Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Cross-linker Control of Vitrimer Flow

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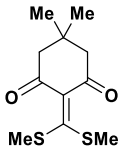
Cross-linker Synthesis

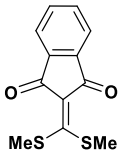
The Meldrum's Acid derived cross-linker (**MA**) and barbituric acid derived cross-linker (**BA**) were synthesized based on previously reported procedures by Wentrup[1] and Kuhn,[2] respectively. All reactions were performed under nitrogen or argon with anhydrous DMF obtained by passing degassed solvents through activated alumina columns. Chemicals were obtained from MilliporeSigma, TCI Chemicals, Alfa Aesar, and Oakwood.

2-(bis(methylthio)methylene)-5,5-dimethylcyclohexane-1,3-dione (CY):



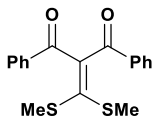
To a solution of 5,5-dimethylcyclohexane-1,3-dione (5 grams, 35.7 mmol, 1 equiv.) and potassium carbonate (K_2CO_3, 24.6 g, 178 mmol, 5 equiv.) under argon and in 100 mL of dry DMF, was added carbon disulfide (2.99 g, 2.69 mL, 44.6 mmol, 1.25 equiv.) dropwise over 5 minutes at room temperature. The mixture flushed dark red and was stirred at room temperature for 2 hours. The flask was then placed in an ice bath, and iodomethane, (5.58 mL, 12.7 g, 89.2 mmol, 2.5 equiv.) was added dropwise over 10 minutes. The mixture was allowed to warm slowly to room temperature over the course of 18 hours. The mixture was then diluted with water, extracted into ethyl acetate, and washed with brine. The organic layers were concentrated in *vacuo* to give a viscous red liquid and triturated in pentane to yield an orange solid, which was further recrystallized from hexane to give orange crystals (2.12 g, 24%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.55 (s, 10 H), 1.08 (s, 1H). Spectral data were consistent with literature reports.[3]

2-(bis(methylthio)methylene)-1H-indene-1,3(2H)-dione (IND):



To a solution of 1,3-indanedione (1.0 grams, 6.84 mmol, 1 equiv.) and sodium hydride (NaH {60 wt% in mineral oil}, 0.41 grams, 10.5 mmol, 1.5 equiv.) in 30 mL of dry DMF, was added carbon disulfide (0.4 mL, 6.9 mmol, 1 equiv.) dropwise over 5 minutes. The reaction mixture was stirred for an hour, before iodomethane (0.87 mL, 14.0 mmol, 2 equiv.) was added dropwise over 10 minutes at 0°C using an ice bath. The solution was slowly allowed to reach room temperature and was left to react overnight for 18 hours. The solution was then added to ice water dropwise and allowed to stir for 30 additional minutes. The brown precipitate was collected, and purified *via* flash column chromatography (70:30 Ethyl acetate:Hexanes). The product was obtained as a yellow solid (0.69 grams, 40% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (m, 2 H), 7.65 (m, 2H), 2.58 (s, 6H). Spectral data were consistent with literature reports.[4]

2-(bis(methylthio)methylene)-1,3-diphenylpropane-1,3-dione (DP):



To a solution of 1,3-diphenyl-1,3-propanedione (5.0 grams, 22.3 mmol, 1 equiv.) and potassium carbonate (K_2CO_3, 9.24 grams, 66.9 mmol, 3 equiv.) in 50 mL of dry DMF, was added carbon disulfide (1.41 mL, 23.4 mmol, 1.1 equiv.) dropwise over 5 minutes. The reaction mixture was stirred at room temperature for an hour, before iodomethane (2.9 mL, 46.6 mmol) was added dropwise over 10 minutes at 0°C. The solution was slowly allowed to reach room temperature and was left to react overnight. The solution was then added to ice water dropwise and allowed to stir for 30 additional minutes. The orange precipitate was collected, and recrystallized in methanol as a light yellow solid (1.41 g, 21% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.02 (m, 4H) 7.56 (m, 2H), 7.47 (m, 4H), 2.22 (s, 6H). Spectral data were consistent with literature reports.[5]

