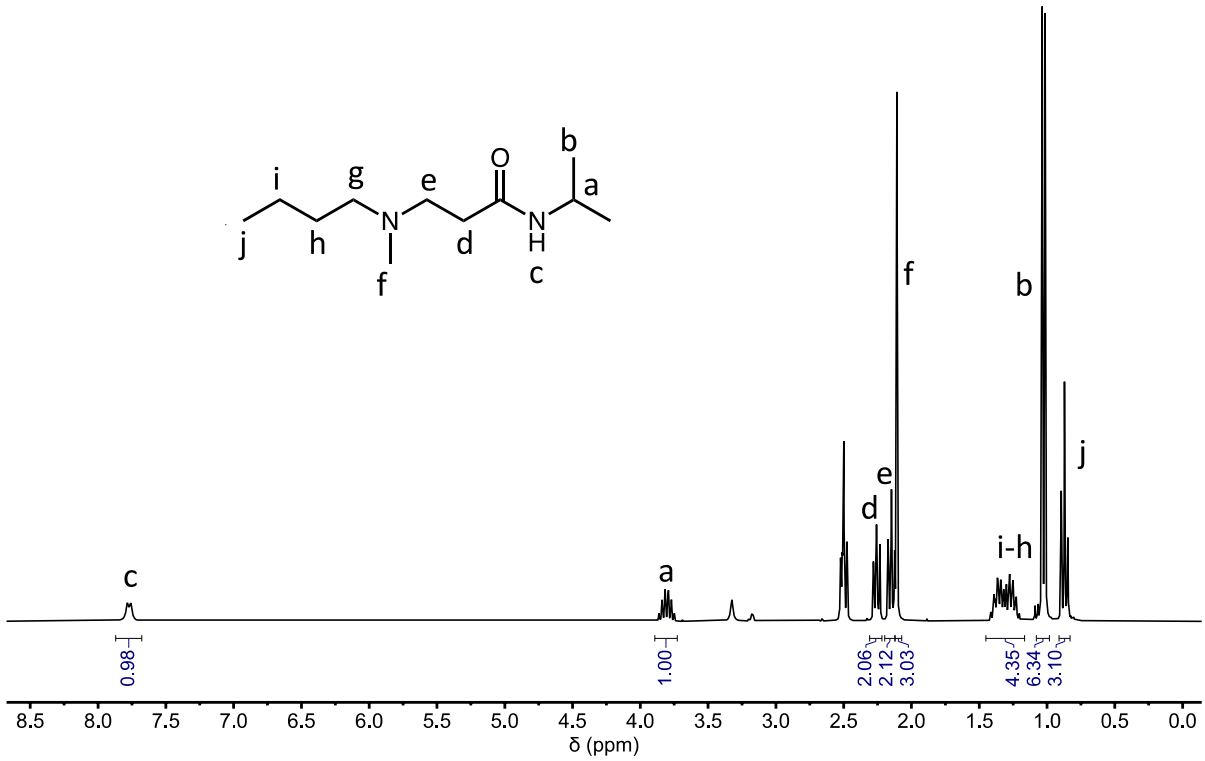


Figure S1. *^{1}H-NMR spectrum in DMSO-d_6 of model compound **1**.*

Synthesis of model compound *N*-(2-ethylhexyl)-3-((2-ethylhexyl)amino)propanamide (2)*: Methyl acrylate (1g, 1 eq.) and 2-ethyl hexylamine (4.5 g, 3 eq.) were mixed in a three necked round bottom flask equipped with a probe for online ATR-IR. The reaction was carried out at 50 °C until total consumption of methyl acrylate was observed by intensity decreasing of the relative C=C stretching band at 989 cm^{-1} (^{1}H NMR is reported in **Figure S2**). The temperature was then increased to 100 °C for 32 h for the amidation reaction. *β*-amino amide formation was assessed by following the diminishing of the ester carbonyl C=O stretching at 1740 cm^{-1} against the increase of the amide carbonyl C=O band at 1666 cm^{-1}. The formation of amino amide **2** was also confirmed by ^{1}H NMR (**Figure S3**).

