Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Tuneable and degradable thermosets possessing dynamic aliphatic disulfide bonds via stereoselective thiol-yne polymerisation

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Experimental methods

All compounds, unless otherwise indicated were purchased from commercial sources and used as received. The following chemicals were vacuum distilled prior to use and stored in Young's tap-ampoules under N_2: propiolic acid (Sigma-Aldrich $\geq$ 97%). Heating was applied using a stirring plate equipped with an oil bath. We acknowledge the molar mass between crosslinks calculator from the Konkolewicz group and Hubbard provided by the Macromolecular Alliance for Community Resources and Outreach.

NMR Spectroscopic Analysis. All NMR spectroscopy experiments were performed at 298 K on a Bruker DPX-400 NMR instrument equipped with a BBFO smart probe operating at 400 MHz for H (100.57 MHz for ^{13}C). ^{1}H NMR spectra are referenced to solvent residual proton (δ = 7.26 for $CDCl_3$) and ^{13}C NMR spectra are referenced to the solvent signal (δ = 77.16 for $CDCl_3$). The resonance multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).

Mass Spectrometry. High Resolution Electrospray Ionization Mass Spectrometry was performed in the School of Chemistry at the University of Birmingham on a Waters Xevo G2-XS QTof Quadrupole Time-of-Flight mass spectrometer.

Fourier-transform Infrared Spectroscopy (FTIR): All FTIR analyses were performed on an Agilent Technologies Cary 630 FTIR spectrometer at a resolution of 4 cm^{-1}. 16 Scans from 600 to 4000 cm^{-1} were performed and the spectra were corrected for background absorbance.

Size Exclusion Chromatography (SEC). SEC measurements were performed on an Agilent 1260 Infinity II Multi-Detector GPC/SEC System fitted with RI and ultraviolet (UV) detectors (λ = 309 nm) and PLGel 3 μm (50 × 7.5 mm) guard column and two PLGel

5 µm (300 × 7.5 mm) mixed-C columns with DMF containing 5 mM NH_4BF_4 as the eluent (flow rate 1 mL/min, 50 °C). A 12-point calibration curve ($M_p = 550$–2,210,000 g×mol^{-1}) based on poly(methyl methacrylate) standards (PMMA, Easivial PM, Agilent) was applied for the determination of molecular weights.

Differential Scanning Calorimetry (DSC). The thermal characteristics of the polymers were determined using differential scanning calorimetry (STARe system DSC3, Mettler Toledo) from −80 to 120 °C at a heating rate of 10 °C·min^{-1} for three heating/cooling cycles unless otherwise specified. The glass transition temperature (T_g) was determined from the inflection point in the second heating cycle of DSC. Total enthalpy of melting (ΔH_m) was calculated from the integration and normalization of all endothermic peaks present using the STARe software. The melting temperature was determined from the minimum value of the endothermic peak using the STARe software.

Thermogravimetric Analysis (TGA). TGA thermograms were obtained using a Q550 Thermogravimetric Analyzer (TA instruments). Thermograms were recorded under an N_2 atmosphere at a heating rate of 10 °C·min^{-1}, from 10 to 600 °C, with an average sample weight of *ca.* 5 mg. Aluminium pans were used for all samples. Decomposition temperatures were reported as the 5% weight loss temperature ($T_{d,5\%}$).

Dynamic Mechanical Analysis (DMA): Dynamic mechanical thermal analysis (DMTA) data were obtained using a Mettler Toledo DMA 1 star system and analysed using the software package STARe V13.00a. Thermal sweeps were conducted using films (L × W × thickness = 15 mm × 6 mm × 0.5 mm) cooled to −80 °C and held isothermally for ca. 5 minutes. Storage and loss moduli, as well as the loss factor (ratio of *E*" and *E*', tan δ) were probed as the temperature was swept from −80 to 180 °C, 5 °C·min^{-1}, displacement of 1 µm, frequency of 1 Hz. Stress-relaxation experiment was performed using films (L × W × thickness = 15 mm × 6 mm × 0.5 mm) cut from the networks, applying a displacement of 10 µm at 150 °C for 20 minutes.

Rheology: The flow characteristics of the polymers were studied using Anton Paar MCR302 rheometer with Peltier controlled heating. All tests were performed using parallel plates on disk-shape samples of 8 mm in diameter. For frequency sweep measurement, the frequency was varied from 100 Hz to 0.01 Hz at 25 °C, with a strain amplitude of 5%. For strain sweep measurements, strain was varied between 0.1% to 500% with a frequency of 1 rad/s.

Tensile testing. Dogbone shaped samples were cut using custom ASTM Die D-638 Type 5. Uniaxial tensile testing was performed using a Testometric M350-5CT universal mechanical testing instrument fitted with a load cell of 10 kN. Each specimen was clamped into the tensile holders and subjected to an elongation rate of 10 $mm \cdot min^{-1}$ until failure with an applied pretension of 0.1 N. All tensile tests were repeated 3 times (unless otherwise stated), and an average of the data was taken to find the ultimate tensile stress and strain. Data was analysed using winTest™ Analysis software (v.5.0.34) and OriginPro® software. Young modulus was calculated by taking the slope of the tensile curve at 1% strain. Toughness was calculated as the area under the curve up to break.

Reprocessing. Networks flakes were reprocessed with a 3 Specac Atlas™ Manual Hydraulic Press 15T fitted with Specac heated plates. The pieces were added into a stainless-steel mold and placed into a pre-heated press at 150 °C. The sample was heated for 20 min (3000 kg pressure) before degassing 3 × (3000 kg pressure/release). Then, the samples were left to cool under pressure until the temperature reached 25 °C.

Swell testing and gel fraction: Networks were taken and cut into disks (6.7 × 0.5 mm) and weighed before being submerged in chloroform ($CHCl_3$) and allowed to swell until equilibrium swelling was reached after 30 hours. The initial mass (W_i) and swelling mass (W_s) were used to calculate the swelling ratio (%) as shown in equation S1, where W_s is given by subtracting W_i from the sample mass measured rapidly after being removed from the solvent. The swollen networks were resubmerged in new $CHCl_3$ and finally dried after filtration to get the dry mass (W_d). This was used to calculate the gel fraction (%) as shown in equation S2.

Equation S1[1]

$$Swelling\ ratio\ (\%) = \frac{W_s}{W_i} \times 100$$

Equation S2[1]

$$Gel\ fraction\ (\%) = \frac{W_d}{W_i} \times 100$$

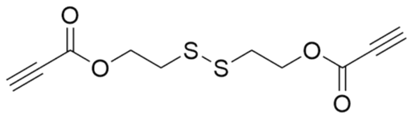
Equation S3[1, 2]

$$M_c = 3\frac{\rho RT}{E^{\prime}_{rubbery}}$$

Equation S4

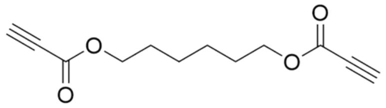
$$\%Wt_{SSbond} = \frac{\left({}^{MW_{SS}} \big/ {}_{MW_{C_2SS}} \right) \times m_{C_2SS}}{total\ m_{network}} \times 100$$

Synthetic procedures



Disulfide dipropiolate (C_2SS): Monomer C_2SS was prepared by adapting a procedure reported by Hüppe *et al.*[3] Bis(2-hydroxyethyl) disulfide (5.3 g, 34.5 mmol), propiolic acid (9.7 g, 137.8 mmol) and *para*-toluenesulfonic acid (*p*-TsOH) (0.66 g, 3.45 mmol) were solubilised in toluene (150 mL) under stirring in a two-necks round bottom flask (250 mL) equipped with a Dean-Stark apparatus and degassed with N_2 gas for 10 minutes. Temperature was increased until reflux occurred (ca. 130 °C) and the reaction was left running overnight (ca. 16 h). The reaction mixture was then allowed to cool down at room temperature and excess of propiolic acid was neutralised *via* the addition of $NaHCO_{3(aq.)}$ sat. solution under vigorous stirring. The mixture was then transferred to a separatory funnel and washed with $NaHCO_{3(aq.)}$ sat. solution (3×30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *via* a rotary evaporator to obtain a dark viscous fluid. The product was purified *via* column chromatography performed following the procedure described by Still *et al.*[4] using a mixture of ethyl acetate and hexane (1:3 v/v) as the mobile phase. The product was isolated as a slightly yellow liquid that solidified upon standing. The solid product was recrystallised from ethyl acetate/hexane to obtain colourless crystals (4.11 g, 46% yield) with characterisation data in agreement with previously reported results.[3]

^1H NMR (400 MHz, Chloroform-*d*) $\delta = 4.46$ (t, $J = 6.6$ Hz, 4H), 2.98 (t, $J = 6.6$ Hz, 4H), 2.92 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) $\delta = 152.48, 75.54, 74.45, 64.04, 36.86$. HRMS (TOF-MS-EI$^+$) (m/z): $[M]^+$ calculated for $C_{10}H_{10}O_4S_2$, 259.0049; found, 259.0047.



Hexane dipropiolate (C_6): 1,6-hexanediol (5 g, 42.31 mmol), propiolic acid (7.81 mL, 126.93 mmol) and *p*-toluenesulfonic acid monohydrate (4.02 g, 21.15 mmol) were stirred in toluene (90 mL) in a 250 mL round bottom flask equipped with a Dean-Stark apparatus. The temperature was raised until reflux occurred and the reaction was left running for 17 h. The solvent was removed *via* a rotary evaporator and column chromatography (Hex:EtOAc 2:1) was performed on the crude reaction mixture. The product was further purified *via* recrystallisation (hexane) to yield white crystals (7.5 g, 80%) with spectroscopic data in agreement with previously published results.[5]

^{1}H NMR (400 MHz, Chloroform-*d*) $\delta = 4.20$ (t, $J = 6.6$ Hz, 4H), 2.87 (s, 2H), 1.69 (q, $J = 6.5$ Hz, 4H), 1.47 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) $\delta = 152.9$, 74.9, 74.8, 66.3, 28.3, 25.6. HRMS (TOF-MS-EI$^+$) (m/z): $[M+Na]^+$ calculated for $C_{12}H_{14}O_4Na$, 245.0790: found, 245.0788.

General synthesis of network: Dipropiolate monomers in the desired ratio were solubilised in $CHCl_3$ in the presence of trimethylolpropane tris(3-mercaptopropionate) (3-AT) to achieve a final thiol:alkyne ratio of 1:1 or 1.5:1, keeping the concentration of thiol at 0.3 M. The mixture was cooled for 10 minutes in an ice bath. The catalyst (triethylamine (Et_3N) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)) was then added to the mixture and was subsequently poured into a Teflon beaker covered with tin foil. The solvent was left evaporating inside a fumehood until free standing films could be recovered. Networks were then dried in a vacuum oven at 50 °C until a constant weight was reached.

