Supporting information

Exploring Transamidation and Chemical Recycling of β-Amino Amide-Derived Covalent Adaptable Networks

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Contents

1. Materials

Methyl acrylate (stabilized with MEHQ, ≥99%) and trimethyl hexamethylenediamine (2,2,4- and 2,4,4- mixture, ≥99%), n-octylamine (≥98%), methyl n-octanoate (≥99%), were purchased from TCI Chemicals Europe. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (**TBD**, ≥98%), p-toluenesulfonic acid (**p-TsOH**, ≥98%), methanesulfonic acid (**MSA**, ≥99%), trifluoromethanesulfonic acid (**TfOH**, ≥99%), ethanolamine (≥98%) were purchased from Sigma-Aldrich. N-benzylacrylamide (≥96%) was purchased from Fisher Scientific. Dichloromethane (DCM), Acetonitrile (ACN), and chloroform ($CHCl_3$) were purchased from Acros Organics. Priamine (1074) was kindly provided by Croda. All chemicals were used without further purification unless stated otherwise.

2. Instruments and methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance Ultrashield 300 or 400 MHz spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent. Chemical shifts are given in parts per million (ppm).

(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.

Matrix-assisted laser desorption/ionization (MALDI) For the MALDI measurements stock solution of the matrix dithranol (30 mg mL^{-1}) and sodium trifluoroacetate (NaTFA, 10 mg mL^{-1}) were prepared in tetrahydrofuran. Samples were solubilised in tetrahydrofuran (10 mg mL^{-1}). 45 µl of the matrix solution, 15 µl of the salt and 15 µl of the sample solution were mixed and subsequently spotted on the MALDI plate. The spots were dried at room temperature and loaded into an Applied Biosystems Sciex 4800+ MALDI ToF analyser, controlled by 4000 Series Explorer software (Applied Biosystems, Germany). The instrument was operated in reflective positive ion mode.

Electrospray Ionization - Mass Spectrometry (ESI-MS) was used to measure absolute mass values. Spectra were recorded on Q-Exactive Plus stand-alone benchtop Orbitrap mass spectrometer (Thermo Fisher Scientific), equipped with a heated electrospray ionization source (HESI). The instrument was calibrated in the m/z range of 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using

ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150, and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), an auto sampler (WPS3000TSL), and a temperature-controlled column department (TCC 3000). The injection volume used for analysis was 10 µL of a 0.05 mg/mL solution (in ACN).

Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA851e instrument under an air atmosphere at a heating rate of 10 $K \cdot min^{-1}$ from 25 to 800 °C. Isothermal analysis was performed at 180 °C under an air atmosphere for 60 min.

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

Dynamic mechanical thermal analysis (DMTA, shear mode) was performed on a SDTA861e DMTA equipment from Mettler Toledo instrument, at a heating rate of 3 $K \cdot min^{-1}$ from −100 to 50 °C in oscillatory mode on discs of 8 mm diameter. The amplitude was set to 2 µm, and the frequency was 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. *Amplitude sweep* experiments were performed using a frequency of 1 Hz, a constant normal force of 1 N, and a variable shear strain that was ramped up logarithmically from 0.01 to 10% to determine the linear viscoelastic region (LVER). *Stress-relaxation experiments* were performed at different temperatures (200 - 170 °C, with intervals of -10 °C) using a constant shear strain within the LVER of the samples, and a constant normal force of 1 N. The shear moduli were followed as a function of time. The obtained characteristic relaxation time (τ) derived from the Kohlrausch–Williams–Watts (KWW) stretched model (**Equation S1**) was used to calculate the activation energy.

$$G(t) = G_0 e^{-(\frac{t}{\tau})^{\beta}} \quad \textbf{(Equation S1)}$$

(Re)processing experiments were conducted on a Carver Bench Top Standard Heated Press, equipped with a four-column hydraulic lab press manually operated with digital heated platens.

(Re)processability was investigated by breaking the cross-linked material into pieces of about 0.5 cm, which were then placed into a steel mold for compression molding. This assembly was placed in a preheated compression press at designated temperatures (180 – 160 °C) for 1 min under 0.5 metric tons of pressure. Then, the pressure increased to 3 tons and kept constant for an additional 30 min. After this time, the sample was carefully removed from the mold.

Solubility tests were carried out with dry samples of approximately 2 mm in diameter and 2 mm in thickness, and a weight of around 10 - 20 mg in 40 mL of chloroform. Those tests were performed for 24 h at 25 °C. The solvent was then removed, and the samples were dried under vacuum overnight at 100 °C. The soluble fraction (**Equation S2**) and swelling degree (**Equation S3**) were calculated as follows:

$$\text{soluble fraction (\%)} = \frac{m_i - m_d}{m_i} \quad \textbf{(Equation S2)}$$

$$\text{swelling degree (\%)} = \frac{m_s - m_i}{m_i} \quad \textbf{(Equation S3)}$$

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

3. Experimental procedures

3.1. Synthesis of model compound N-benzyl-3-(methyl(octyl)amino)propenamide (M)

In a flask, 2 g (1 eq) of N-benzyl acrylamide dissolved in 5 ml methanol was slowly added into 2.13 g (1.2 eq) of n-methyl-n-octylamine, while being continuously stirred. The reaction was performed at 70 °C under a nitrogen atmosphere for 48 h. The crude mixture was then taken up in 20 mL of *chloroform*, washed with HCl 1M (1 x 20 mL), water (2 × 20 mL), brine (1 × 20 mL), and dried over $MgSO_4$. After which solvent was removed by rotary evaporation and in a vacuum oven overnight at 40 °C resulting in a pale yellow oil (yield = 61 %, 2.3 g). The obtained product was characterized by ^{1}H-, ^{13}C-NMR and ESI-MS as shown in **Figure S1-3**.

3.2. Synthesis of n-octyloctanamide (Ref-M).

Methyl n-octanoate (1 eq) and octylamine (1.2 eq) were introduced in a flask. The reaction was performed at 120 °C under a nitrogen atmosphere for 48 h. The crude mixture was then taken up in 20 mL of chloroform, washed with HCl 1M (x1), water (x2), brine (x1), and dried over $MgSO_4$. After which solvent was removed by rotary evaporation and in a vacuum oven overnight at 40 °C

resulting in a transparent brownish oil. The obtained product was characterized by ^{1}H-NMR as shown in **Figure S8**.

3.3. Synthesis of 2,2,4-trimethyl hexamethylenediamine tetra amino-ester crosslinker (TMH-4E)

In a flask, 5 eq of methyl acrylate (diluted in DCM) was added slowly into 1 eq of 2,2,4-trimethyl hexamethylenediamine. The reaction was conducted at reflux condition for 24 h. The crude reaction mixture was then cooled down. The product TMH-4E was isolated by extractions with DCM/water three times and dried over $MgSO_4$ and under vacuum at 40 °C overnight resulting in a transparent oil (yield = 75 %). The obtained product was characterized by ^{1}H-NMR as shown in **Figure S9**.

3.4. Synthesis of Priamine tetra amino-ester crosslinker (P4E)

In a flask, 5 eq of methyl acrylate (diluted in DCM) was added slowly into 1 eq of priamine 1074. The reaction was conducted at reflux condition for 24 h. The reaction mixture was then cooled down and washed with water (3 × 50 mL), brine (1 × 50 mL), and dried over $MgSO_4$. After which solvent was removed by rotary evaporation and in a vacuum oven overnight at 40 °C resulting in a pale yellow oil (yield = 83 %). The obtained product was characterized by ^{1}H-NMR as shown in **Figure S18**.

3.5. Synthesis of β-amino amide-based covalent adaptable networks

In a vial equipped with a magnetic stirring bar, the cross-linker (either TMH-4E or P4E) and Priamine were introduced in the following ratio (NH_2 : ester = 1:1 mol/mol). In the catalyst-containing systems, an additional catalyst (TBD, or pTsOH, or MSA, or TfOH) was added, with a ratio of 5 mol% to the designated β-amino amides. The network formation via polyamidation was performed at 120 °C for 16 h, followed by a post-curing at 120 °C for 1 h under vacuum. Obtained networks were compression molded into 1-2 mm thick samples for further characterizations.

3.6. Chemical degradation

The P-BAAN network, synthesized from P4E and Priamine, was immersed in amino compound (either n-octylamine or ethanolamine) in a sealable vial (sample/amino compound = 10 wt.%). The degradation tests were performed at 140 °C under a nitrogen atmosphere. The degraded mixture was collected at different time intervals, worked-up by extraction (DCM/water) and subjected to characterizations (i.e., ^{1}H-NMR spectroscopy and MALDI mass spectrometry).