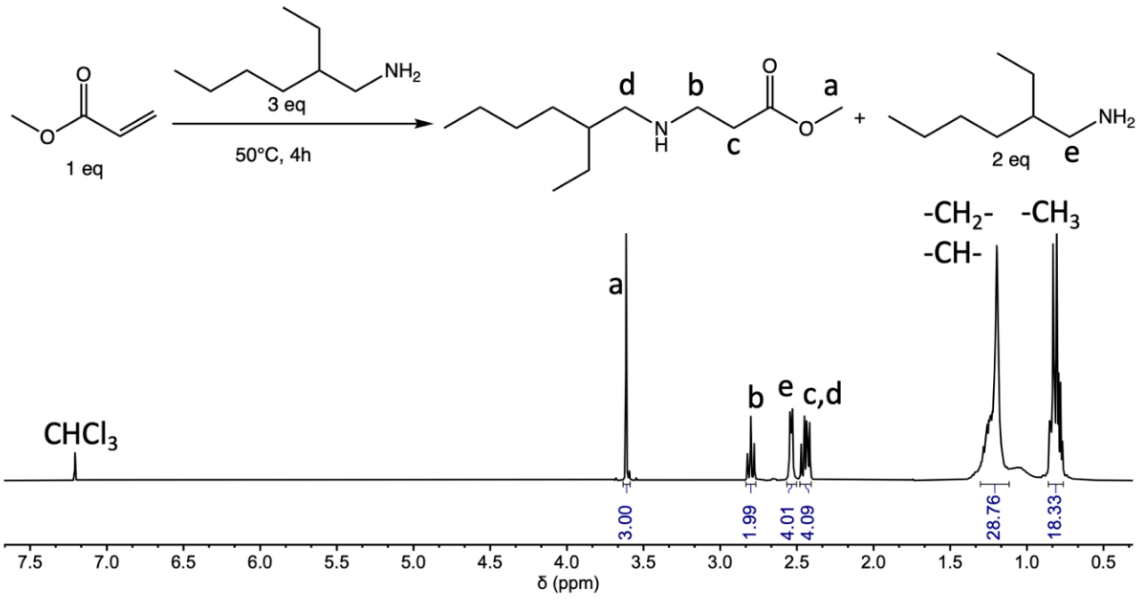


Figure S2*. [1]H-NMR spectrum in $CDCl_3$ of model study mixture after step 1 at 50 ˚C for 4 h which includes methyl 3-((2-ethylhexyl)amino)propanoate as Michael adduct and residual 2-ethyl-1-hexylamine (2 eq, confirmed by integral value of proton* ***e****).*