Degradation experiment: Disks used to perform *gel-sol* analysis were placed in DMF with a final concentration of 20 mg/mL in a 7 mL vial. SEC analysis was performed to evaluate the presence of oligomers after the addition of the solvent and after a 24-hour period revealing the absence of degradation. Dithiothreitol (DTT) (1 equiv. to disulfide equivalent) was added to the vials that were stirred on an orbital shaker at 250 rpm until the networks were not visible anymore (*ca.* 60 h). Aliquotes (50 µL) were taken throughout the experiment to monitor the degradation *via* SEC. The experiment was conducted at room temperature. The oligomers were isolated by diluting the reaction mixture with $LiCl_{aq.}$ 10% w/w and extracted with dichloromethane (CH_2Cl_2).

NMR spectroscopy of synthesised monomers

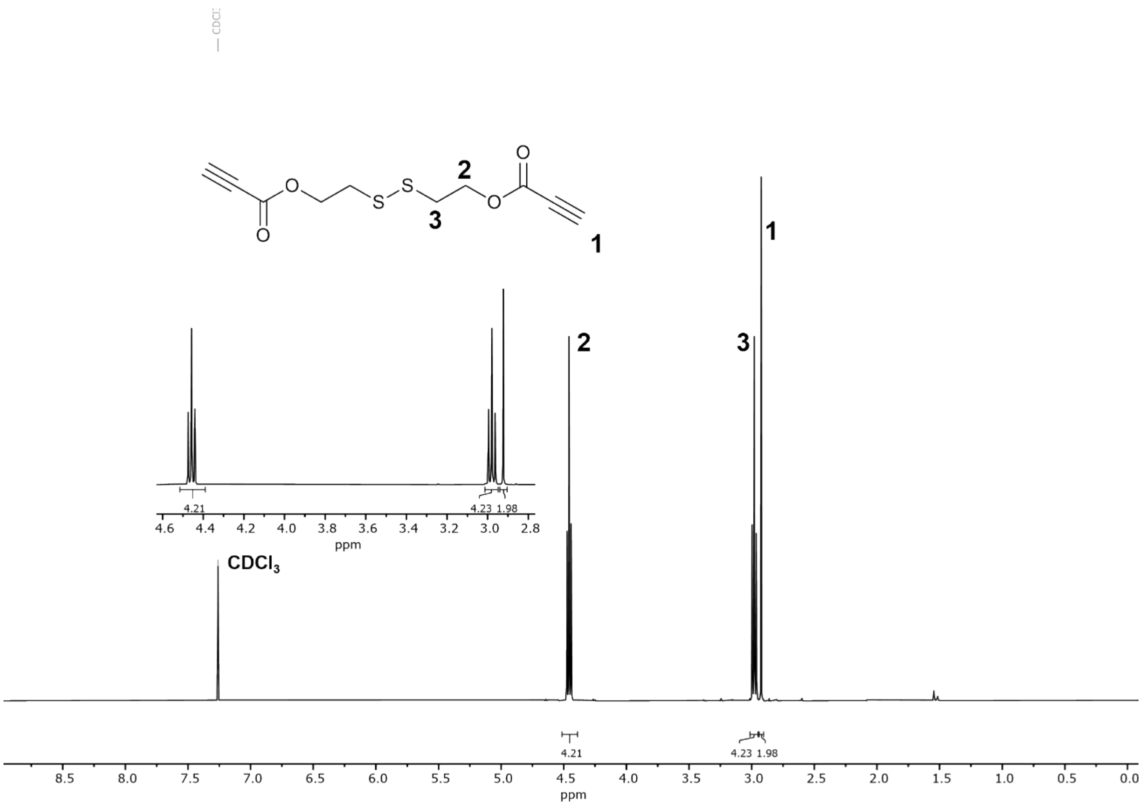


Figure S1. C_2SS ^1H NMR spectrum – 400 MHz, 298 K, $CDCl_3$.

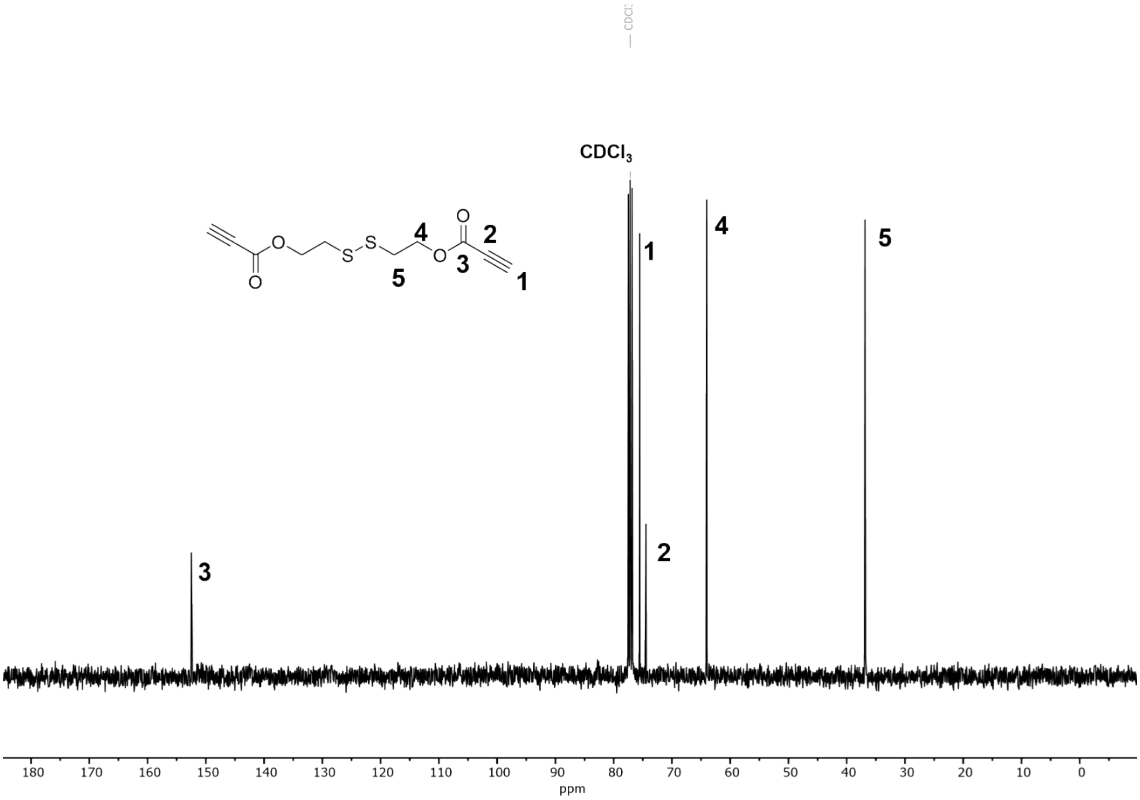


Figure S2. C_2SS ^{13}C NMR spectrum – 100.57 MHz, 298 K, $CDCl_3$

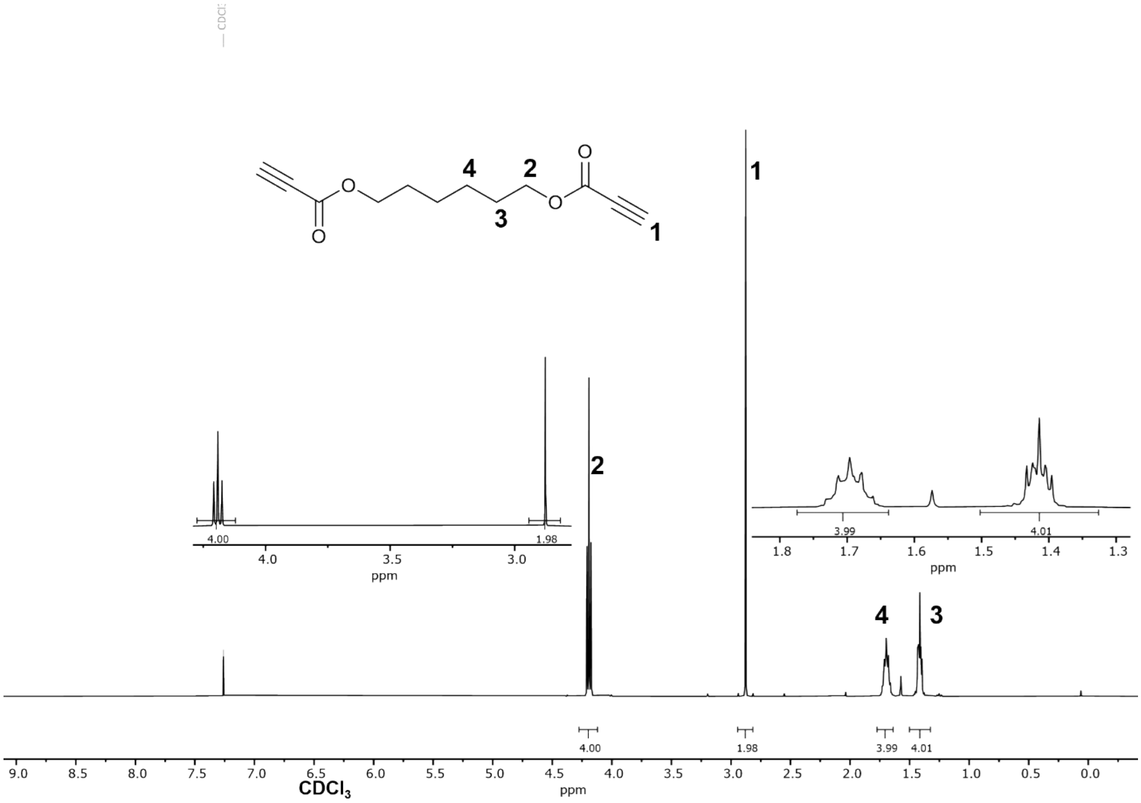


Figure S3. C_6 ^1H NMR spectrum – 400 MHz, 298 K, $CDCl_3$.