4. Supporting figures

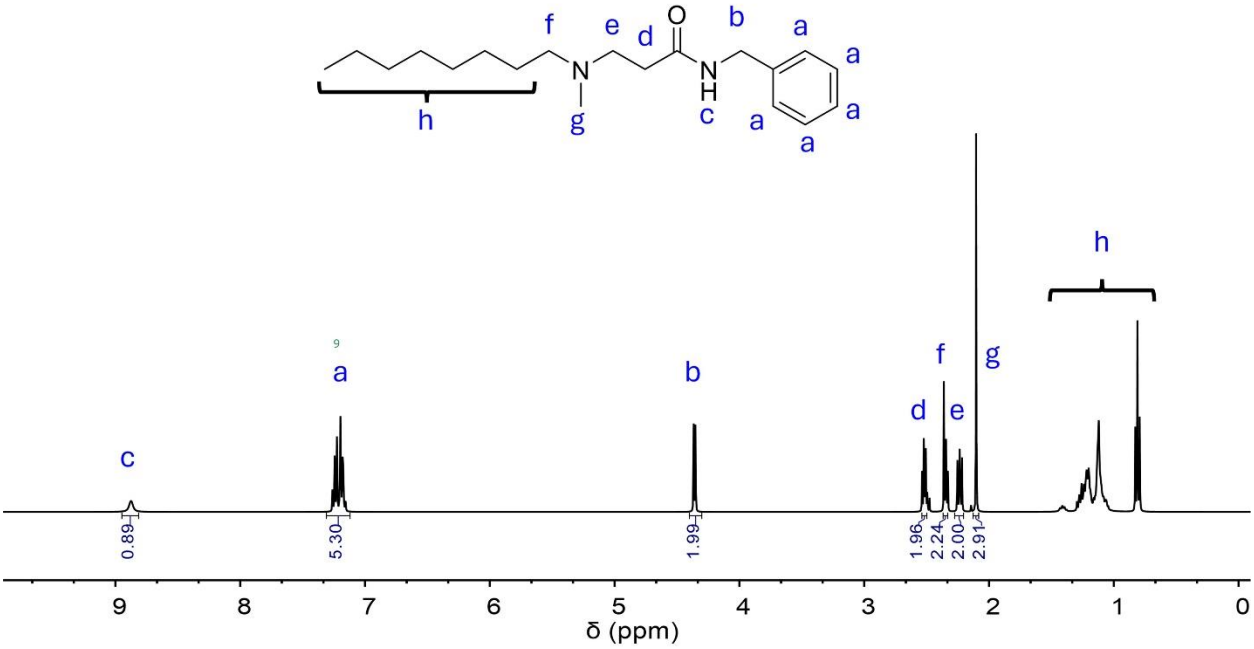

Figure S1. ^{1}H-NMR spectrum of N-benzyl-3-(methyl(octyl)amino)propenamide (M). ^{1}H NMR (400 MHz, $CDCl_3$) **δ (ppm):** 3.56 (s, 2H), 3.15 (td, 2H), 2.71 (t, 2H), 2.43 (t, 2H), 2.22 (s, 3H), 1.49 – 1.35 (m, 2H), 1.33 – 1.21 (m, 2H), 0.86 (td, 4H).

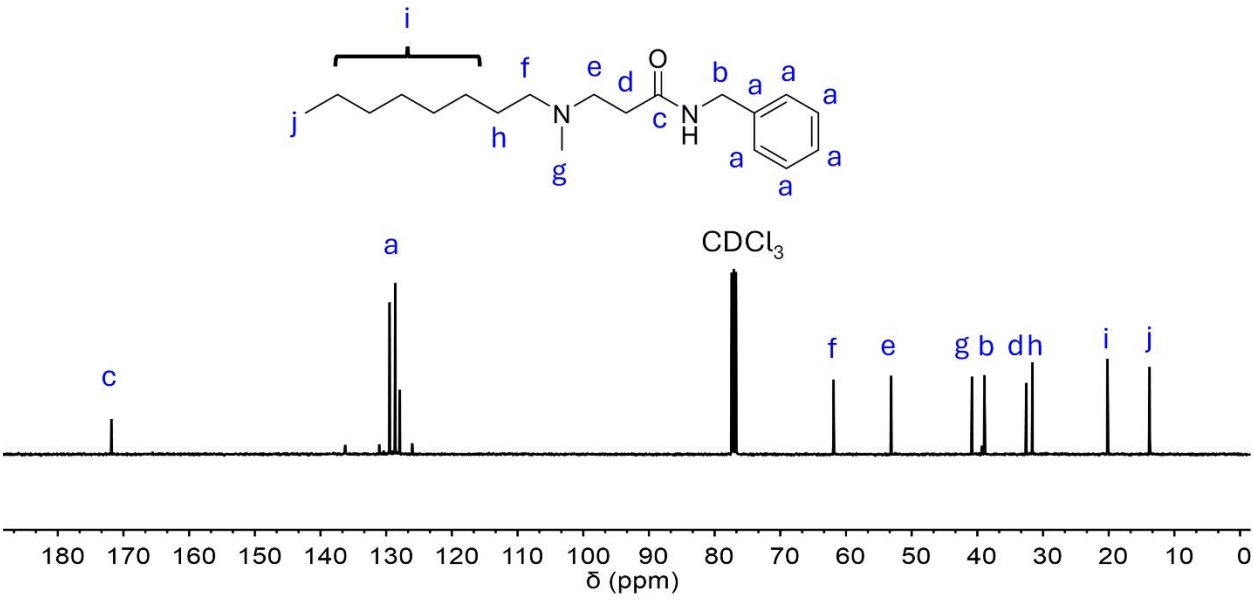

Figure S2. ^{13}C-NMR spectrum of N-benzyl-3-(methyl(octyl)amino)propenamide (M). ^{13}C NMR (400 MHz, $CDCl_3$) **δ (ppm):** 171.82, 129.49, 128.63, 127.94, 61.90, 53.13, 40.82, 38.91, 32.56, 31.63, 20.20, 13.79.

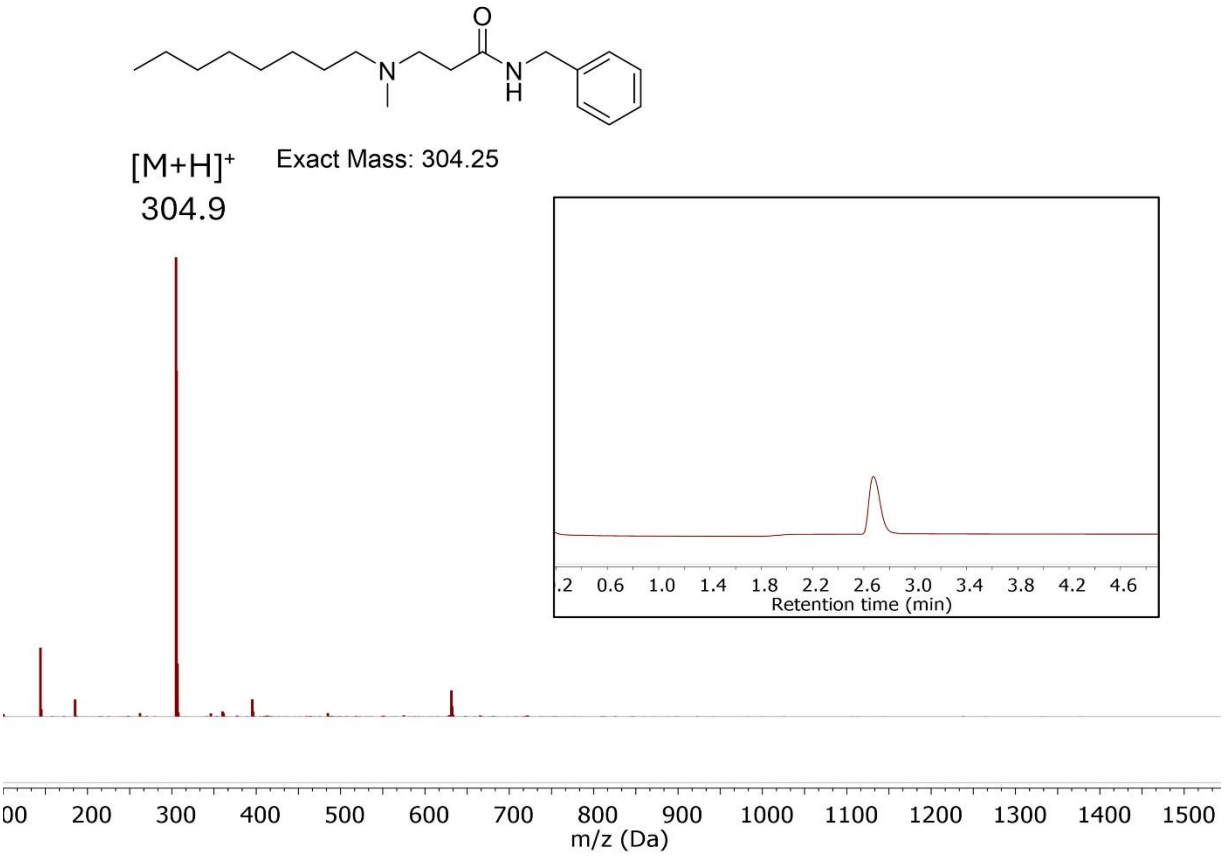

Figure S3. ESI-MS of N-benzyl-3-(methyl(octyl)amino)propenamide (**M**).