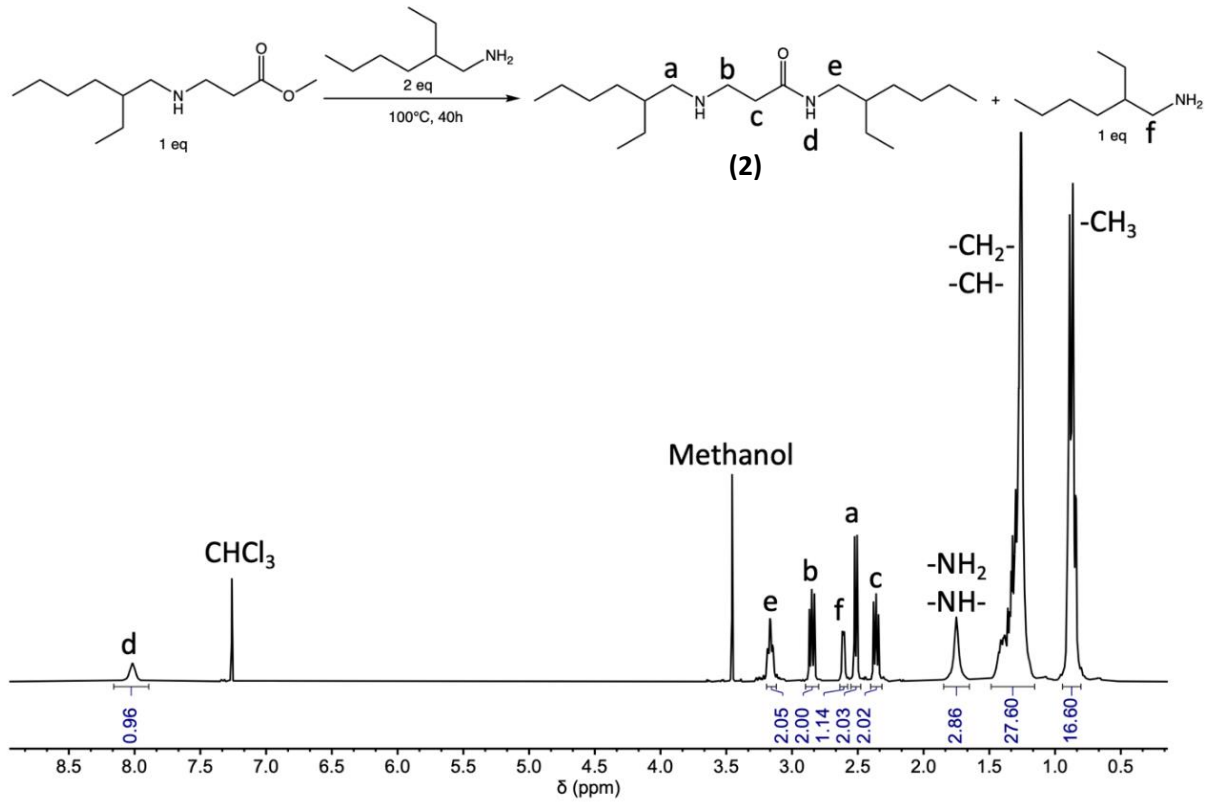


***Figure S3**. [1]H-NMR spectrum in $CDCl_3$ of model compound **2** after amidation step at 100 ˚C for 40 h, showing also 1 eq residual of 2-ethyl-1-hexylamine (see integral of proton **f**).*

Synthesis of tetra amino-ester crosslinker (I)*:* 1,3-Cyclohexanebis(methylamine) (5g, 1 eq.) was dissolved in 20 ml methanol. The solution was then cooled down in an ice batch followed by the dropwise addition of methyl acrylate (5 eq.). The reaction mixture was stirred for 1 h at room temperature, and then for 24 h at 65 °C. The solvent and residual methyl acrylate were removed under reduced pressure resulting in a pale-yellow oil (yield = 95%). [1]H-NMR spectrum (300 MHz, $CDCl_3$) is given in **Figure S4**. δ ppm 3.66 (s, 12H), 2.83-2.66 (m, 8H), 2.52 – 2.37 (m, 8H), 2.21 (d, 7.6 Hz, 4H), 1.84 – 1.11 (m, 8H), 0.75 – 0.24 (m, 2H).

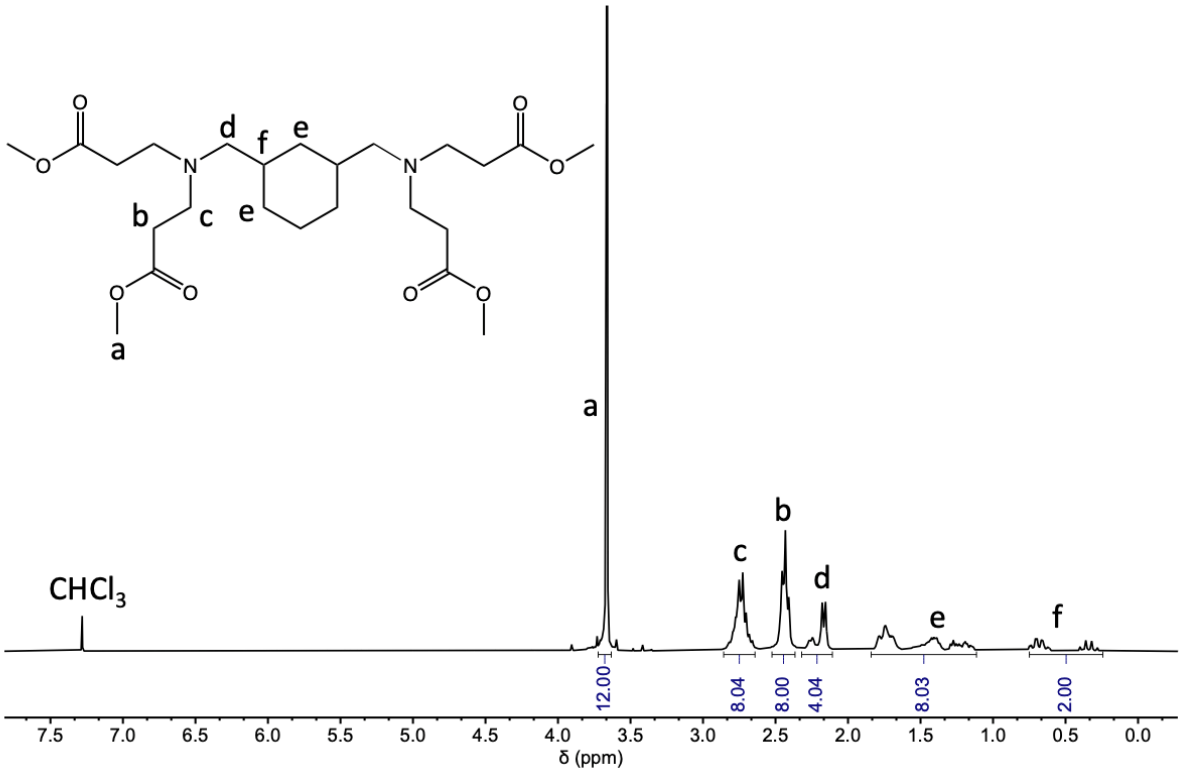


Figure S4. *^{1}H-NMR spectrum in $CDCl_3$ of 1,3-bis(aminomethyl)cyclohexane tetra(amino-ester) crosslinker.*