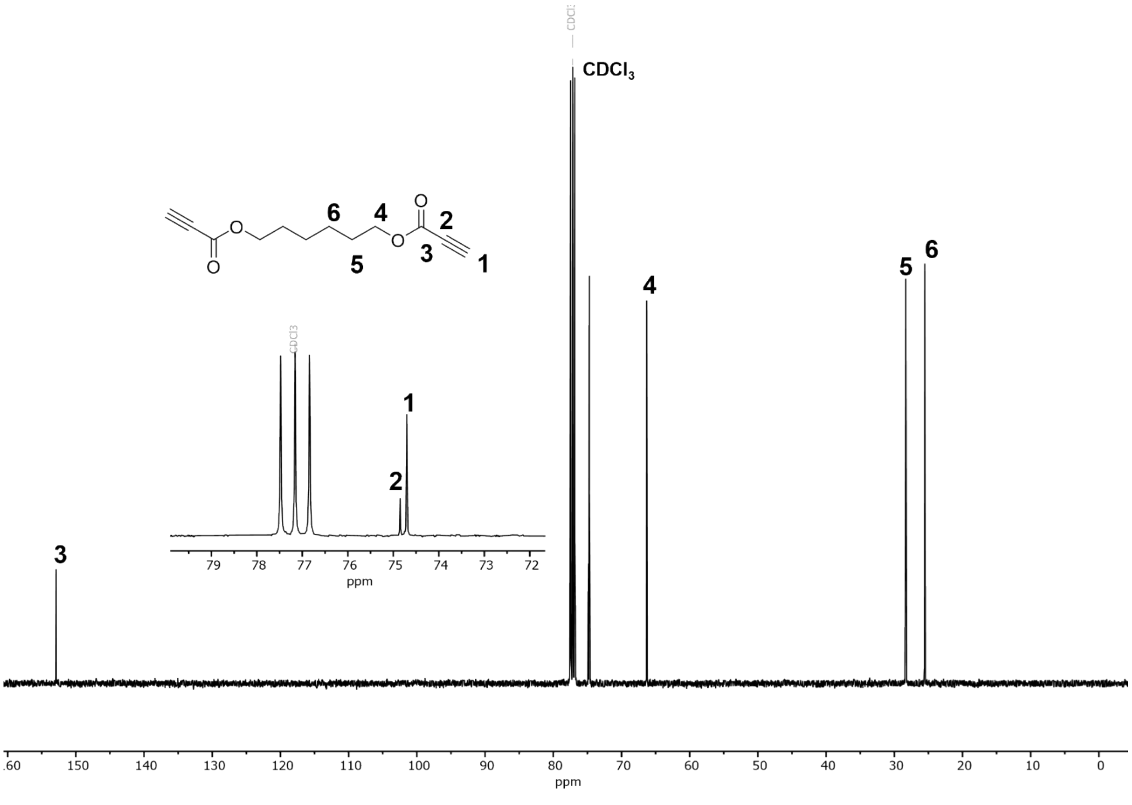


Figure S4. C_6 ^{13}C NMR spectrum – 100.57 MHz, 298 K, $CDCl_3$

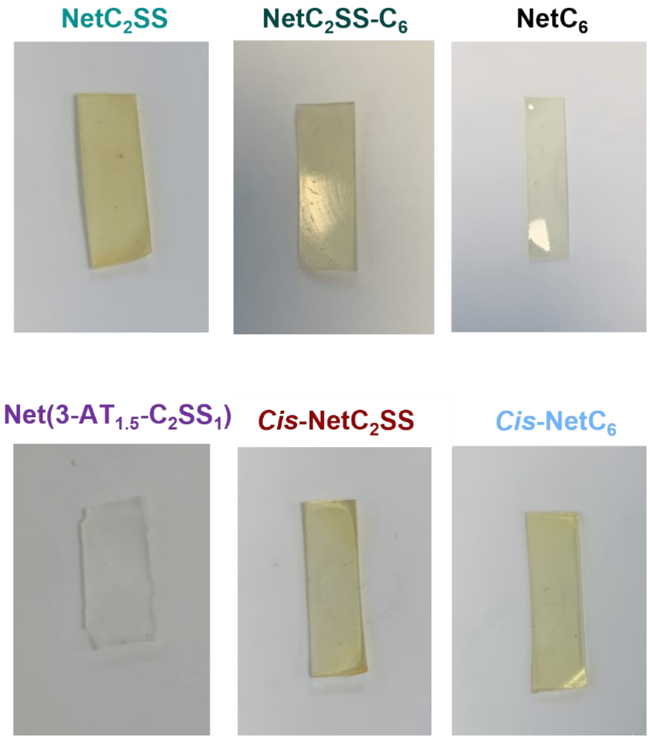


Figure S5. Exemplar DMA testing bars cut from the networks synthesised in this work.

Thermomechanical characterisation

Table S1. Summary of swelling ratio and gel content for the networks synthesised in this work

Name	**Swelling ratio[a] [%]**	**Gel fraction [%]**
Trans-NetC$_2$SS	358±90	91.3±0.7
Trans-Net(C$_2$SS-C$_6$)	335±49	91.6±0.6
Trans-NetC$_6$	466±43	92.3±1
Trans-Net((3-AT$_{1.5}$-C$_2$SS$_1$)	285±41	83.6±0.4
Cis-NetC$_2$SS	247±17	91.6±0.9
Cis-NetC$_6$	506±19	90.4±3.7

[a]*Determined via gravimetry (Equation S1)*

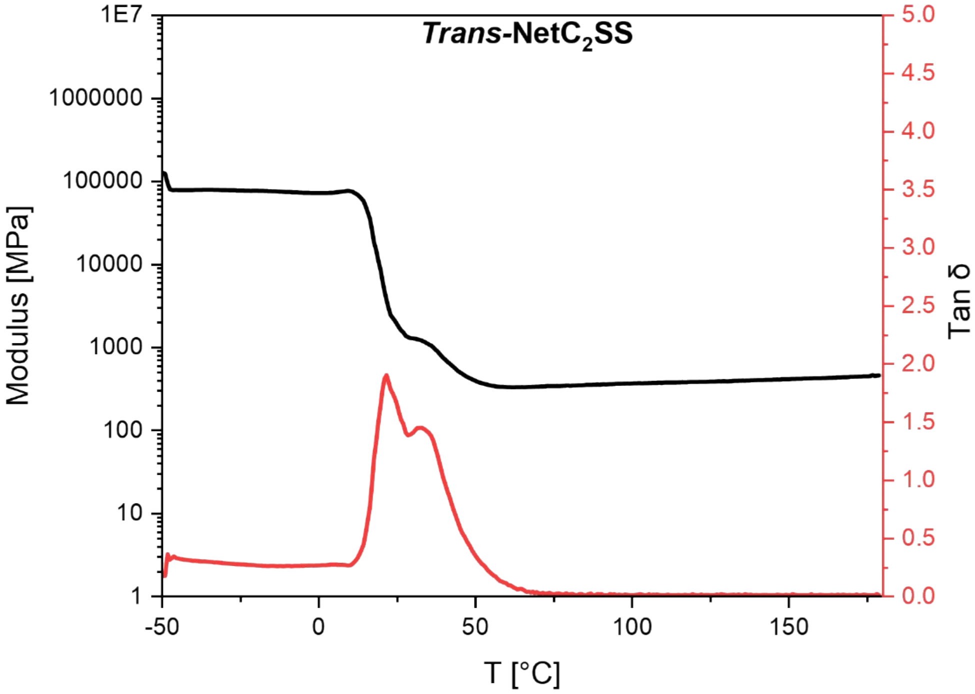


Figure S6. DMA thermogram (−50 – 180 °C, 1 Hz, 1 µm) of *Trans*-NetC$_2$SS.

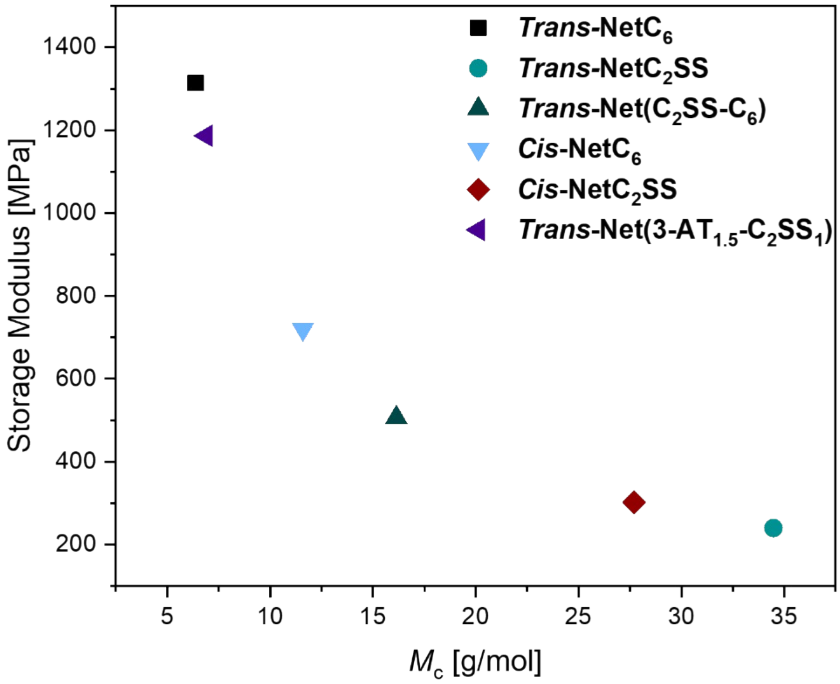


Figure S7. Correlation between M_c and storage modulus calculated at T_g + 50 °C.

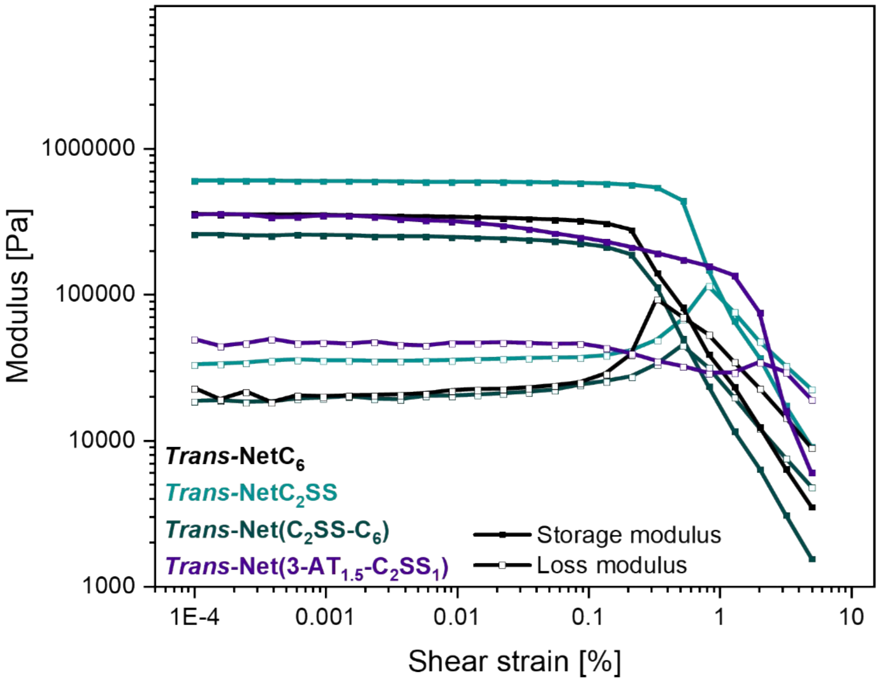


Figure S8. Amplitude sweeps (25 °C, 0.1 to 500% strain, 1 rad/s) of networks.