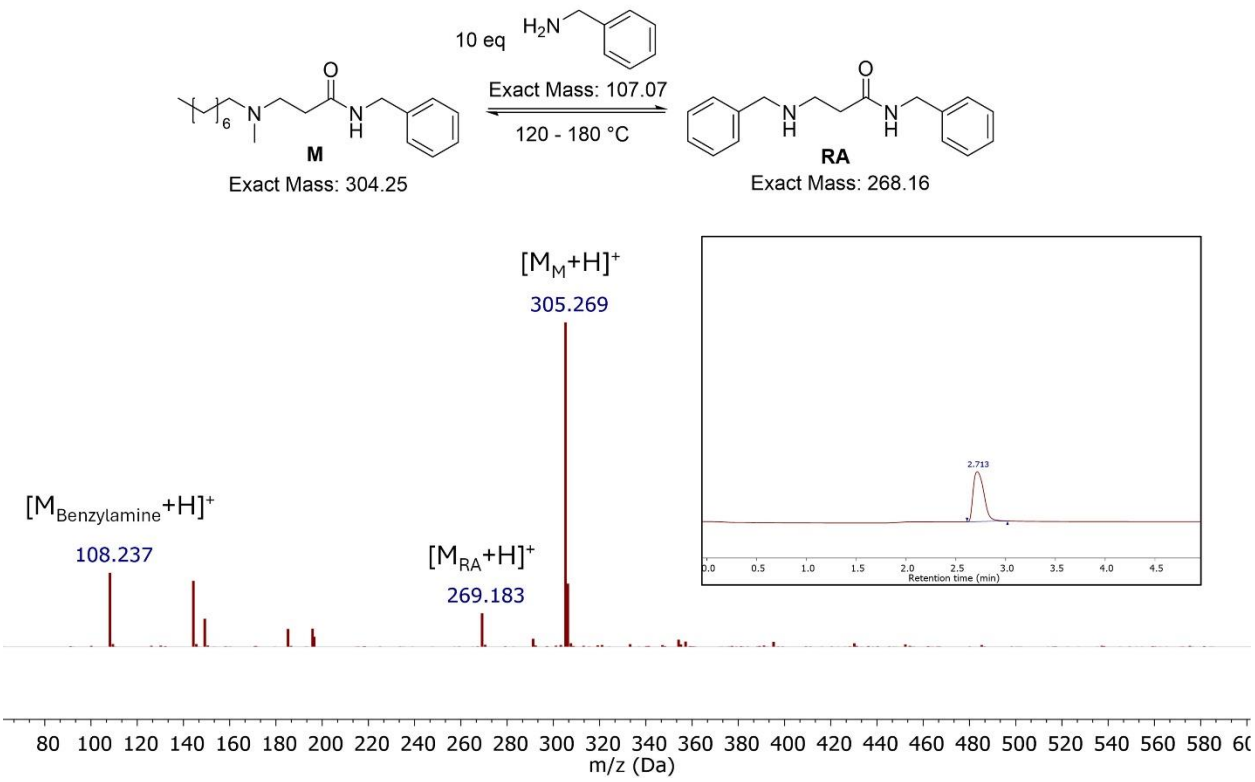

Figure S4. ESI-MS of a crude mixture of a model (retro) aza-Michael exchange reaction at 180 °C after 2h, which shows the mass of exchange adduct RA.

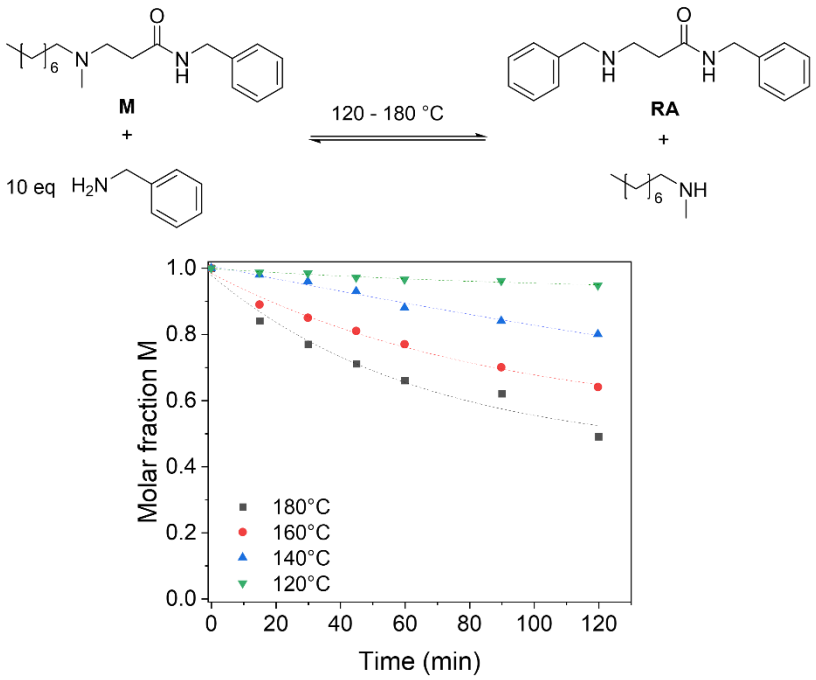

Figure S5. Overlay of the remaining molar fraction of model BAA compound **M** as a function of time during the (retro) aza-Michael exchange at temperatures varying from 120 to 180 °C.

Table S 1. Summary of data from the kinetic study on the (retro) aza-Michael exchange used to construct the Arrhenius plots.

Temperature (°C)	1000/T (K^{-1})	K (s^{-1})	ln(K)
180	2.207	5.00 x 10^{-6}	7.31 x 10^{-6}
160	2.309	4.00 x 10^{-6}	4.83 x 10^{-6}
140	2.420	1.96 x 10^{-6}	2.71 x 10^{-6}
120	2.544	0.77 x 10^{-6}	0.58 x 10^{-6}

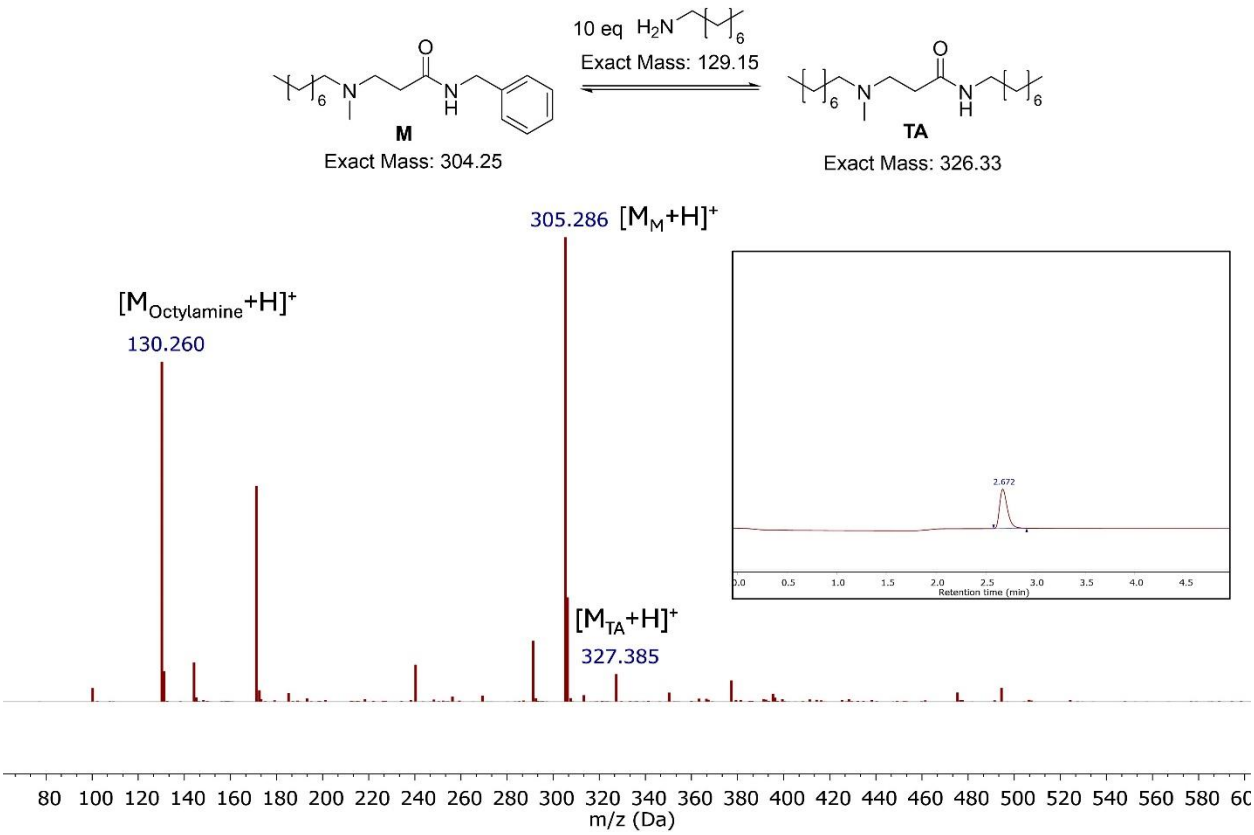

Figure S6. ESI-MS of a crude mixture of a model transamidation exchange reaction at 180 °C after 2h, which displays the mass of exchange adduct TA.

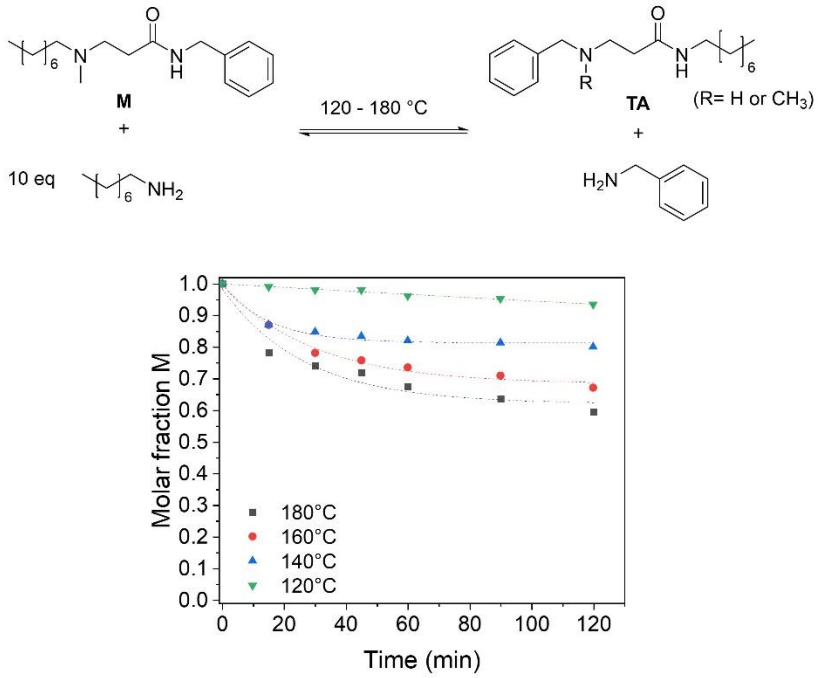

Figure S7. Overlay of the remaining molar fraction of model BAA compound M as a function of time during the transamidation exchange at temperatures varying from 120 to 180 °C.