Activation Energy Calculations

Assuming Maxwell behaviour, $\boldsymbol{\tau}$ can be defined as the time needed for the relaxation modulus to decrease to 1/e of the initial relaxation modulus, G(t), value. For such events, in a vitrimer, $\boldsymbol{\tau}$ is related to the flow activation energy (E_a) of the polymer through an Arrhenius relationship:

$$\boldsymbol{\tau = \tau_0 e^{\frac{-E_a}{RT}}}$$

where R is the ideal gas constant, T is the temperature (in Kelvin), and $\boldsymbol{\tau_0}$ is a pre-exponential factor. The flow activation energies for all the 2 mol% crosslinker/PDMS networks can hence be calculated from the slope of the plot ln(τ) vs. 1/T where the slope of the line is equal to E_a/R.

Five temperatures were used in the study for each cross-linker (100, 120, 130, 140 and 150 ºC). Three independent trials were performed on 3 separate samples (i.e., 3 different samples were made for each cross-linker).

The error corresponding to each individual activation energy ($\sigma E_{a,i}$) was the error calculated from the linear regression fit (i.e., the error of the slope). The three activation energies were then averaged.

BA-Net activation energy calculations

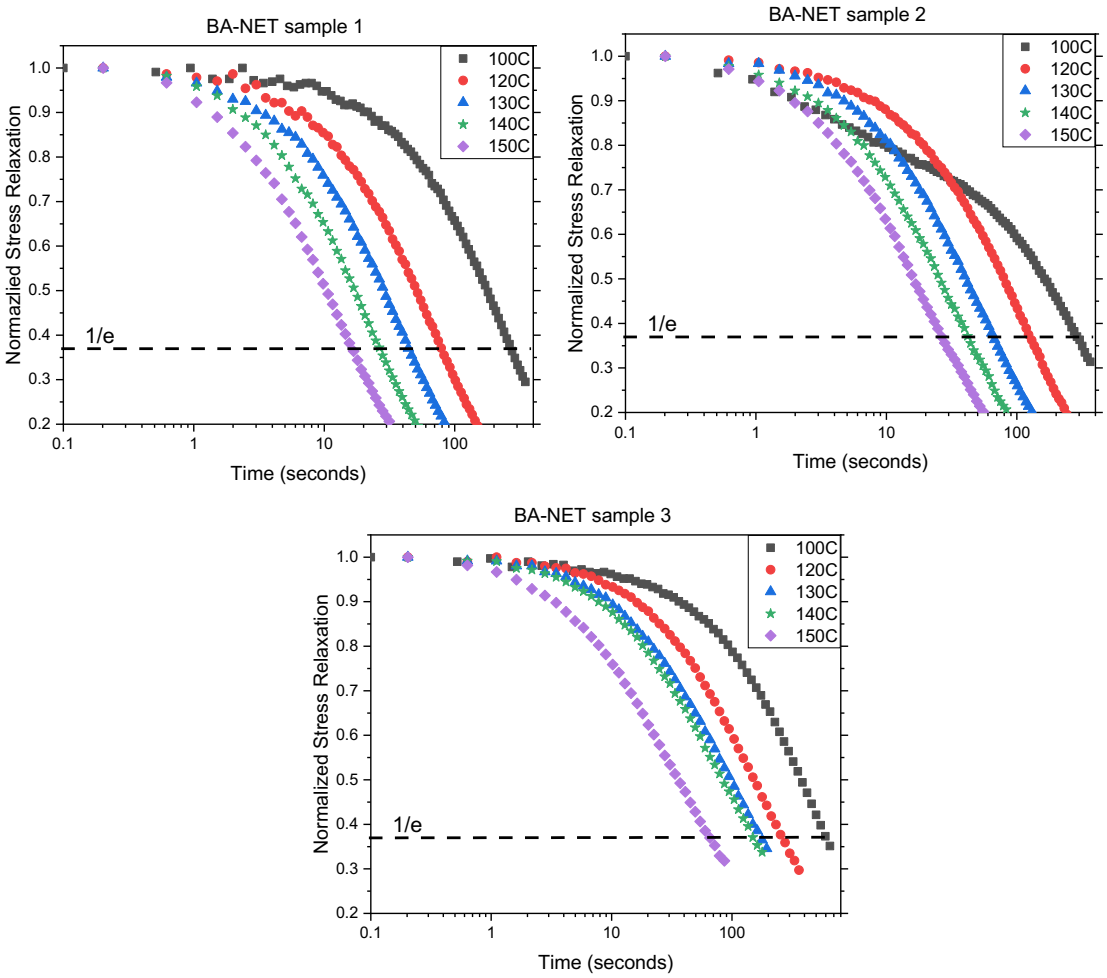


Figure S1. Normalized stress relaxation as a function of time at temperatures ranging from 100 to 150 ºC for 3 different **BA-Net** samples

Table S1. τ^* values calculated for **BA-Net** at different temperatures

Temp (°C)	τ_1	τ_2	τ_3
100	272	299	609
120	80	125	264
130	44.9	66.8	174
140	26.8	42.5	149
150	15.9	26.8	65.6

Table S2. Activation energy values calculated for 3 different **BA-Net** samples and associated errors.

$E_{a,1}$ (kJ/mol)	$\sigma E_{a,1}$ (kJ/mol)	$E_{a,2}$ (kJ/mol)	$\sigma E_{a,2}$ (kJ/mol)	$E_{a,3}$ (kJ/mol)	$\sigma E_{a,3}$ (kJ/mol)	$E_{a,avg}$ (kJ/mol)	$\sigma E_{a,avg}$ (kJ/mol)
74.42	3.09	64.03	2.73	62.91	7.99	67.12	4.60