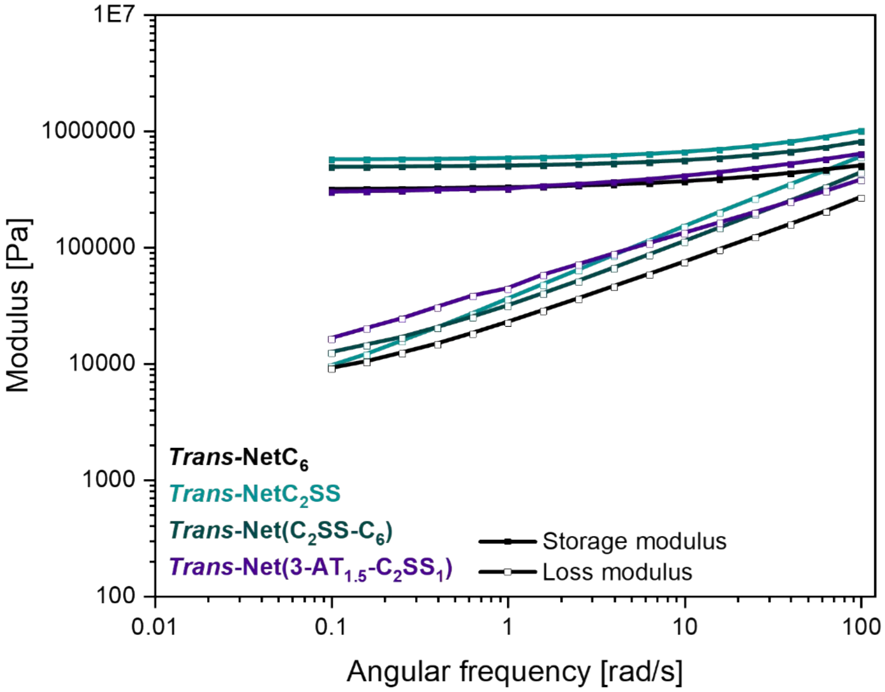


Figure S9. Frequency sweeps (25 °C, strain amplitude 5 %) of networks.

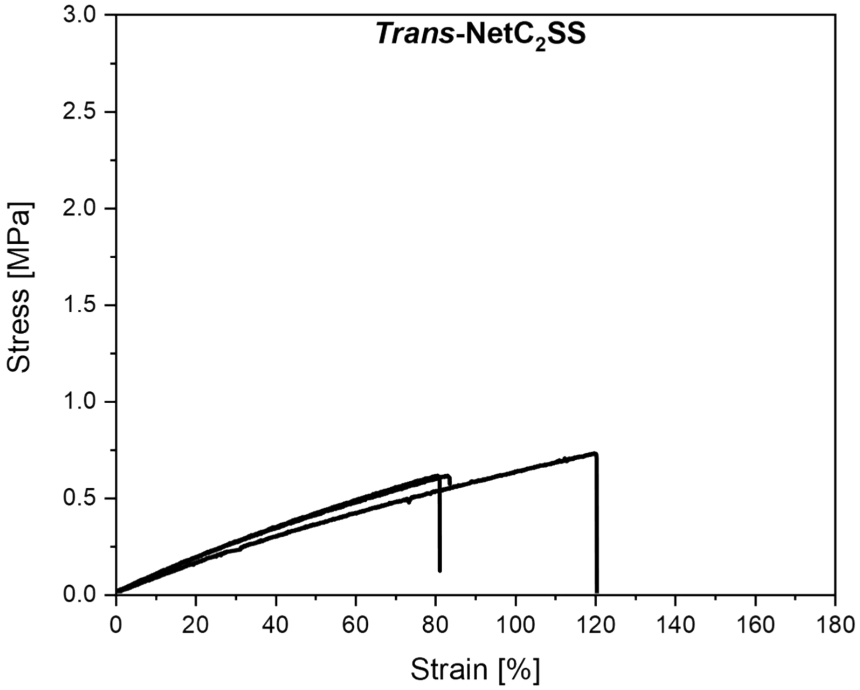


Figure S10. Stress *vs*. strain curves obtained from uniaxial tensile testing (22 °C, 10 mm/min) of *Trans*-NetC$_2$SS.

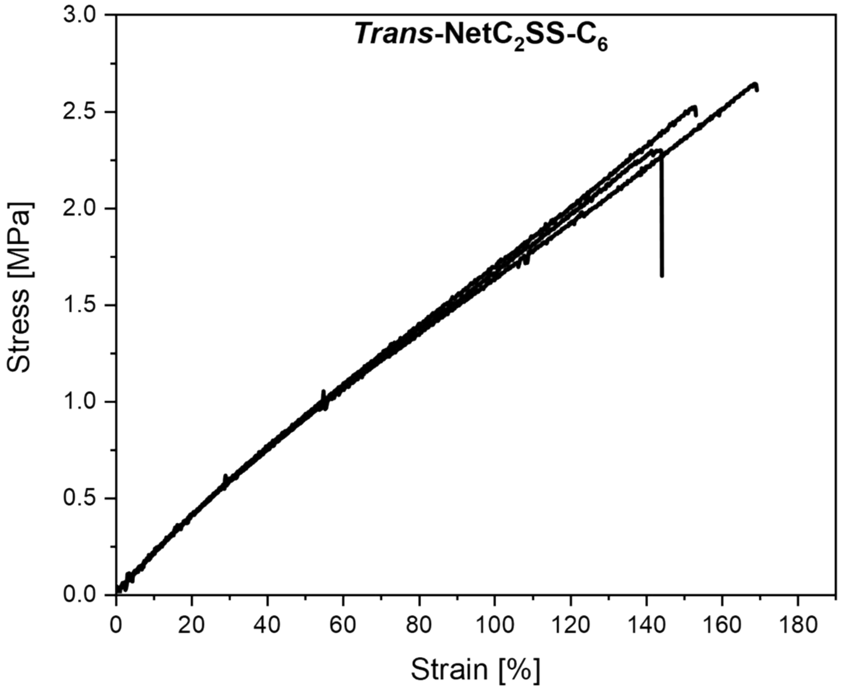


Figure S11. Stress *vs*. strain curves obtained from uniaxial tensile testing (22 °C, 10 mm/min) of *Trans*-Net(C$_2$SS-C$_6$).

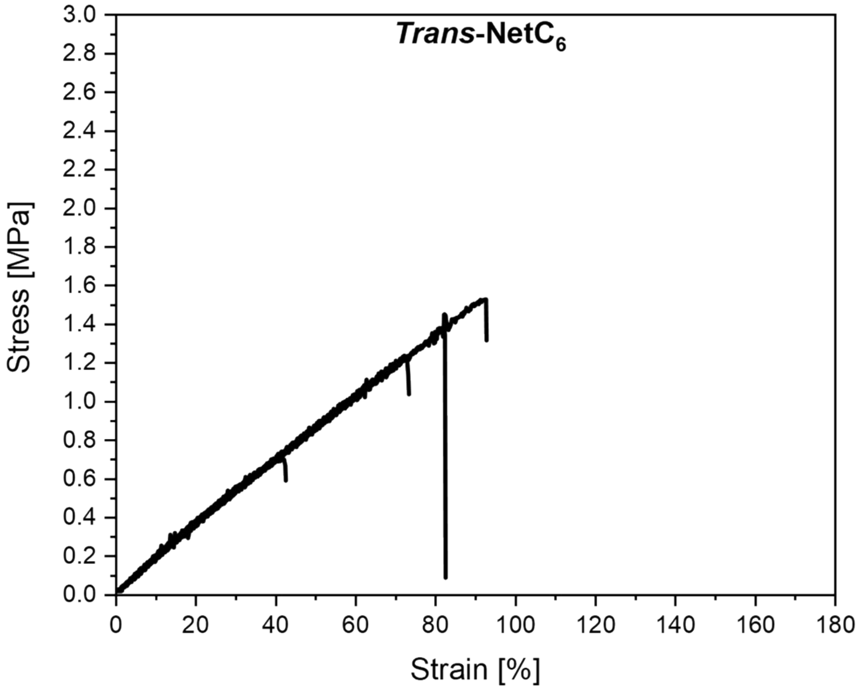


Figure S12. Stress *vs*. strain curves obtained from uniaxial tensile testing (22 °C, 10 mm/min) of *Trans*-NetC$_6$.

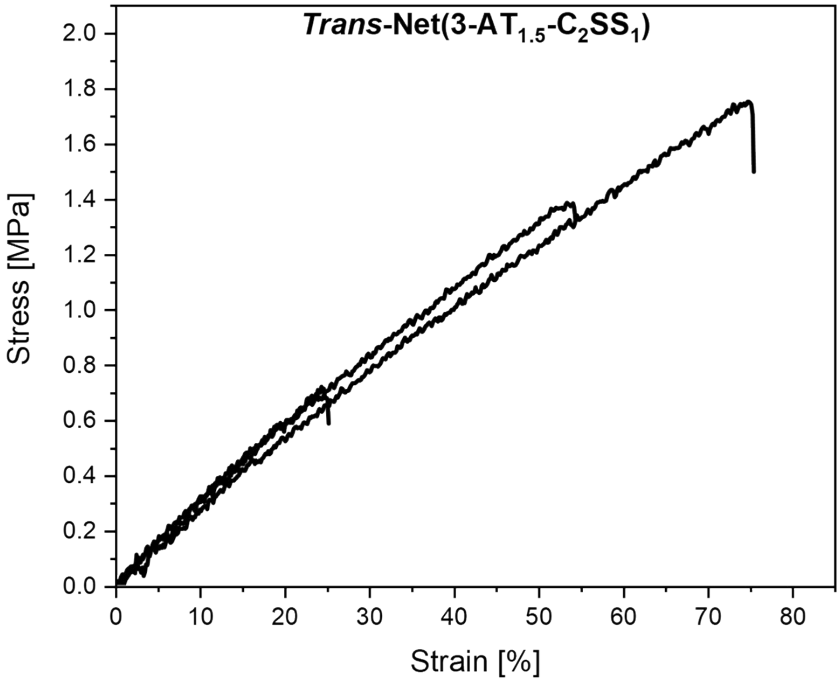


Figure S13. Stress *vs*. strain curves obtained from uniaxial tensile testing (22 °C, 10 mm/min) of *Trans*-Net(3-AT$_{1.5}$-C$_2$SS$_1$).