Table S 2. Summary of data from the kinetic study on the transamidation exchange used to construct the Arrhenius plots.

Temperature (°C)	1000/T (K^{-1})	K (s^{-1})	ln(K)
180	2.207	5.00 x 10^{-6}	-12.206
160	2.309	4.00 x 10^{-6}	-12.428
140	2.420	1.96 x 10^{-6}	-13.145
120	2.544	0.77 x 10^{-6}	-14.082

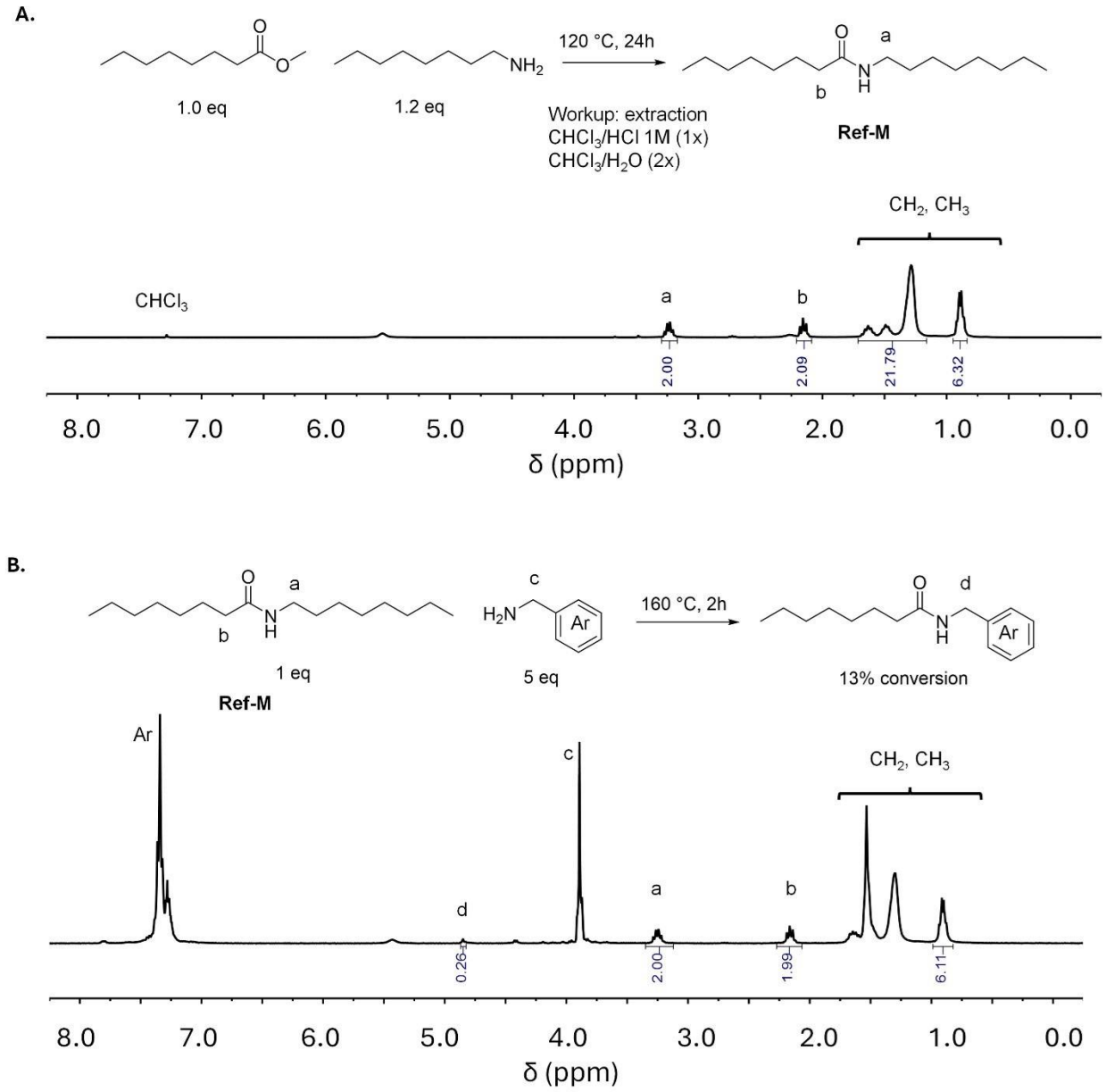

Figure S8. (A) ^{1}H NMR (400 MHz, $CDCl_3$) of (A) n-octyloctanamide (**Ref-M**) as a reference conventional amide, and (B) a crude of benchmark exchange reaction, performed on **Ref-M** at 160 °C for 2 h showed 13% conversion to trans-amidated product, compared to 33% of one conducted on BAA compound **M**. It is worth noting that only a trace conversion was observed in a benchmark reaction conducted at 140 °C after 2 h.

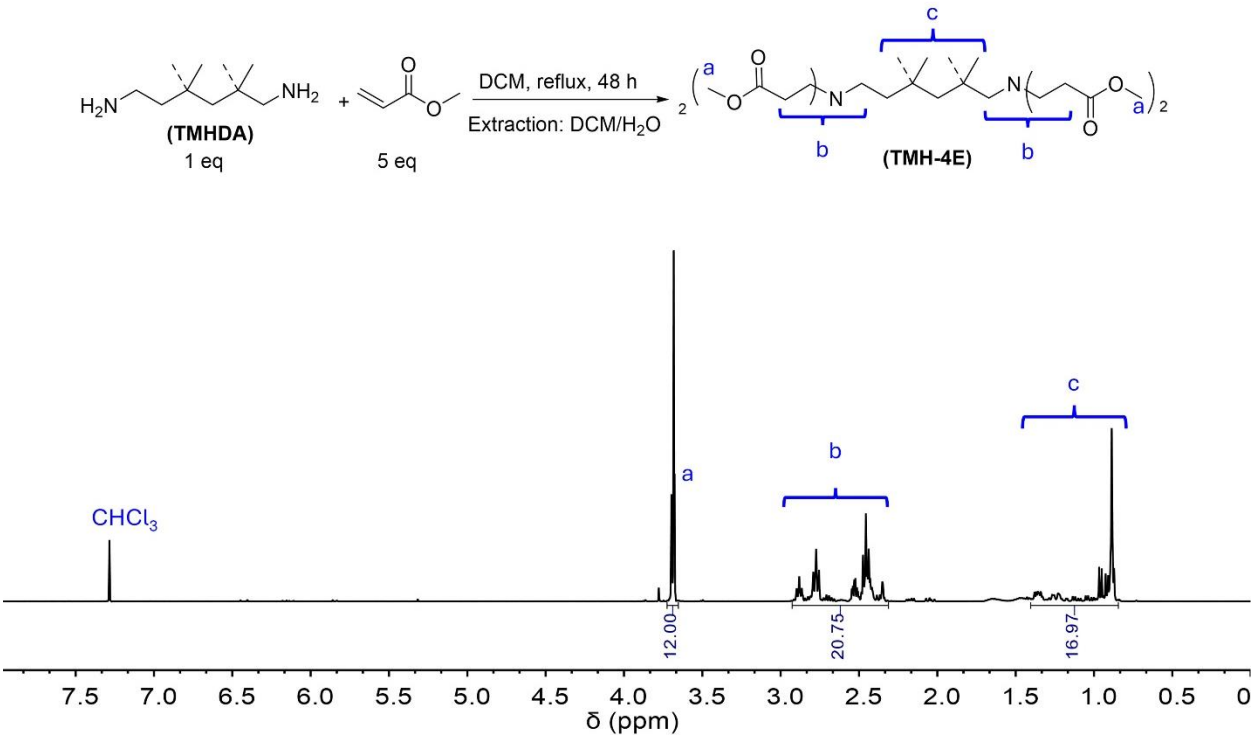

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of cross-linker TMH-4E. **δ (ppm):** 3.72 – 3.65 (m, 12H), 2.93 – 2.31 (m, 20H), 1.40 – 0.84 (m, 17H).

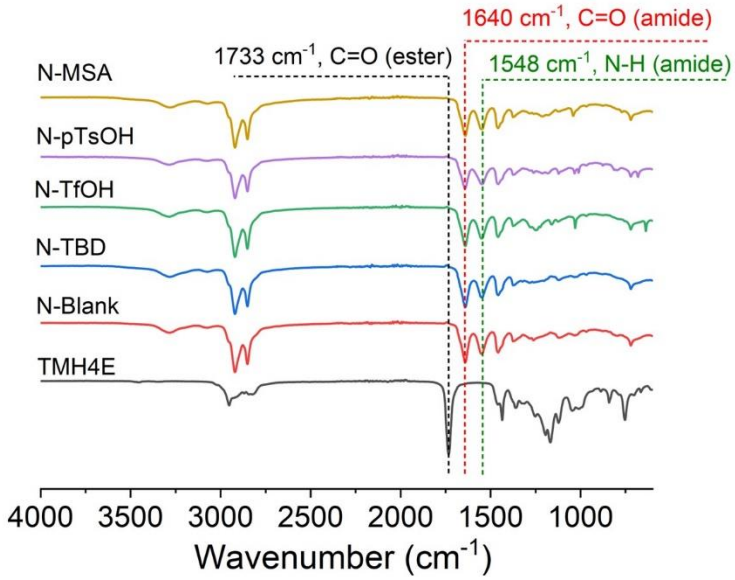

Figure S10. ATR-FTIR spectra of synthesized networks with various catalysts, indicating the formation of BAA bonds via the complete conversion of ester carbonyl (1733 cm^{-1}) to amide carbonyl (1640 cm^{-1}).