Synthesis of covalent adaptable amino-amide network (BAA)*:* 1 Eq. of tetra amino-ester crosslinker (I) and 2 eq. of commercially available diamine compounds were weighted and mixed in a glass vial using a magnetic stirrer. Subsequently, the amino-amide network formation via amidation was conducted at 100 °C for 24 h. Post-curing happened at 120 °C for 24 h under vacuum.

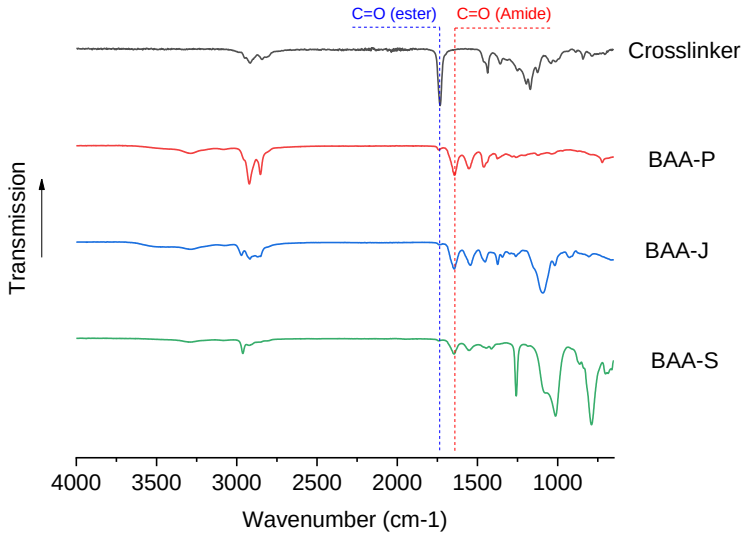


Figure S5. *ATR-FTIR of amino ester crosslinker (I) and resulting amino amide networks.*