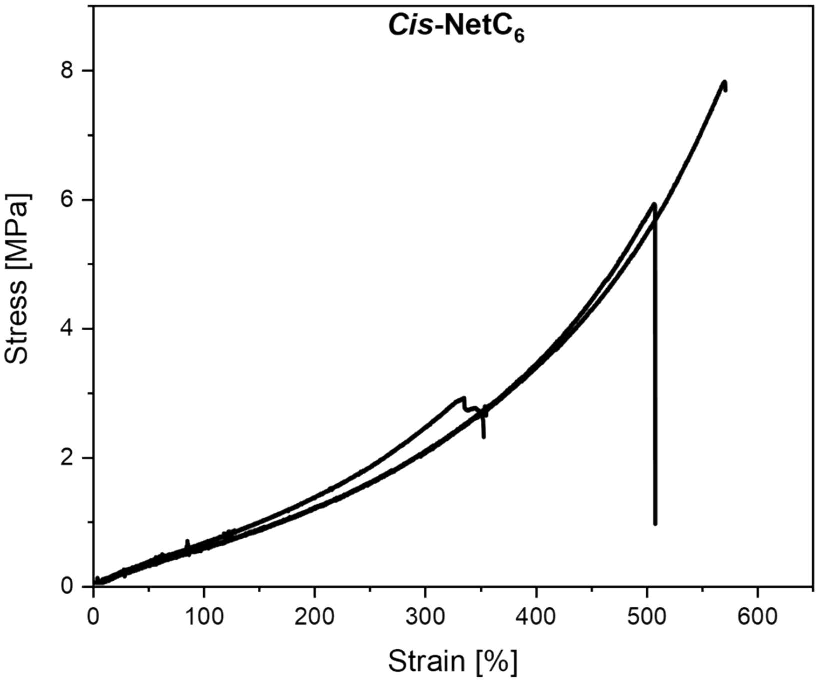


Figure S14. Stress *vs.* strain curves obtained from uniaxial tensile testing (22 °C, 10 mm/min) of *Cis*-NetC$_6$.

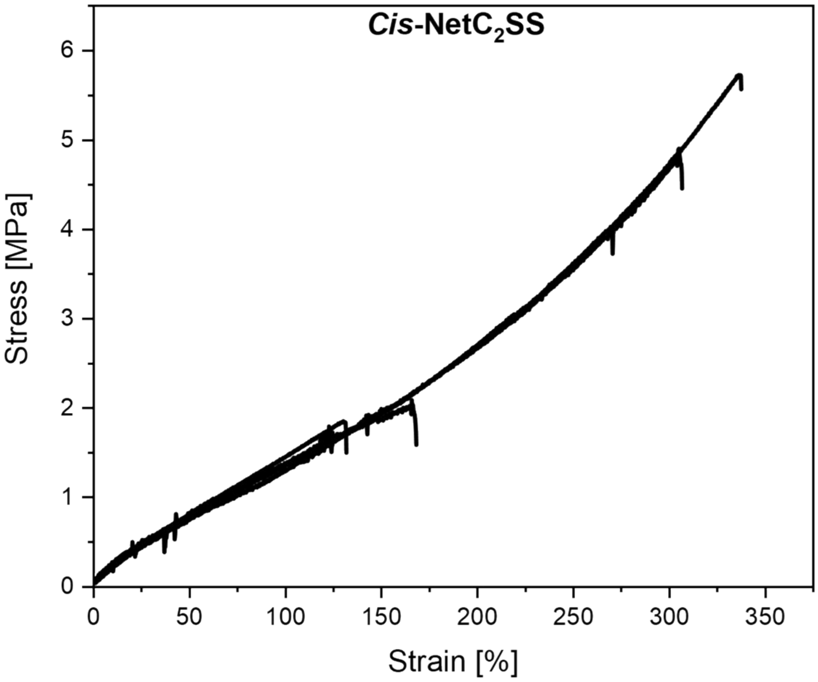


Figure S15. Stress *vs.* strain curves obtained from uniaxial tensile testing (22 °C, 10 mm/min) of *Cis*-NetC$_2$SS.

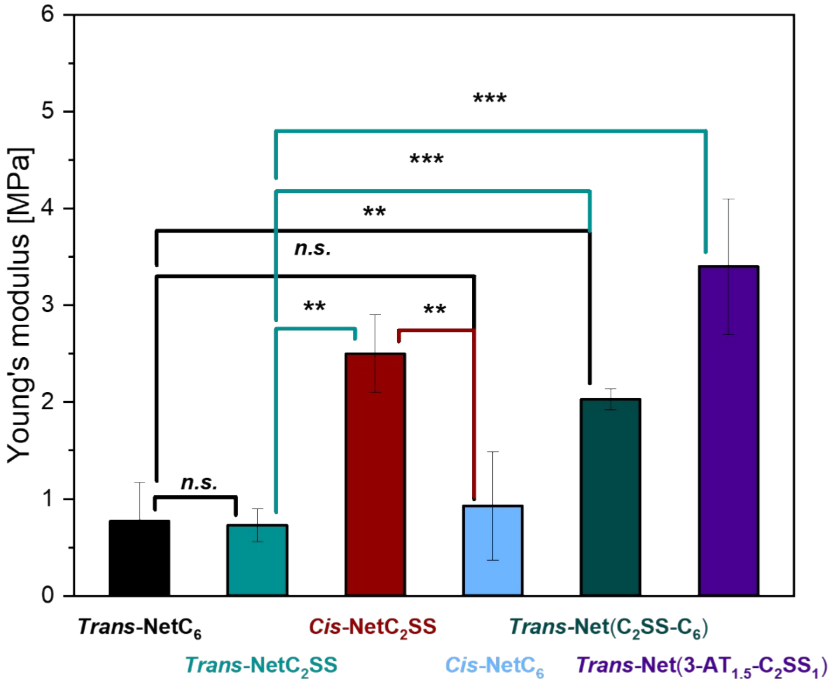


Figure S16. Averaged Young's modulus values [MPa] of different networks. Plot represents the mean, and the error bars represent standard deviation (n = 3, independent samples). Statistical significance and P values are determined by using the two-sided unpaired t test. n.s. = not significant; * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$.

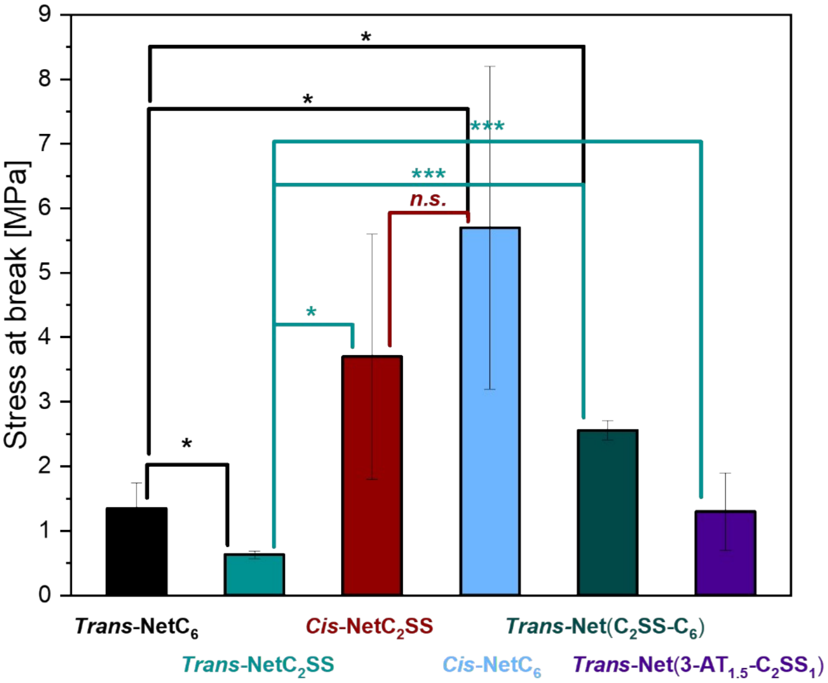


Figure S17. Averaged stress at break values [MPa] of different networks. Plot represents the mean, and the error bars represent standard deviation (n = 3, independent samples). Statistical significance and P values are determined by using the two-sided unpaired t test. n.s. = not significant; * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$.

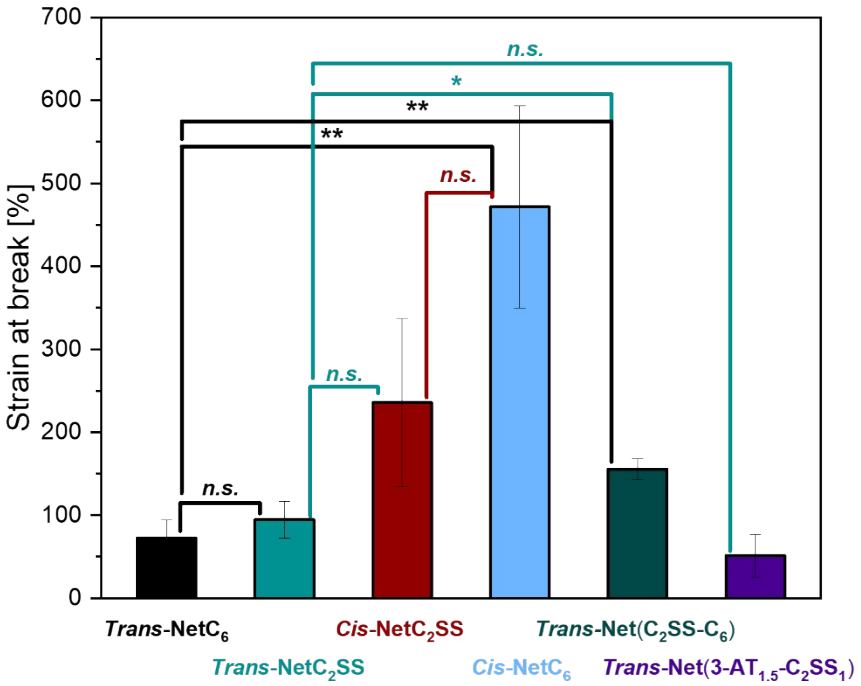


Figure S18. Averaged strain at break [%] of different networks. Plot represents the mean, and the error bars represent standard deviation (n = 3, independent samples). Statistical significance and P values are determined by using the two-sided unpaired t test. n.s. = not significant; * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$.