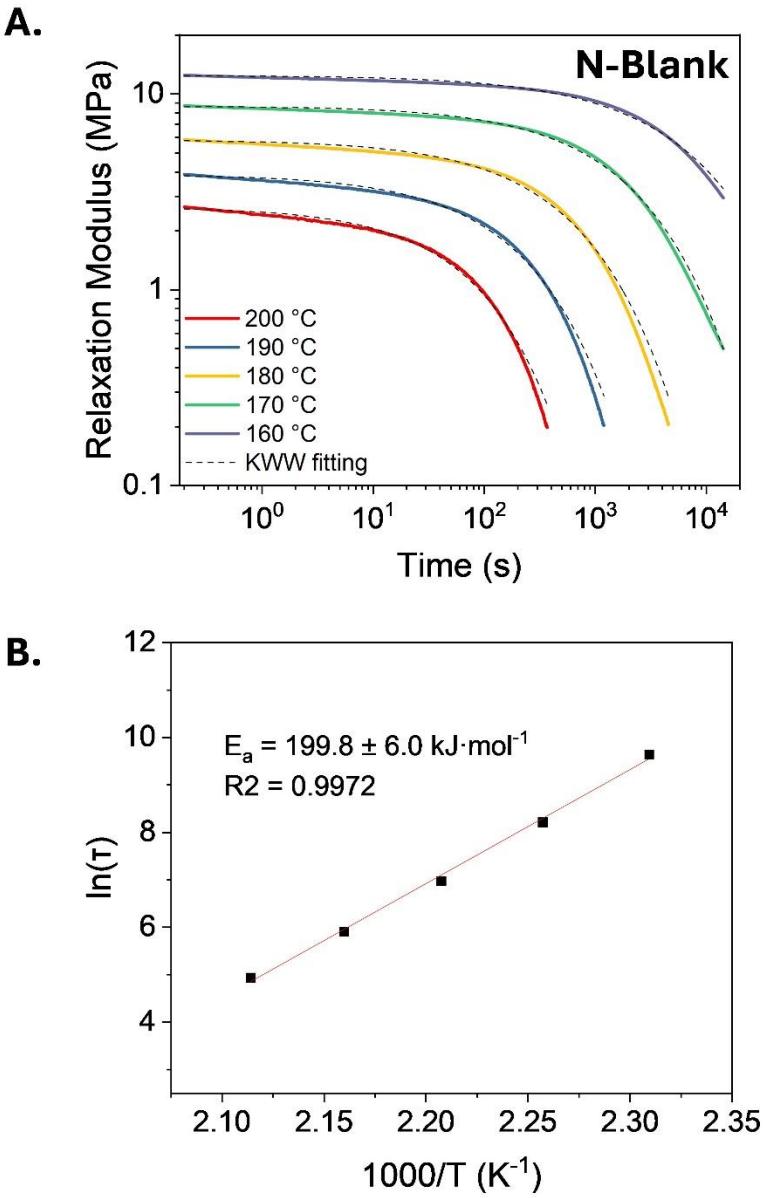

Figure S11. Stress relaxation measurement on the N-Blank network. A) the stress relaxation curves and B) the Arrhenius plot fitted by the Kohlrausch–Williams–Watts (KWW) stretched model.

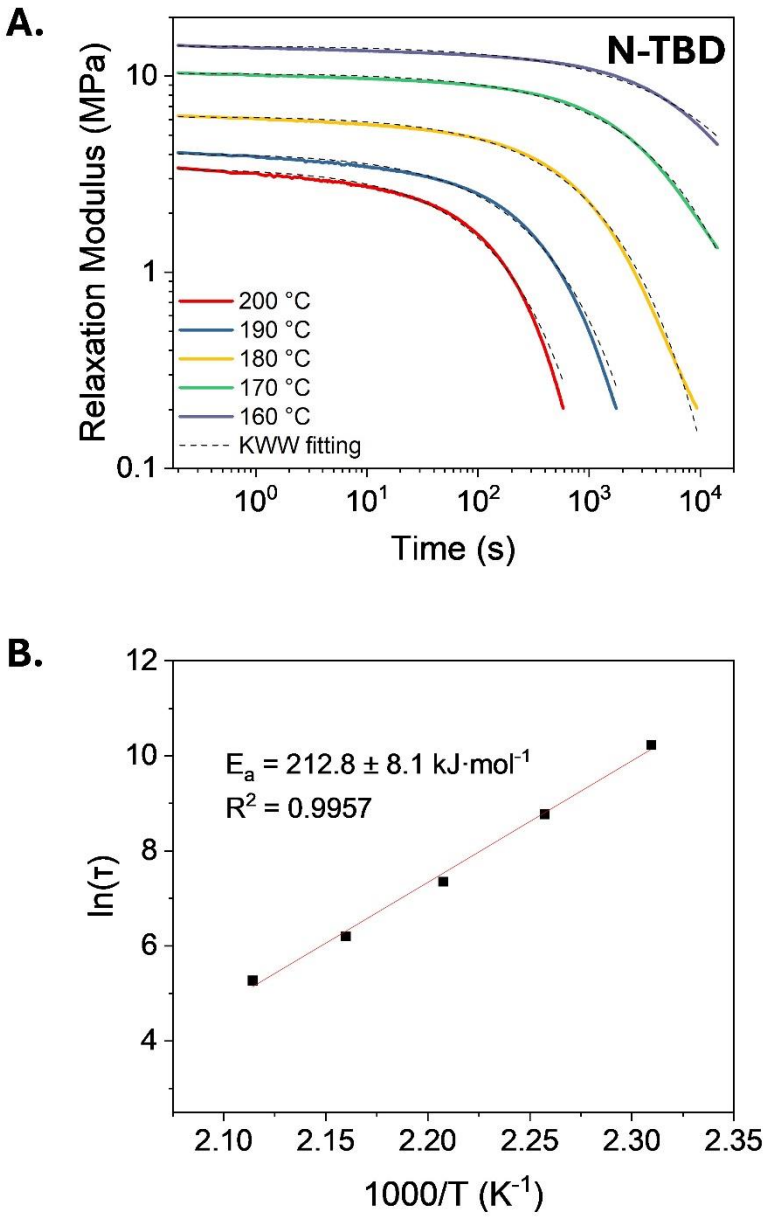

Figure S12. Stress relaxation measurement on the N-TBD network. A) the stress relaxation curves and B) the Arrhenius plot fitted by the Kohlrausch–Williams–Watts (KWW) stretched model.

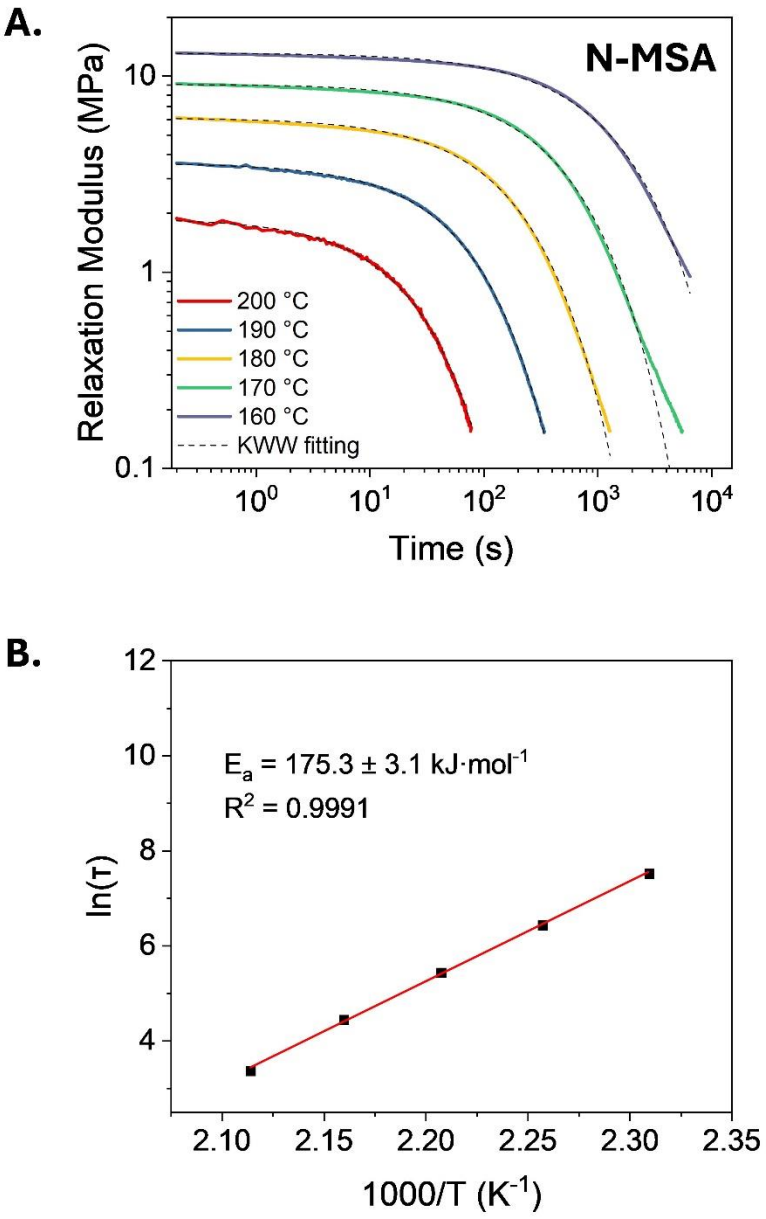

Figure S13. Stress relaxation measurement on the N-MSA network. A) the stress relaxation curves and B) the Arrhenius plot fitted by the Kohlrausch–Williams–Watts (KWW) stretched model.