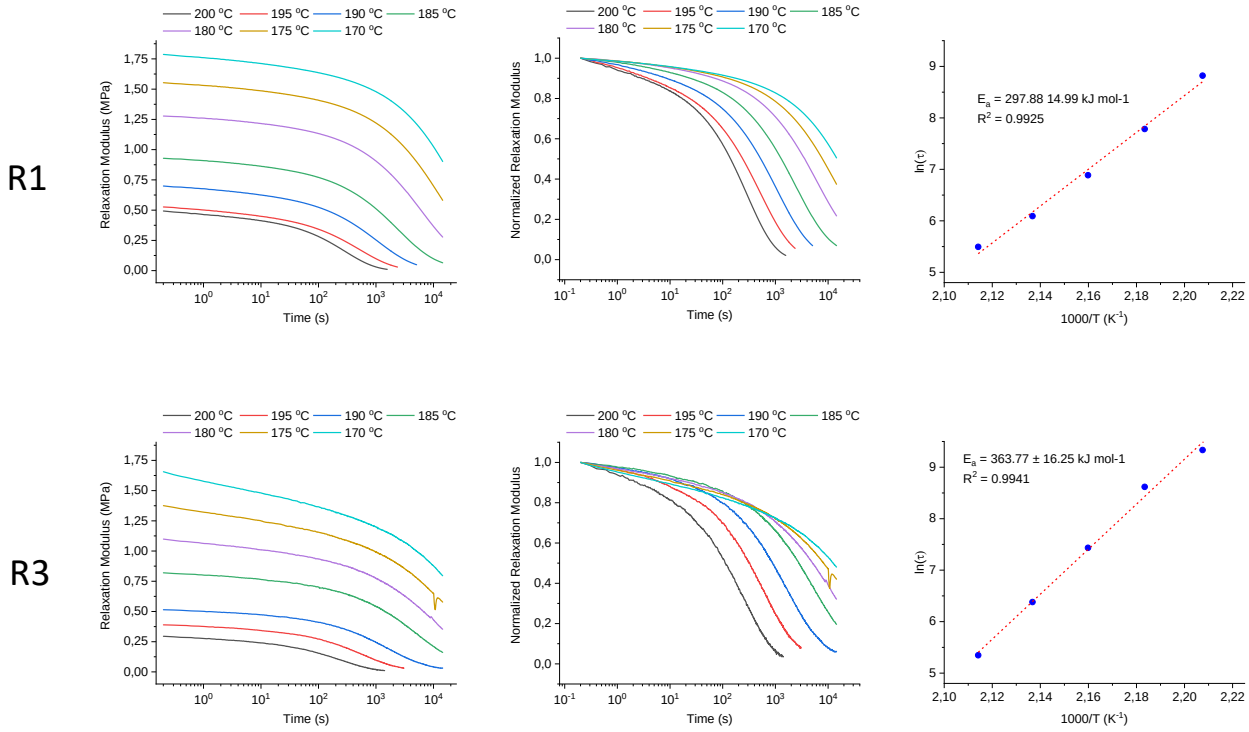


Figure S6. *From left to right are non-normalized, normalized stress relaxation cures and derived Arrhenius plots of BAA-P after the first (top) and the third (bottom) reprocessing cycle.*

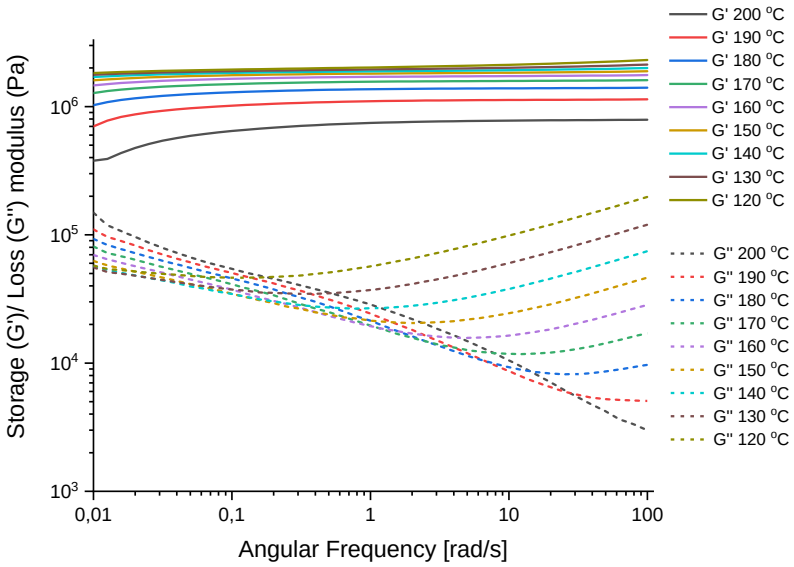


***Figure S7**. Frequency sweep measurements of BAA-P from 200 to 120 °C, indicating a decrease in elastic plateau modulus with temperature.*