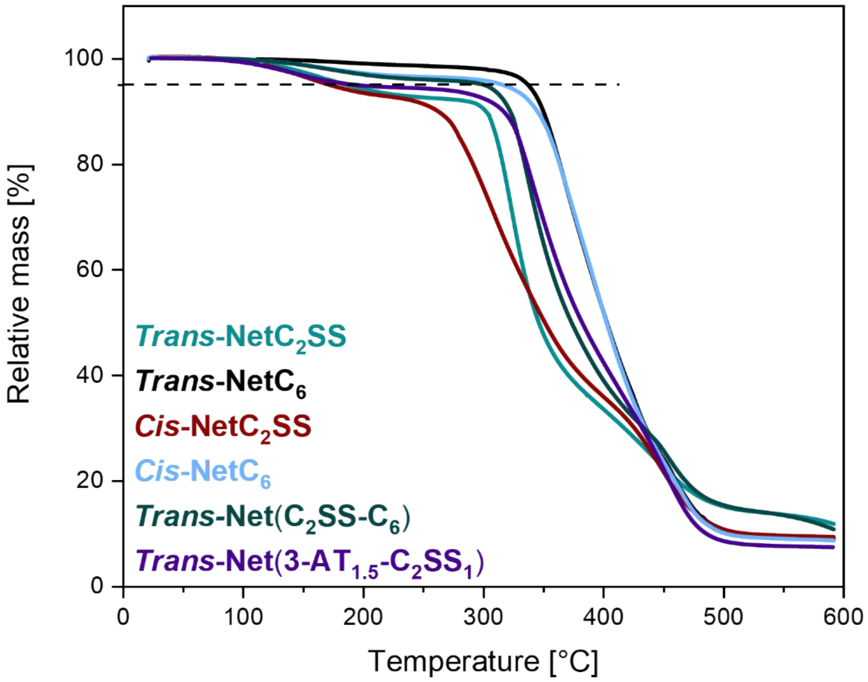


Figure S19. TGA thermogram (25 – 600 °C, N_2) of different networks synthesised in this work.

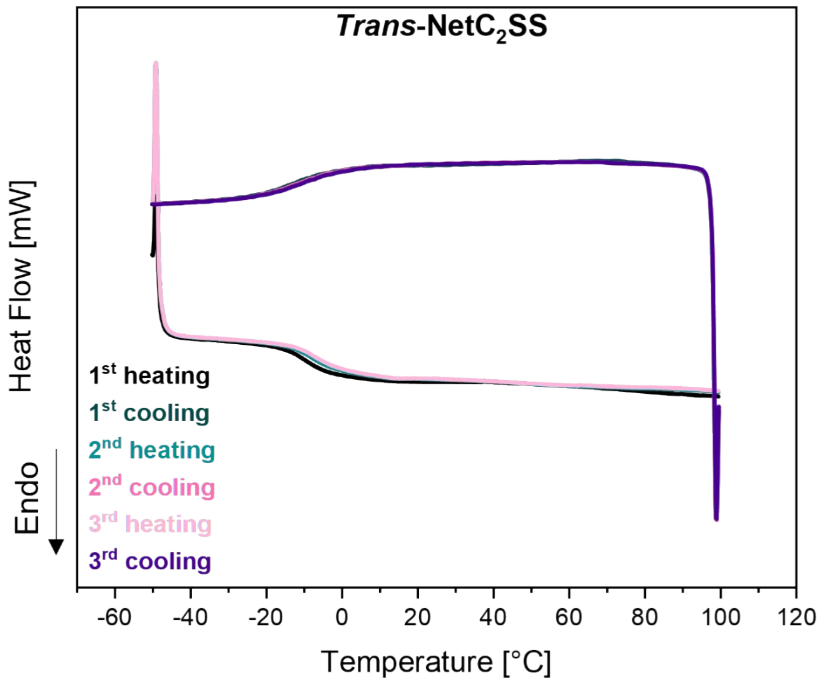


Figure S20. DSC thermogram (−50 – 100 °C, N_2) of *Trans*-NetC_2SS.

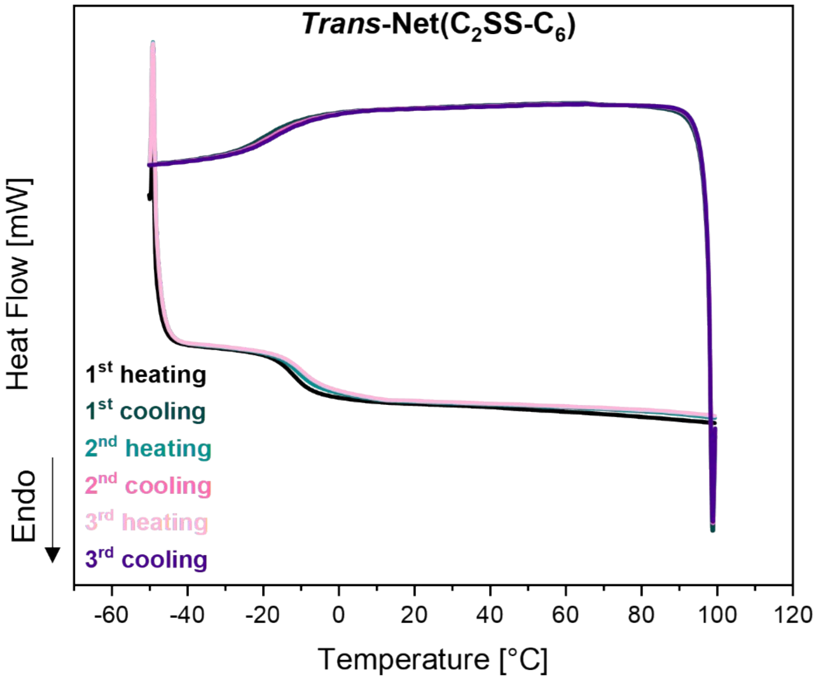


Figure S21. DSC thermogram (−50 – 100 °C, N_2) of *Trans*-Net(C_2SS-C_6).

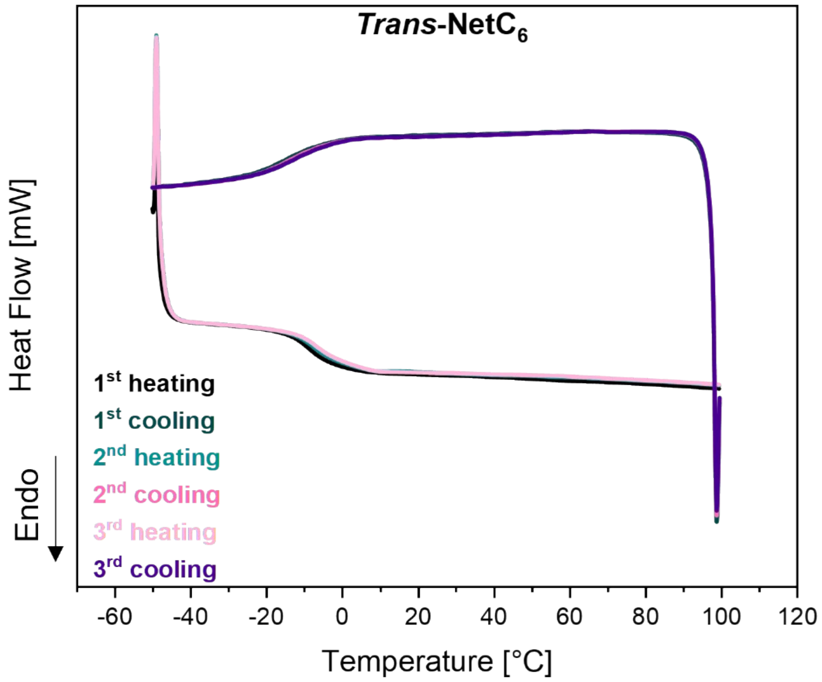


Figure S22. DSC thermogram (−50 – 100 °C, N_2) of *Trans*-NetC_6.

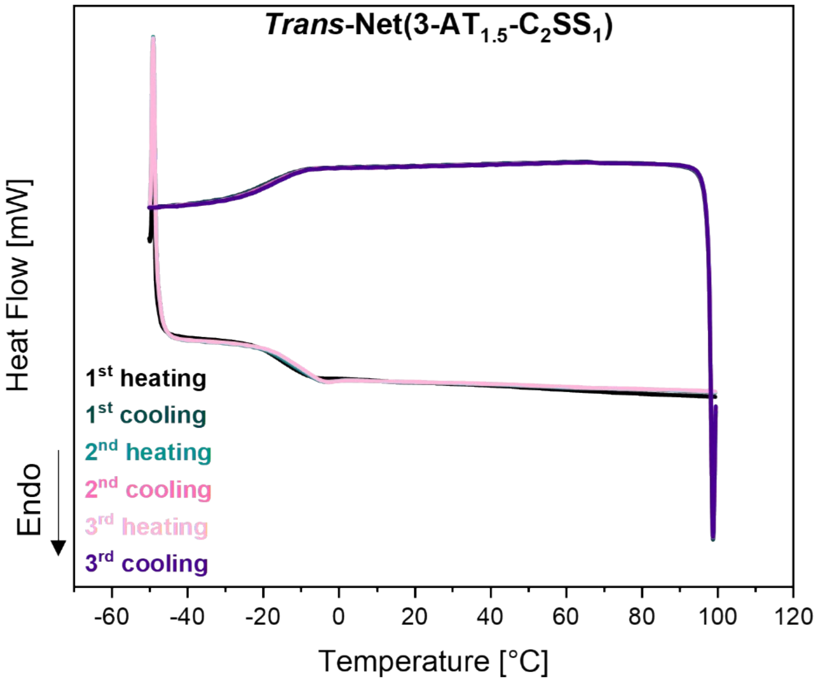


Figure S23. DSC thermogram (−50 – 100 °C, N_2) of *Trans*-Net(3-$AT_{1.5}$-C_2SS_1).