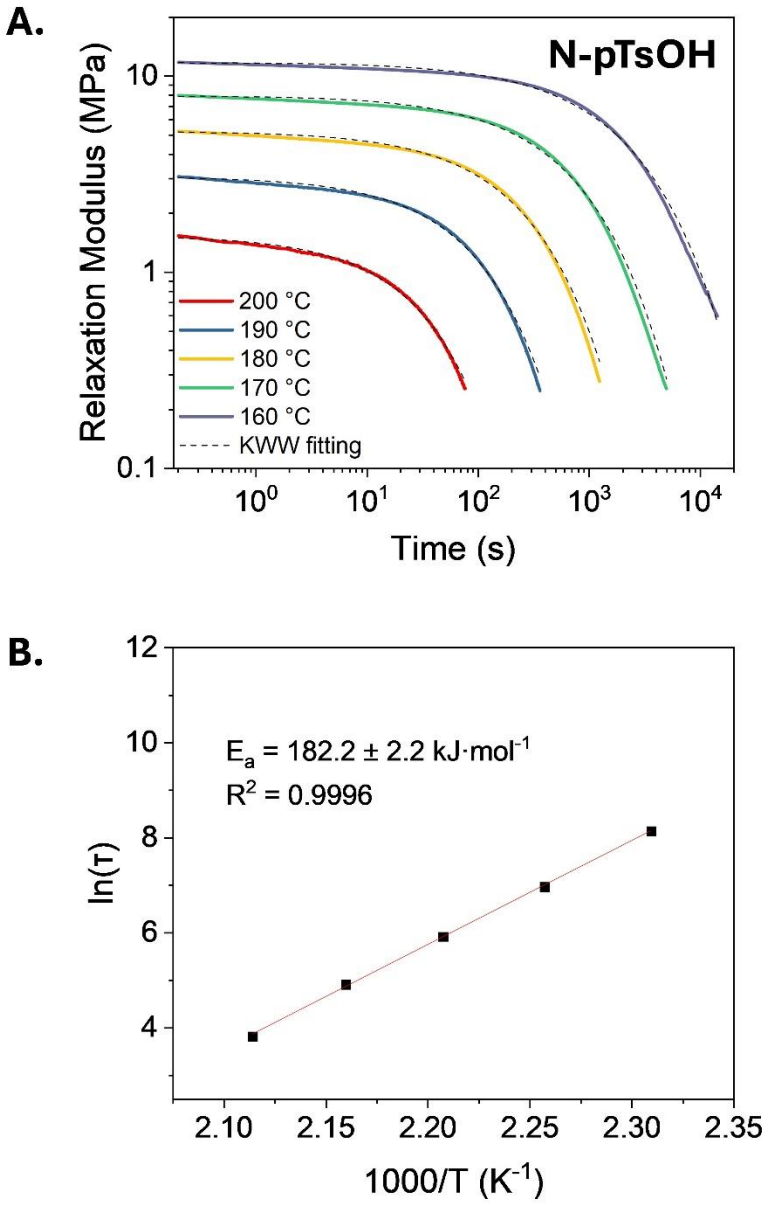

Figure S14. Stress relaxation measurement on the N-pTsOH network. A) the stress relaxation curves and B) the Arrhenius plot fitted by the Kohlrausch–Williams–Watts (KWW) stretched model.

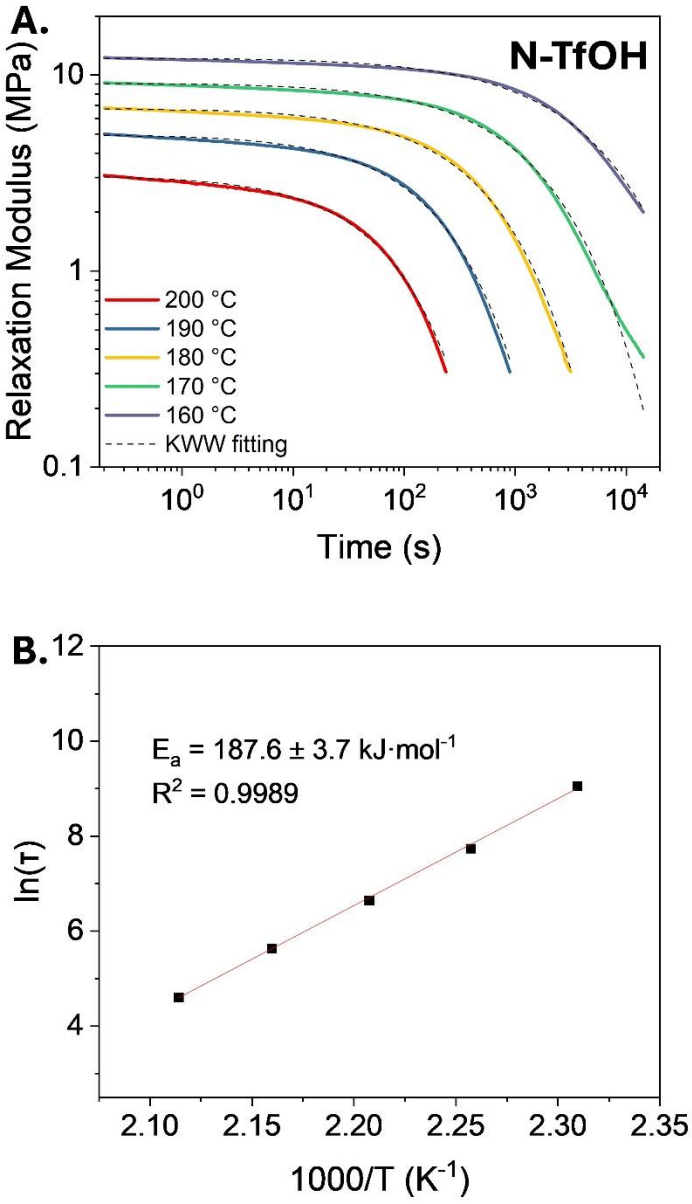

Figure S15. Stress relaxation measurement on the N-TfOH network. A) the stress relaxation curves and B) the Arrhenius plot fitted by the Kohlrausch–Williams–Watts (KWW) stretched model.

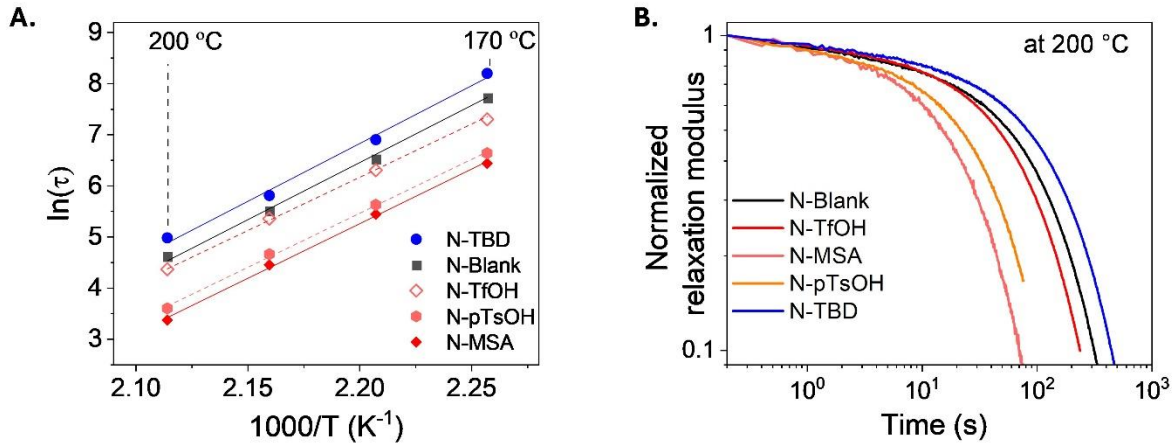

Figure S16. Overlayed Arrhenius plots (A) and relaxation curves at 200 °C (B) of BAAN with and without additional catalysts.

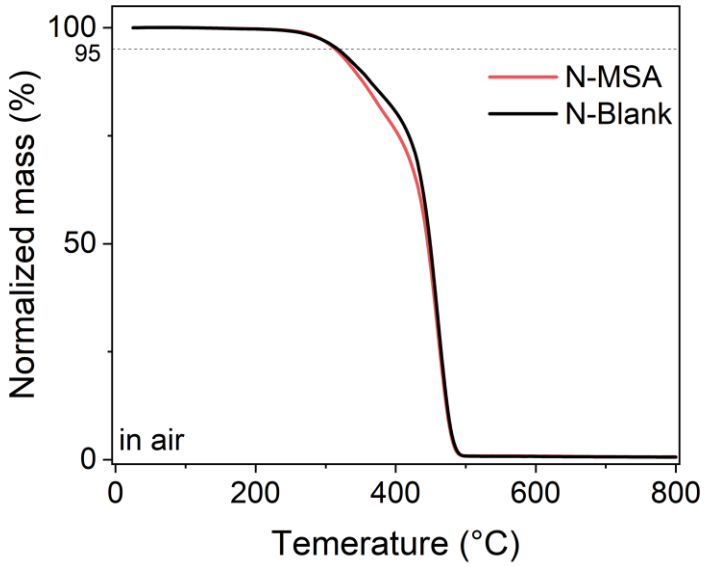

Figure S17. Thermogravimetric analysis (TGA) revealed no significant differences between N-MSA (5 mol% of MSA catalyst) and N-Blank (no catalyst), with onset temperatures at 5 % weight loss of 313 °C and 317 °C, respectively, indicating that the catalyst has a negligible impact on thermal stability.