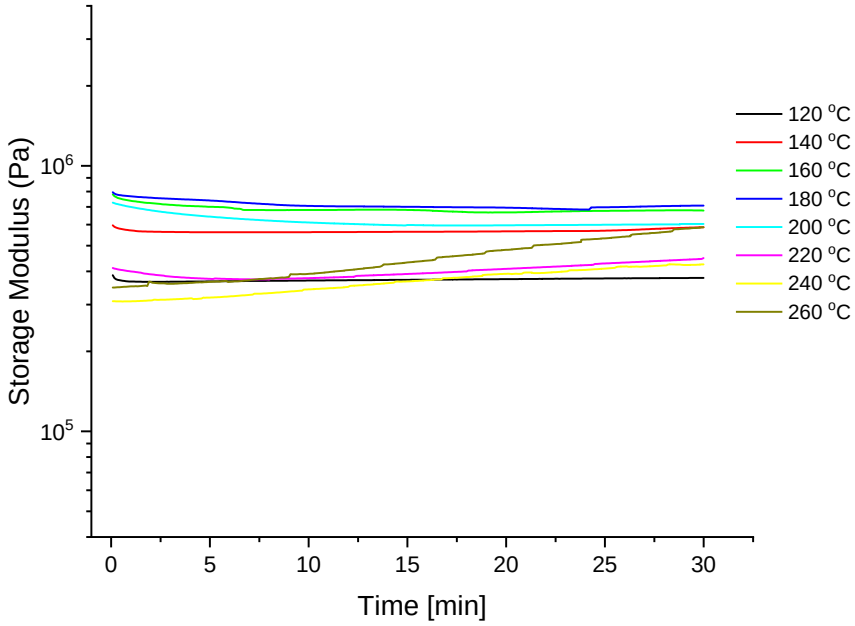


***Figure S8**. Time sweep experiments of BAA-P results indicating the increase in storage modulus beyond 200 °C.*

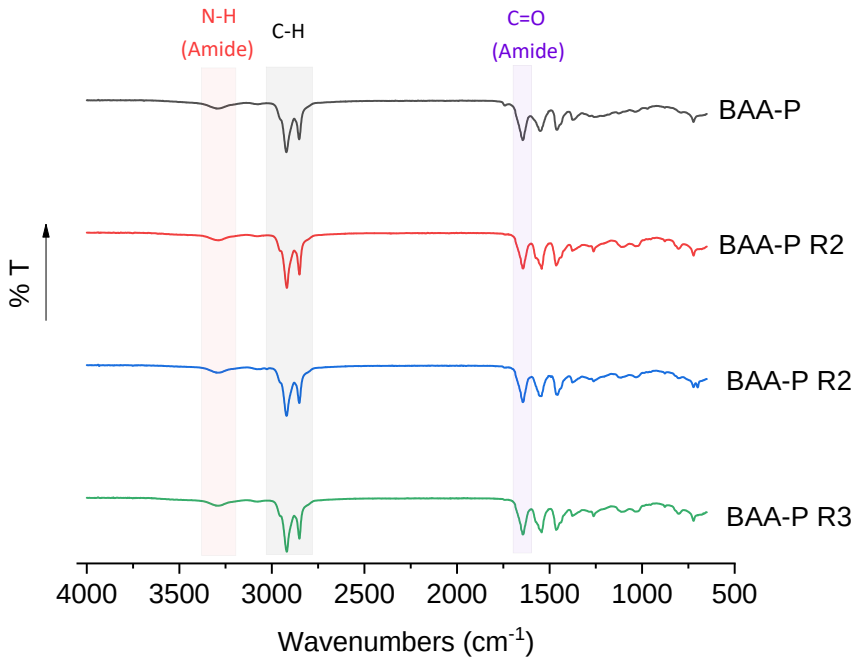
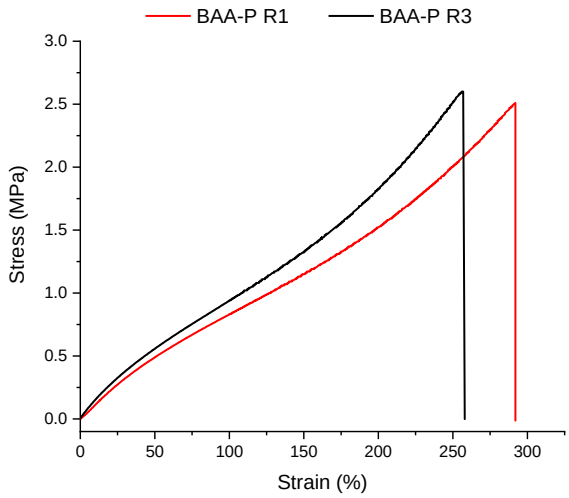
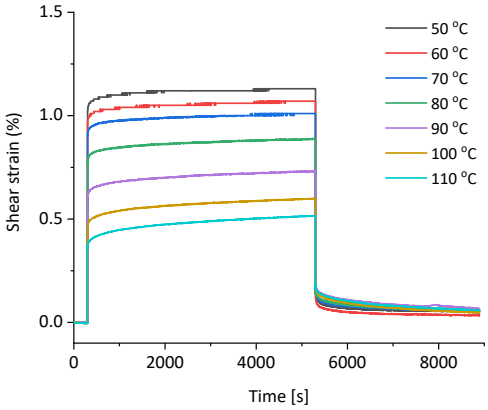


Figure S9. *IR spectrum of the initial BAA-P network and after 1 to 3 cycles of (re)compression molding (top to bottom).*



Sample	Ultimate stress (MPa)	Total elongation (%)	Modulus (MPa)
BAA-P R1	2.40 ± 0.45	279 ± 27	1.19 ± 0.16
BAA-P R3	2.62 ± 0.42	261 ± 21	1.41 ± 0.13

Figure S10. *Stress-strain curves (graph) and corresponding tensile test results (table) of BAA-P network after the first (BAA-P R1, red) and the third (BAA-P R3, black) remoulding cycle.*



Temperature (°C)	Creep rate ε ($\%.s^{-1}$)	Creep Compliance [1/Pa]	Remaining strain (%)
50	7,88E-19	5.66E-06	0,05
60	$1{,}08 \times 10^{-6}$	5.35E-06	0,03
70	$1{,}66 \times 10^{-6}$	5.05E-06	0,05
80	$4{,}90 \times 10^{-6}$	4.43E-06	0,05
90	$6{,}14 \times 10^{-6}$	3.65E-06	0,06
100	$8{,}52 \times 10^{-6}$	3.00E-06	0,05
110	$9{,}57 \times 10^{-6}$	2.58E-06	0,06

Figure S11. *Creep recovery (graph), corresponding creep rates, creep compliance and remaining strain after recovery (table) of BAA-P.*