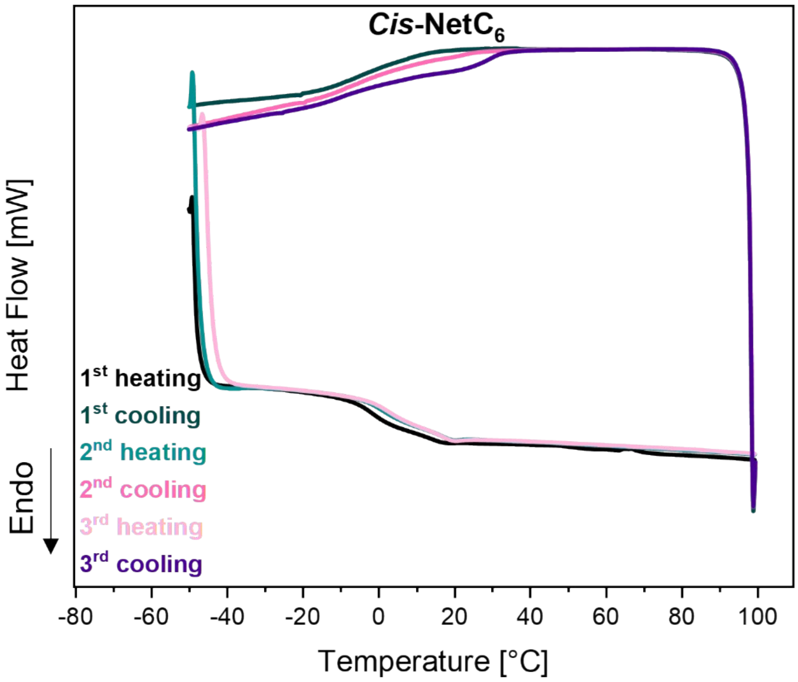


Figure S24. DSC thermogram (−50 – 100 °C, N_2) of *Cis*-NetC$_6$.

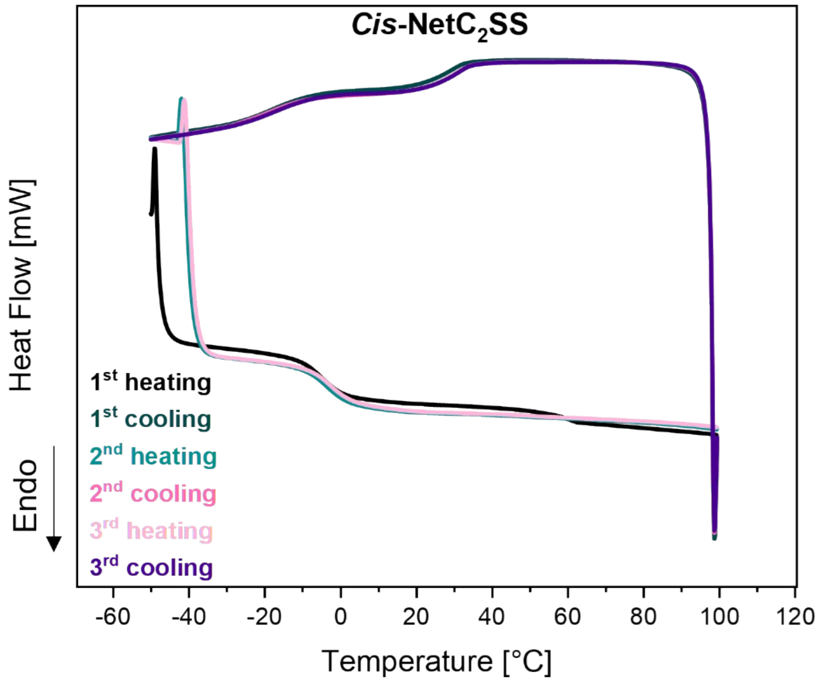


Figure S25. DSC thermogram (−50 – 100 °C, N_2) of *Cis*-NetC_2SS.

Degradation study

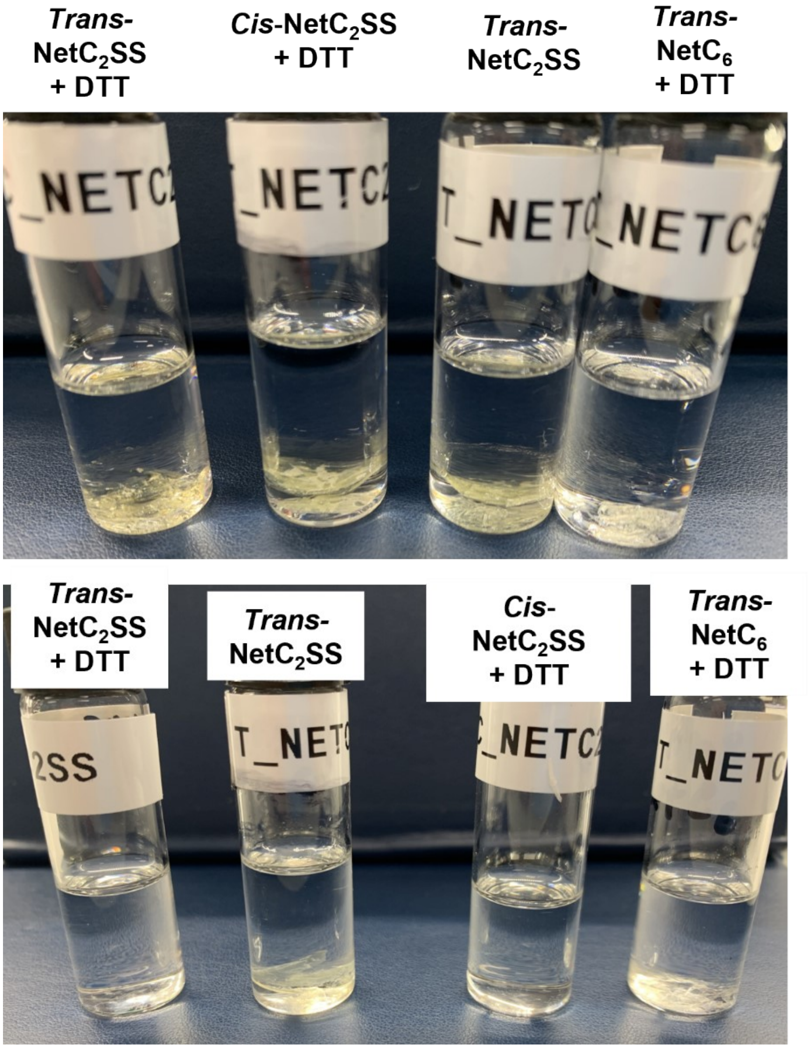


Figure S26. Networks in DMF (20 mg/mL) before (top) and after (bottom) DTT induced degradation.

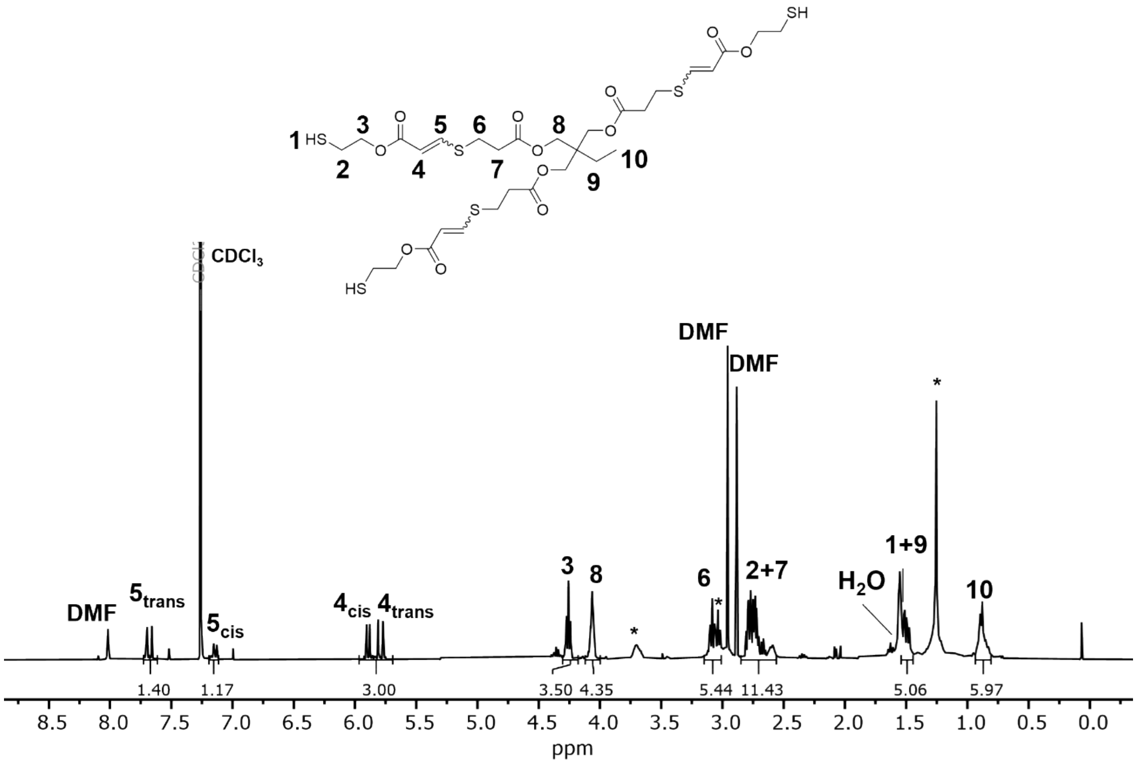


Figure S27. ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of the reaction crude after aqueous washing obtained from *Cis*-NetC_2SS degradation. Residual DTT marked with asterisk.