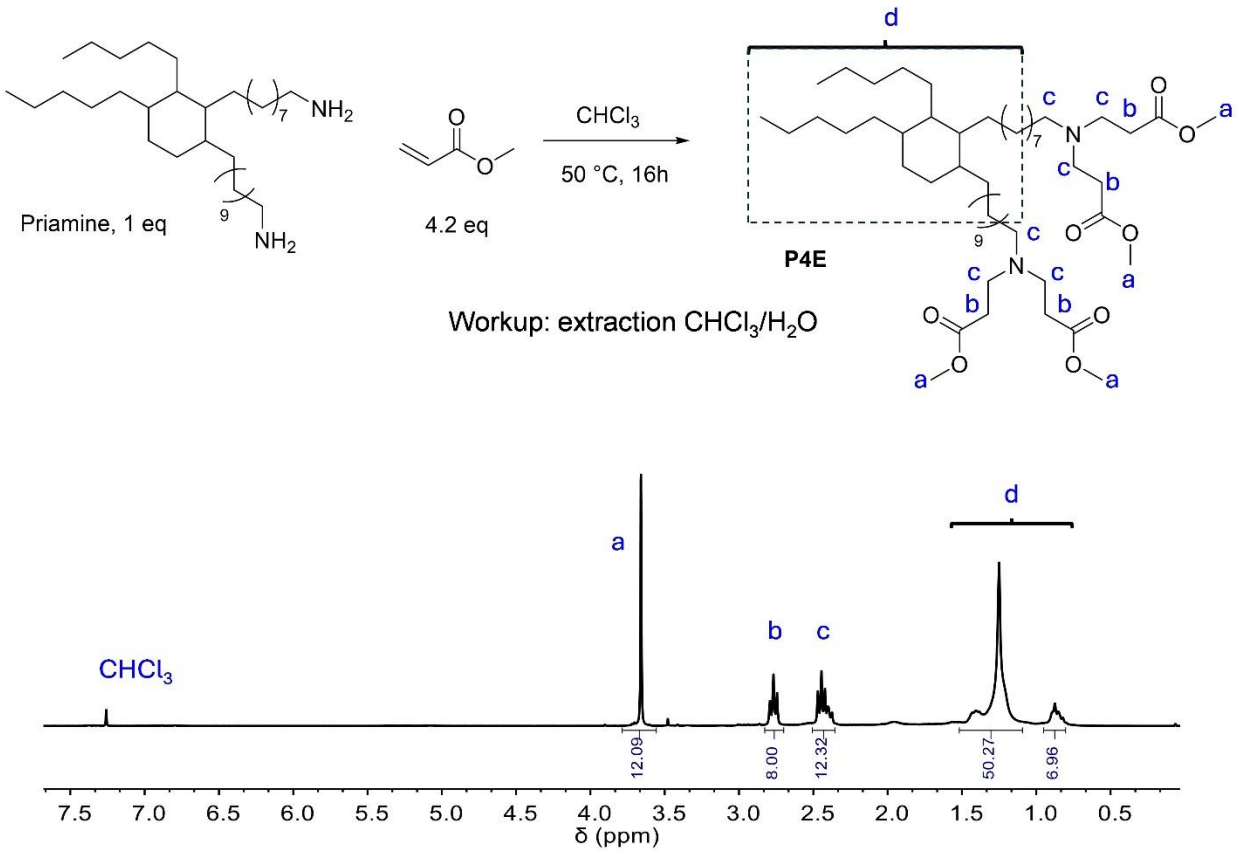

Figure S18. Synthesis of cross-linker Priamine tetraester (P4E) from Priamine for the synthesis of P-BAAN network. ^{1}H NMR (400 MHz, $CDCl_3$) **δ (ppm):** 3.66 (s, 12H), 2.77 (t, 8H), 2.42 (dt, 12H), 1.25 (s, 50H), 0.86 (q, 7H).

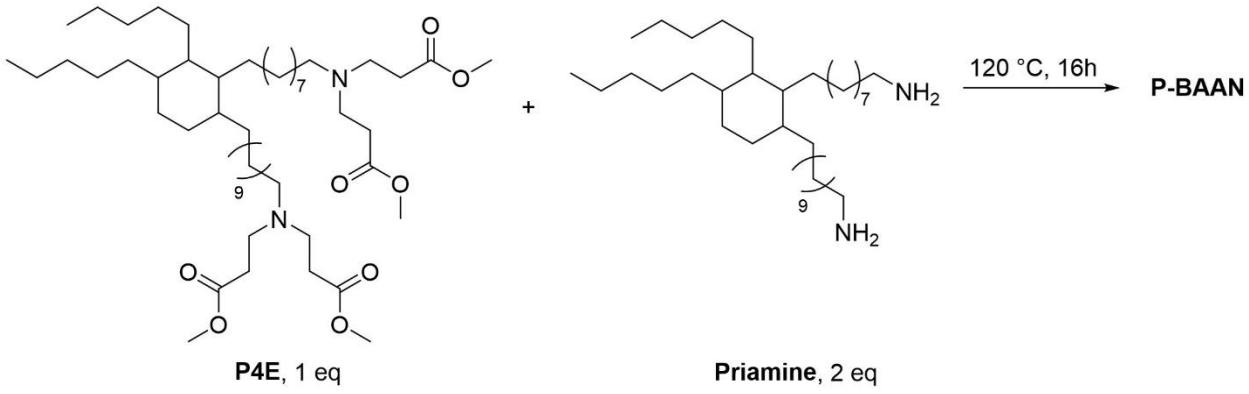

Figure S19. Synthesis of P-BAAN network from P4E cross-linker and priamine.

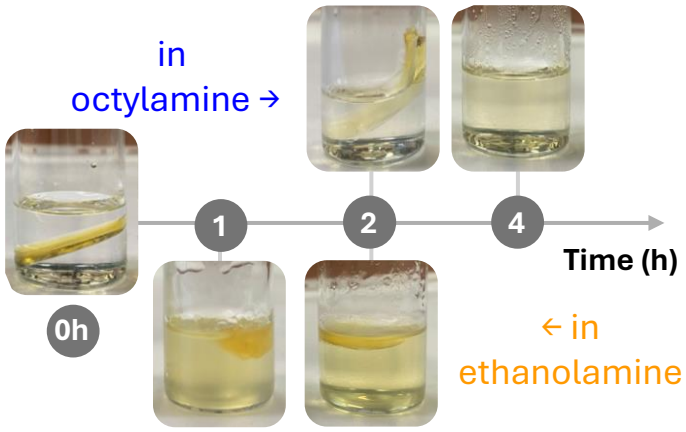

Figure S20. Visualization of the degradation of P-BAAN in n-octylamine (top) and ethanolamine (bottom) at 140 °C.

Figure S21. No dissolution of P-BAAN was observed in a benchmark depolymerization performed in DMSO at 140 °C for 24 h.

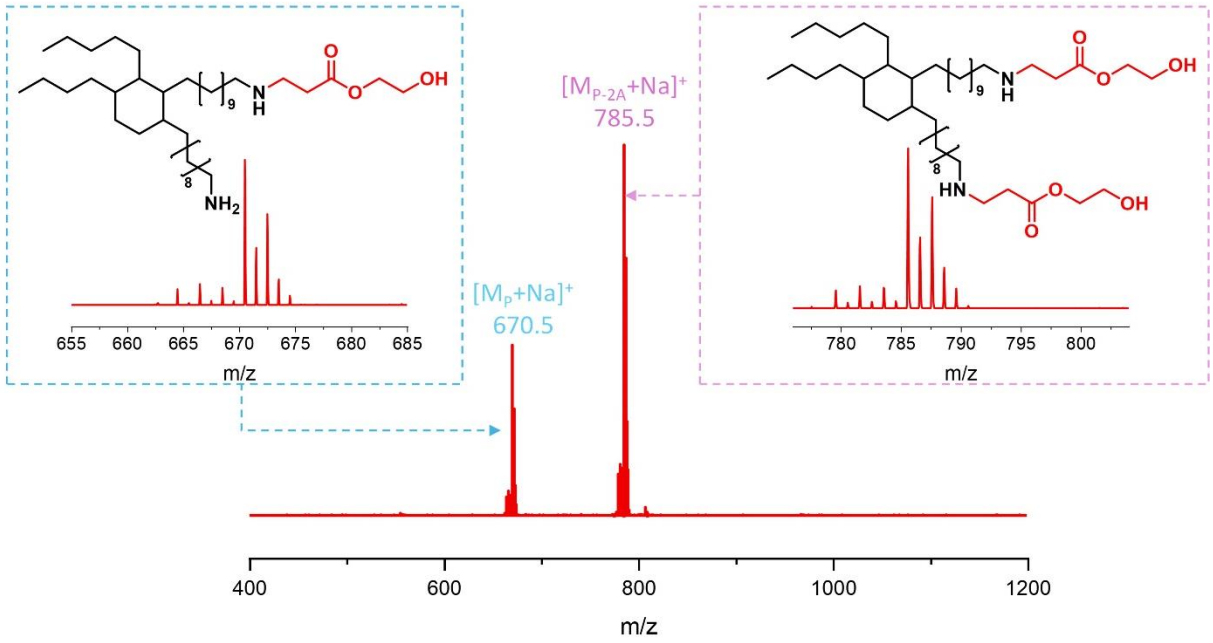

Figure S22. MALDI-ToF result of degraded mixture (extracted with H_2O/DCM) of P-BAAN for 3 days in ethanolamine.