IND-Net activation energy calculations

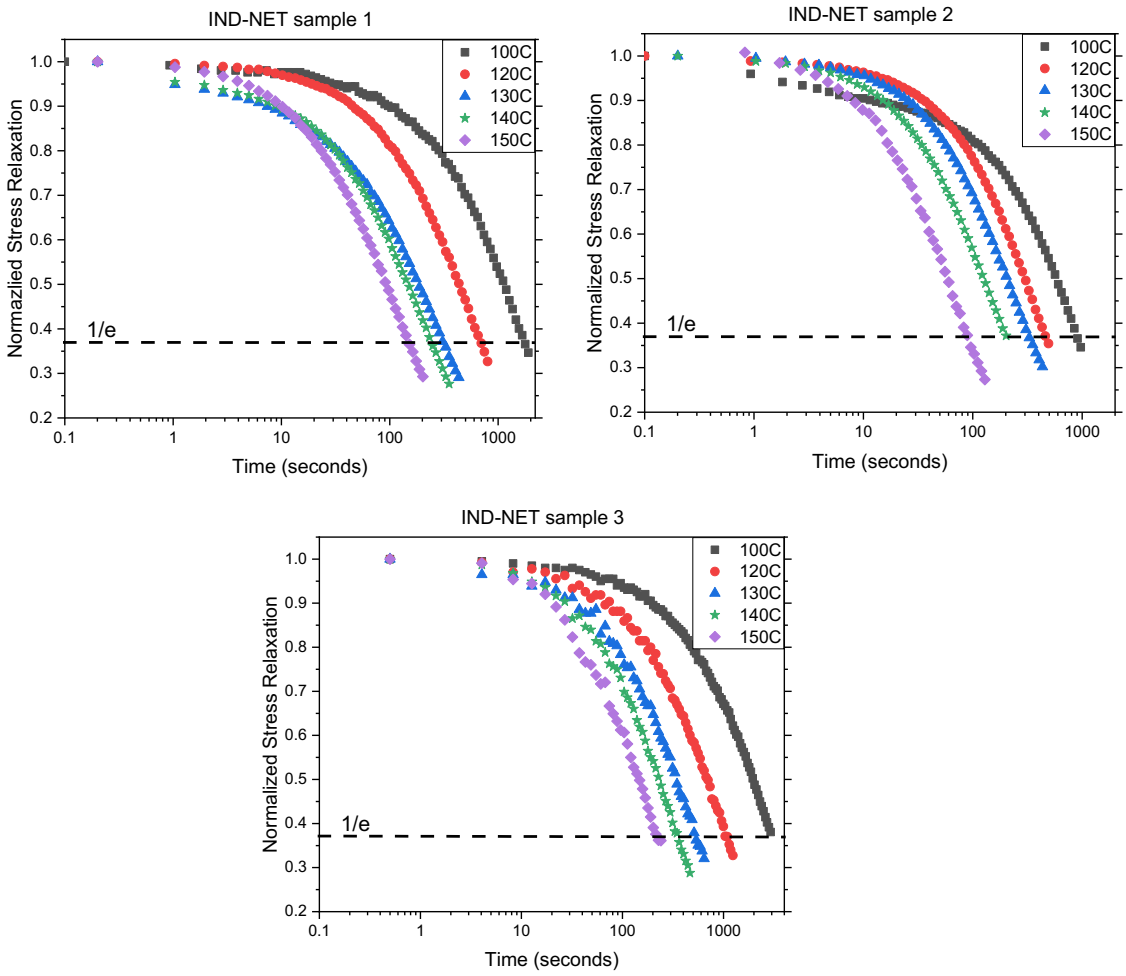


Figure S2. Normalized stress relaxation as a function of time at temperatures ranging from 100 to 150 ºC for 3 different **IND-Net** samples.

Table S3. τ values calculated for **IND-Net** at different temperatures

Temp (°C)	τ_1	τ_2	τ_3
100	1790	1440	2900
120	699	699	1120
130	315	465	536
140	232	274	356
150	150	83.8	210

Table S4. Activation energy values calculated for 3 different IND-NET samples and associated errors.

$E_{a,1}$ (kJ/mol)	$\sigma E_{a,1}$ (kJ/mol)	$E_{a,2}$ (kJ/mol)	$\sigma E_{a,2}$ (kJ/mol)	$E_{a,3}$ (kJ/mol)	$\sigma E_{a,3}$ (kJ/mol)	$E_{a,avg}$ (kJ/mol)	$\sigma E_{a,avg}$ (kJ/mol)
66.40	4.16	69.06	13.02	68.53	3.28	67.99	6.82