Table S1. *Overview of hydrolysis tests of BAA-P under different conditions.*

Condition	**Time (days)**	***Swelling ratio***	***Soluble Fraction***
Water (RT)	3	4.50 ± 1.90	0.69 ± 0.12
	12	9.25 ± 3.64	0.12 ± 0.07
HCl 1M	3	25.7 ± 2.80	0.06 ± 0.01
	12	22.9 ± 5.70	0.78 ± 0.70
NaOH 1M	3	3.84 ± 1.83	0.21 ± 1.29
	12	6.21 ± 0.82	0.14 ± 0.15
Water (100 °C)	2		0.26 ± 0.16

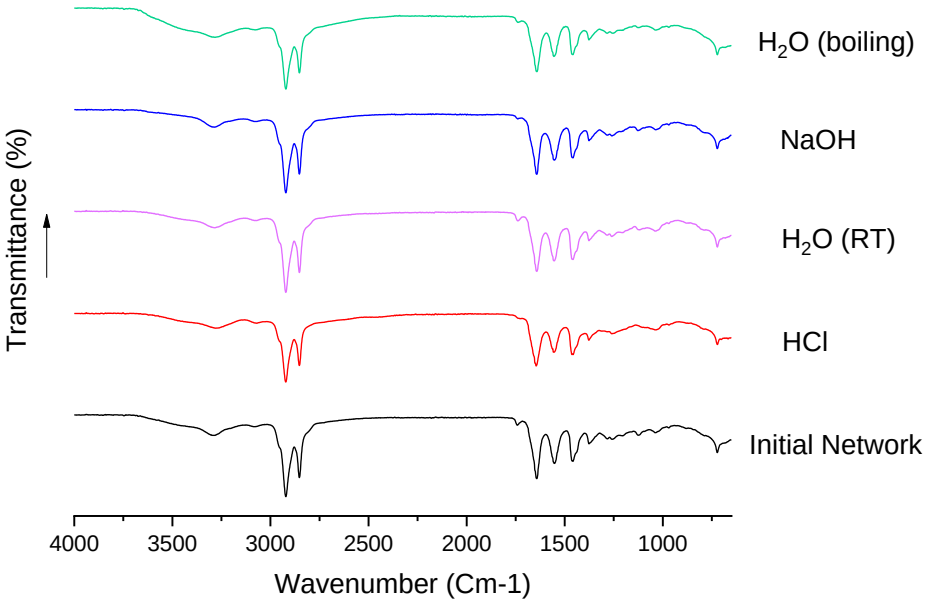


Figure S12. *ATR-IR spectra of initial BAAP-P network and after hydrolysis tests in 1 M HCl, deionized water (room temperature), 1 M NaOH and boiling water (bottom to top, respectively).*

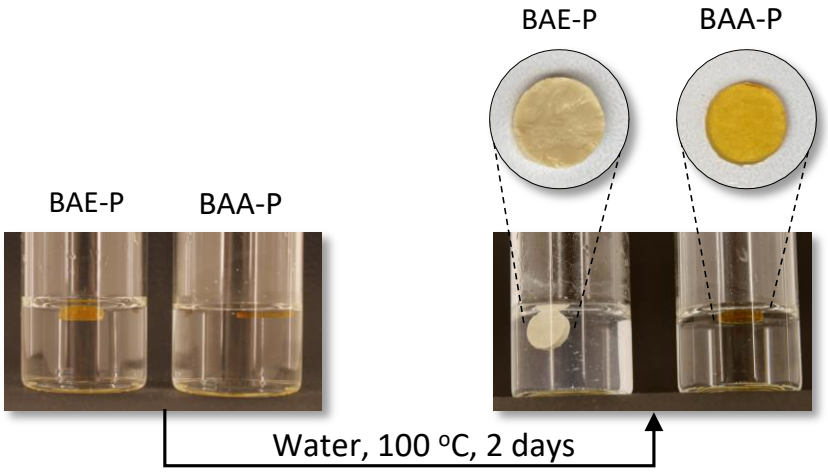


Figure S13. *Appearances of amino ester network (BAE-P) and amino amide network (BAA-P) before (left) and after (right) hydrolysis test in boiling water for 2 days, illustrating the structural loss of BAE-P and the almost unchanged structure of BAA-P.*