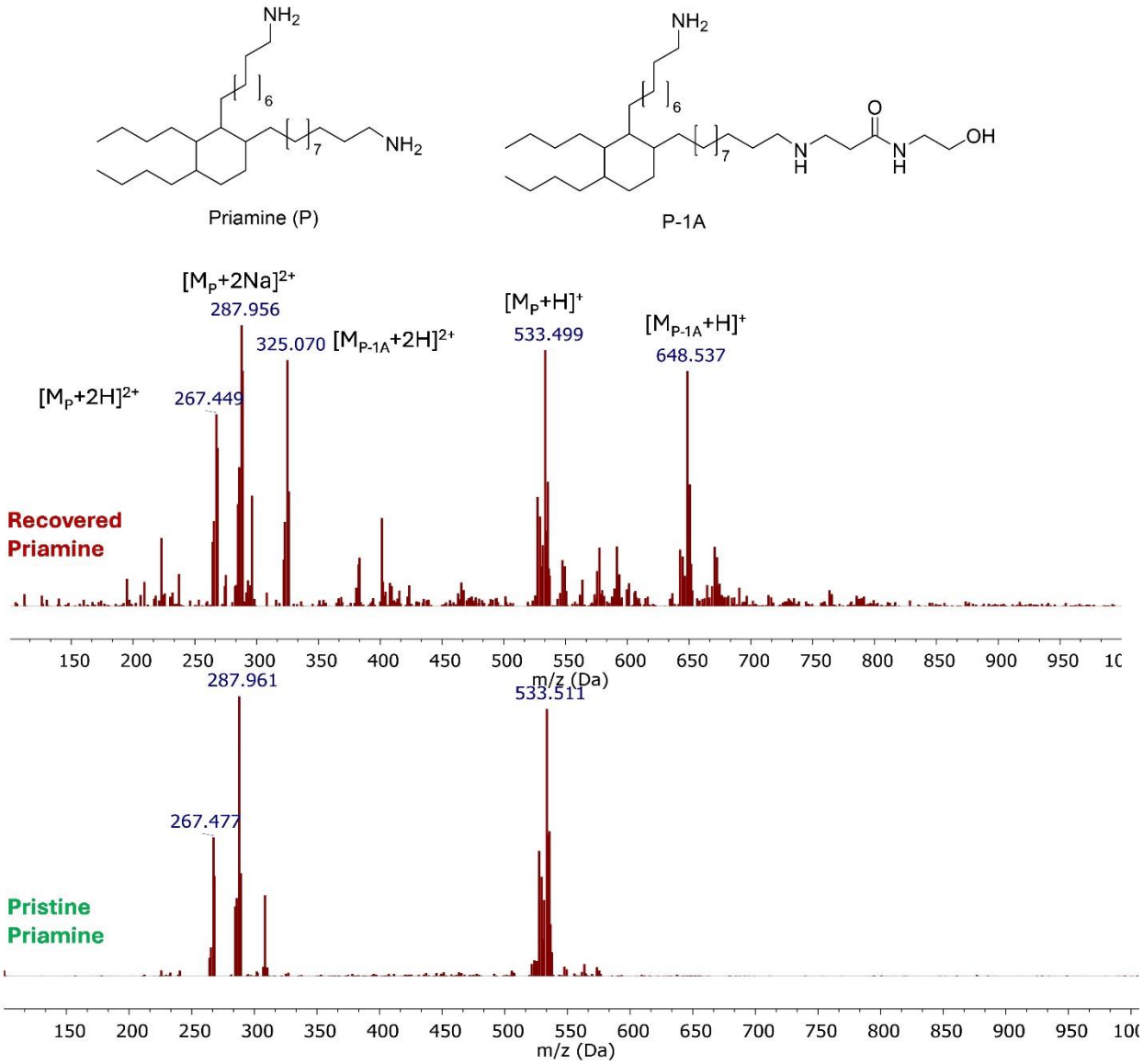

Figure S23. ESI-MS spectra of recovered (top) and pristine (bottom) priamine.

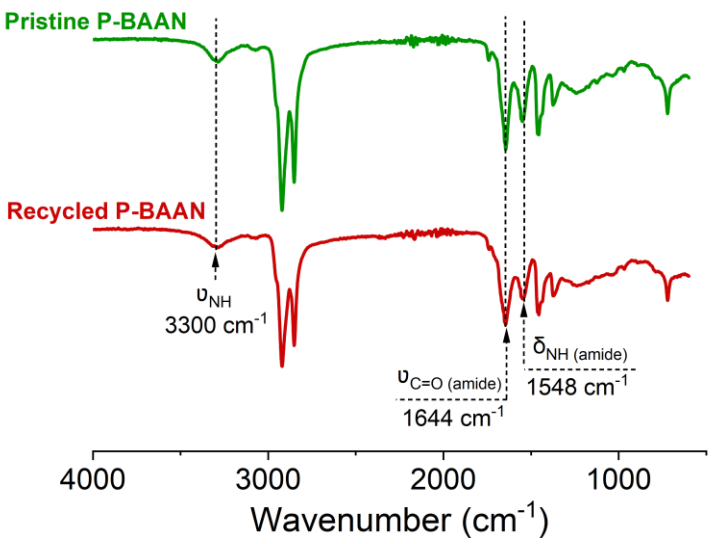

Figure S24. FTIR spectra of recycled P-BAAN in comparison to pristine BAAN.

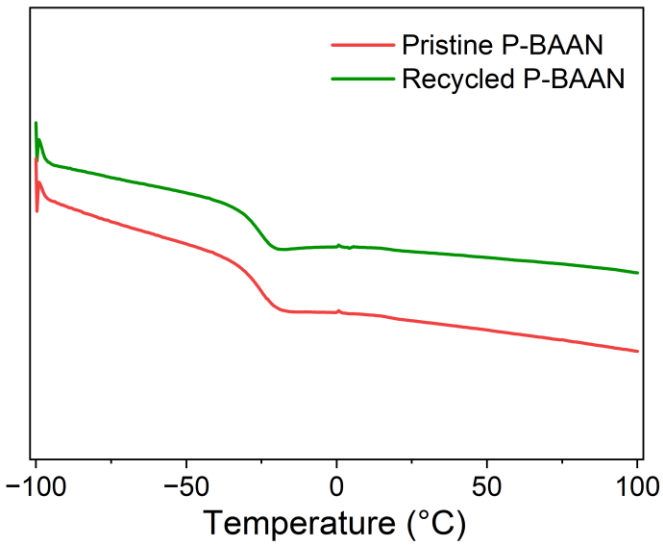

Figure S25. DCS thermogram of recycled P-BAAN in comparison to pristine BAAN.

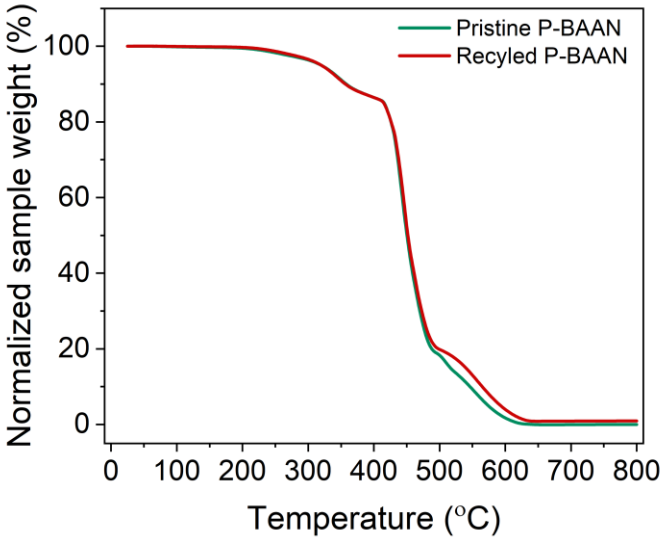

Figure S26. Dynamic TGA result of recycled P-BAAN in comparison to pristine BAAN (heating rate of 10 K·min^{-1} from 25 to 800 °C).

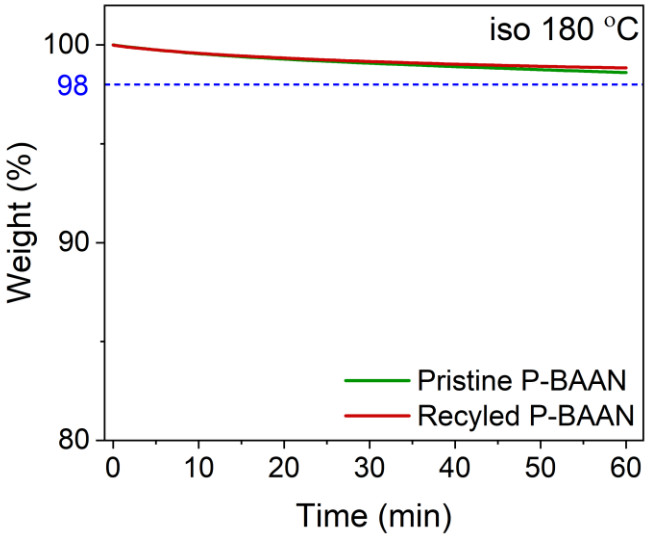

Figure S27. Isothermal TGA at 180 °C of recycled P-BAAN in comparison to pristine BAAN.

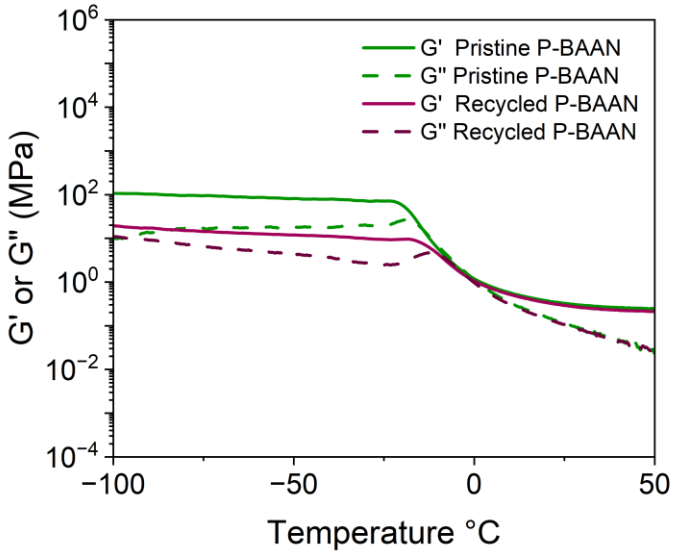

Figure S28. Dynamic mechanical thermal analysis of recycled P-BAAN in comparison to pristine BAAN. G’ and G” correspond to storage and loss moduli, respectively.