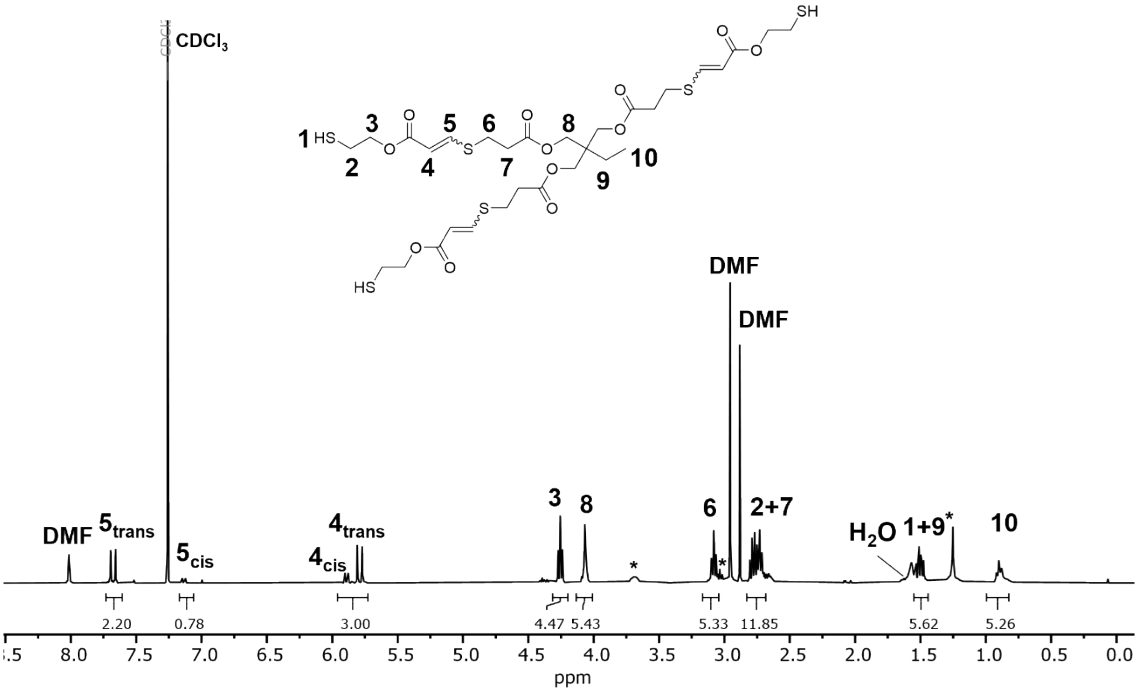


Figure S28. ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of the reaction crude after aqueous washing obtained from *Trans*-NetC_2SS degradation. Residual DTT marked with asterisk.

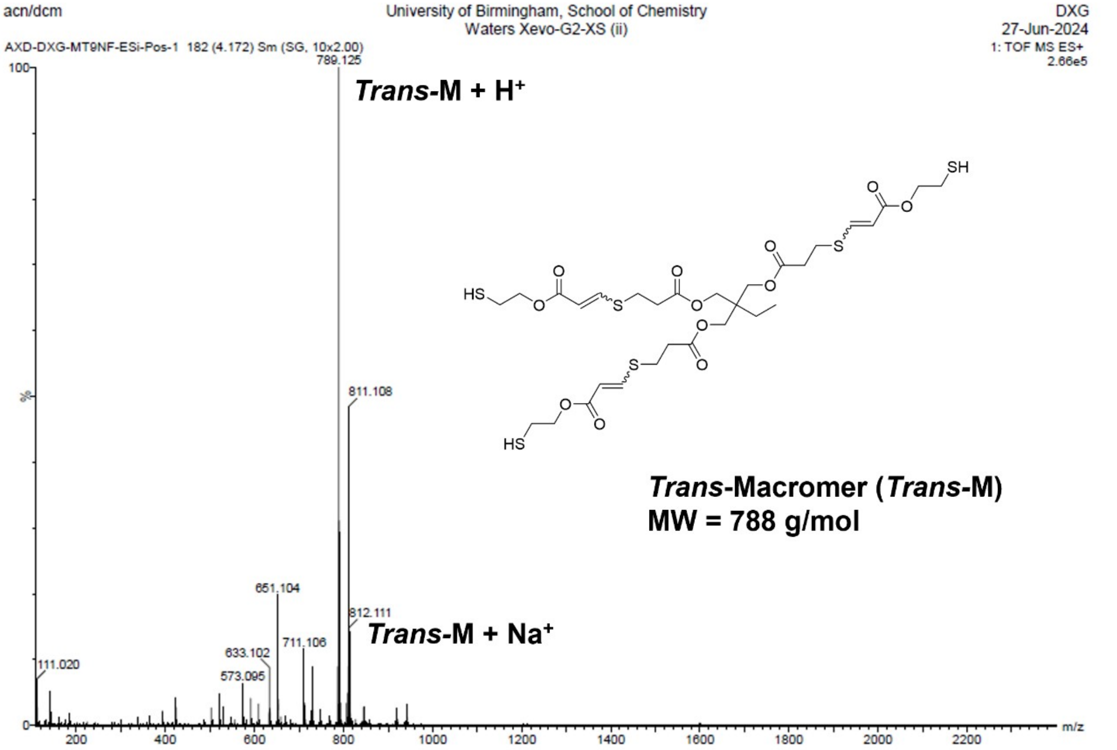


Figure S29. Mass spectrum (ES+) of the reaction crude after aqueous washing obtained from *Trans*-NetC$_2$SS degradation. Plausible structure associated with the most abundant peak is represented.

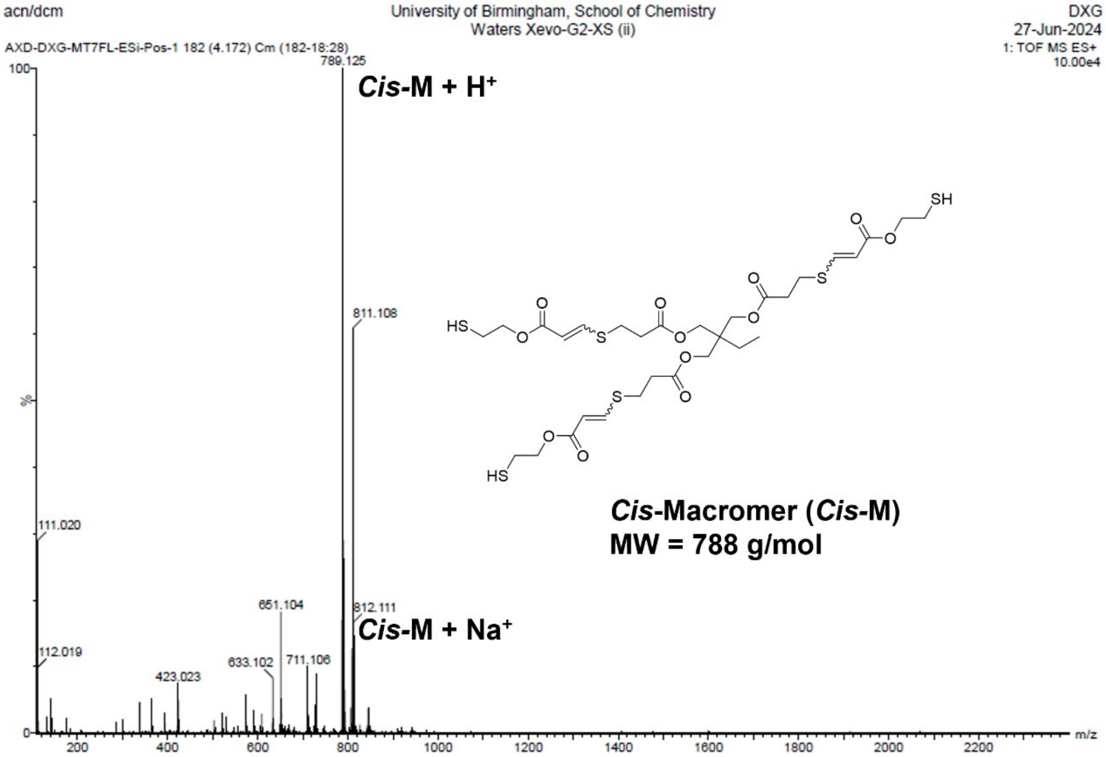


Figure S30. Mass spectrum (ES+) of the reaction crude after aqueous washing obtained from *Cis*-NetC$_2$SS degradation. Plausible structure associated with the most abundant peak is represented.

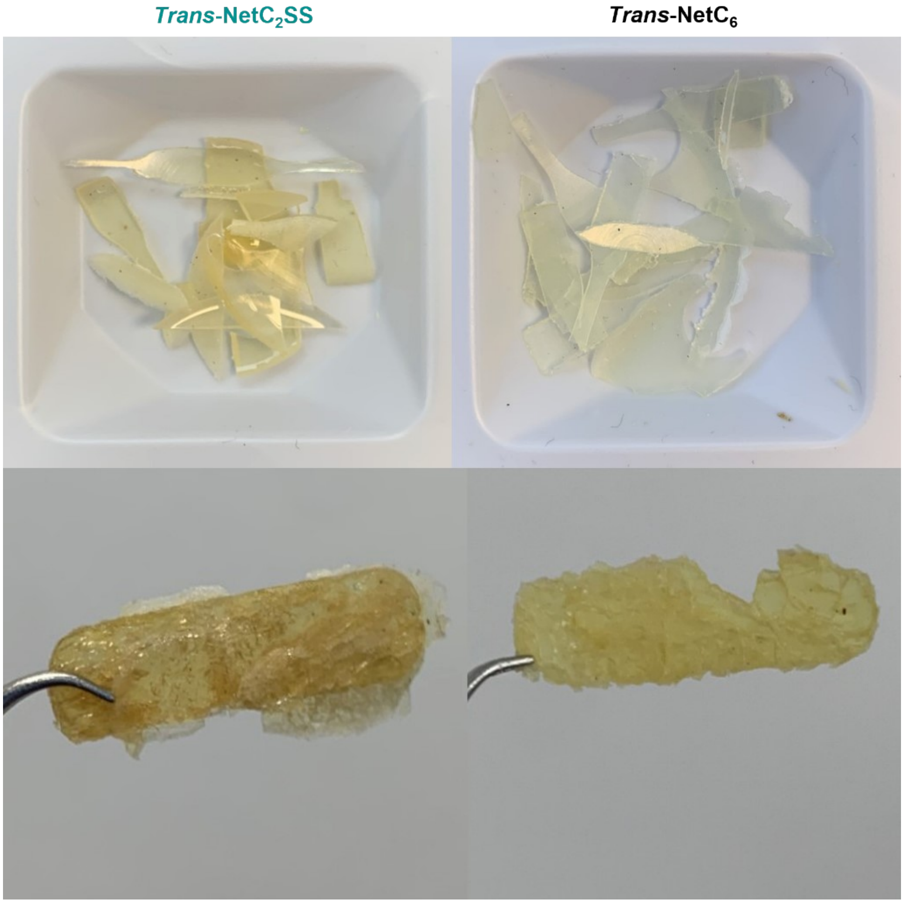


Figure S31. Fragments of *Trans*-NetC$_2$SS and *Trans*-NetC$_6$ (top) that were reprocessed into free-standing films (bottom) after heat compression moulding at 150 °C for 20 minutes, at a pressure of 3000 kg.

References

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