Synthesis of Pripol 2033 diacrylate (II)*:* Pripol 2033 (1 eq.) and TEA (2.4 eq.) were dissolved in DCM (40 mL) and cooled to 0 °C in an ice bath. To this solution, 2.4 eq. of acryloyl chloride in 10mL DCM was added sequentially. The solution was stirred for 1 h at 0 °C and then at room temperature overnight. HCl 1M (20mL) was added to quench the remaining acryloyl chloride, and the layers were separated. The organic layer was washed with aq. HCl (1 M, 2 × 50 mL), aq. $NaHCO_3$ (3 × 50 mL), and brine (50 mL), and dried over $MgSO_4$. Removal of the solvent under vacuum resulted in a yellowish transparent oil (yield = 85%). ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) was shown in **Figure S13**. δ ppm 6.40 (dd, J = 17.3, 1.5 Hz, 2H), 6.12 (dd, J = 17.3, 10.4 Hz, 2H), 5.81 (dd, J = 10.4, 1.5 Hz, 2H), 4.14 (t, J = 6.7 Hz, 4H), 1.70-1.63 (m, 4H), 1.41 – 1.17 (m, 44H), 0.95 – 0.78 (m, 8H).)

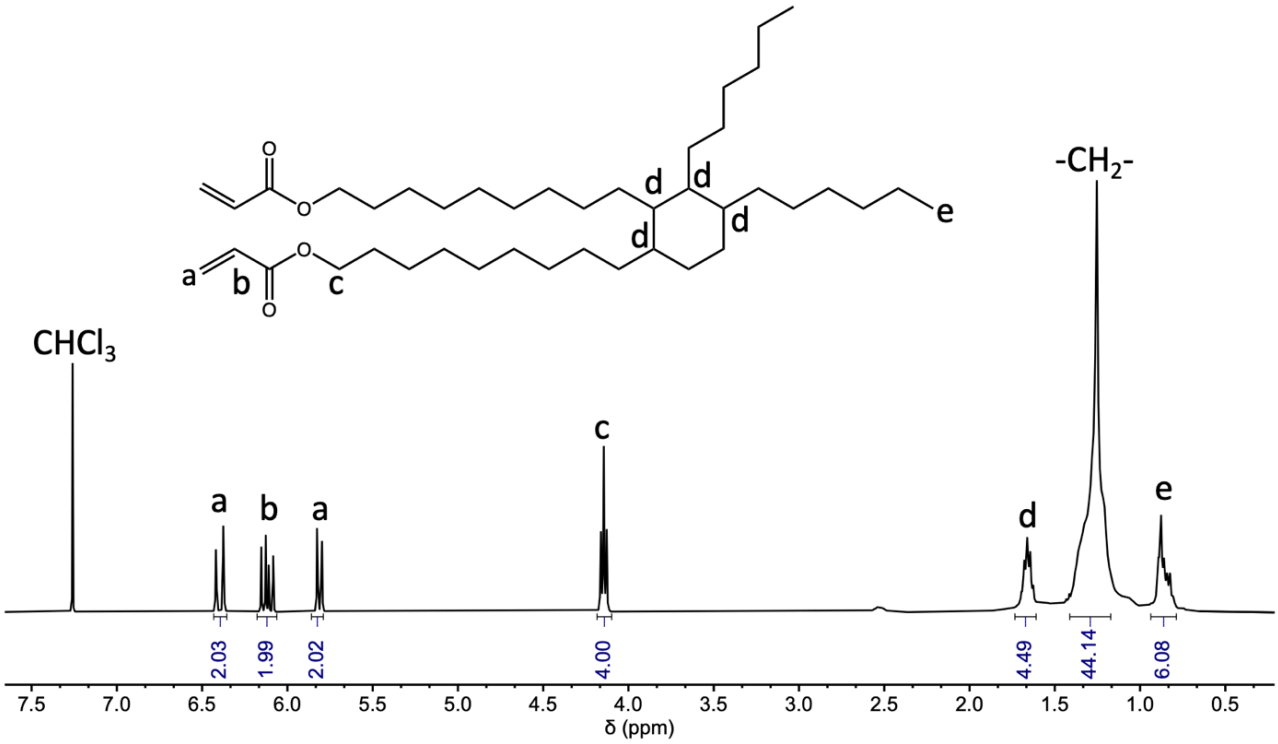


Figure S14. *^{1}H-NMR spectrum in $CDCl_3$ of Pripol 2033-diacrylate.*

Synthesis of reference amino-ester network prepared with Pripol 2033 (BAE-P)*:* 1 Eq. of 1,3-cyclohexanebis(methylamine) and 2 eq. of Pripol 2033 diacrylate (II) ***(Figure S13)*** were weighted and mixed in a polypropylene cup using a DAC 150.1 FVZ speed mixer (mixing condition: 2 min at 2500 rpm). Then, the cup was placed in an oven at 100 °C for 48 h to complete network formation.