CY-Net activation energy calculations

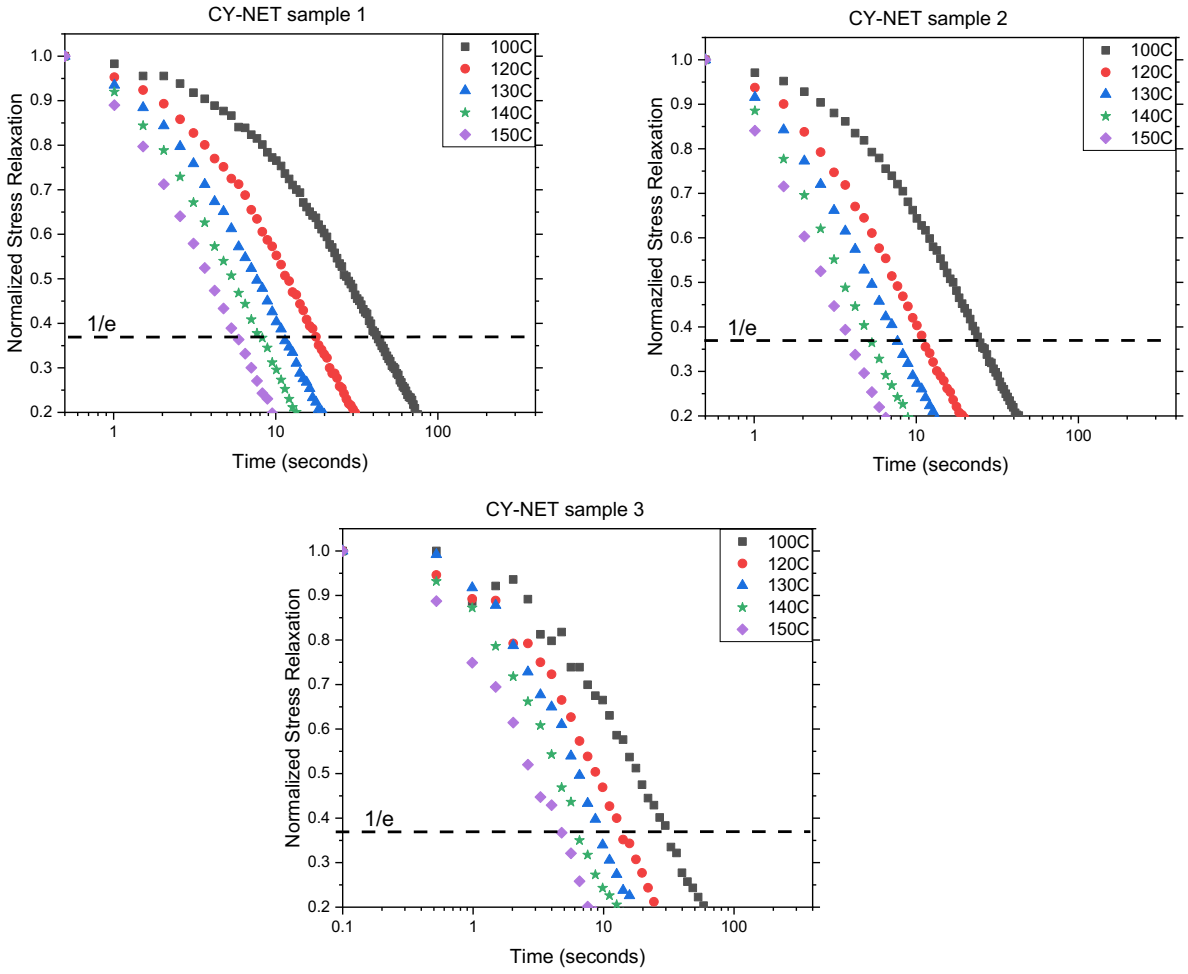


Figure S3. Normalized stress relaxation as a function of time at temperatures ranging from 100 to 150 ºC for 3 different **CY-Net** samples.

Table S5. τ values calculated for **CY-Net** at different temperatures.

Temp (°C)	τ_1	τ_2	τ_3
100	42	40	36
120	17.7	11.6	13.3
130	11.4	7.76	9.5
140	8	5.37	6.5
150	3.5	3.67	3.99

Table S6. Activation energy values calculated for 3 different **CY-Net** samples and associated errors

$E_{a,1}$ (kJ/mol)	$\sigma E_{a,1}$ (kJ/mol)	$E_{a,2}$ (kJ/mol)	$\sigma E_{a,2}$ (kJ/mol)	$E_{a,3}$ (kJ/mol)	$\sigma E_{a,3}$ (kJ/mol)	$E_{a,avg}$ (kJ/mol)	$\sigma E_{a,avg}$ (kJ/mol)
61.84	6.23	62.19	3.54	56.29	1.95	60.11	3.91

MA-Net activation energy calculations

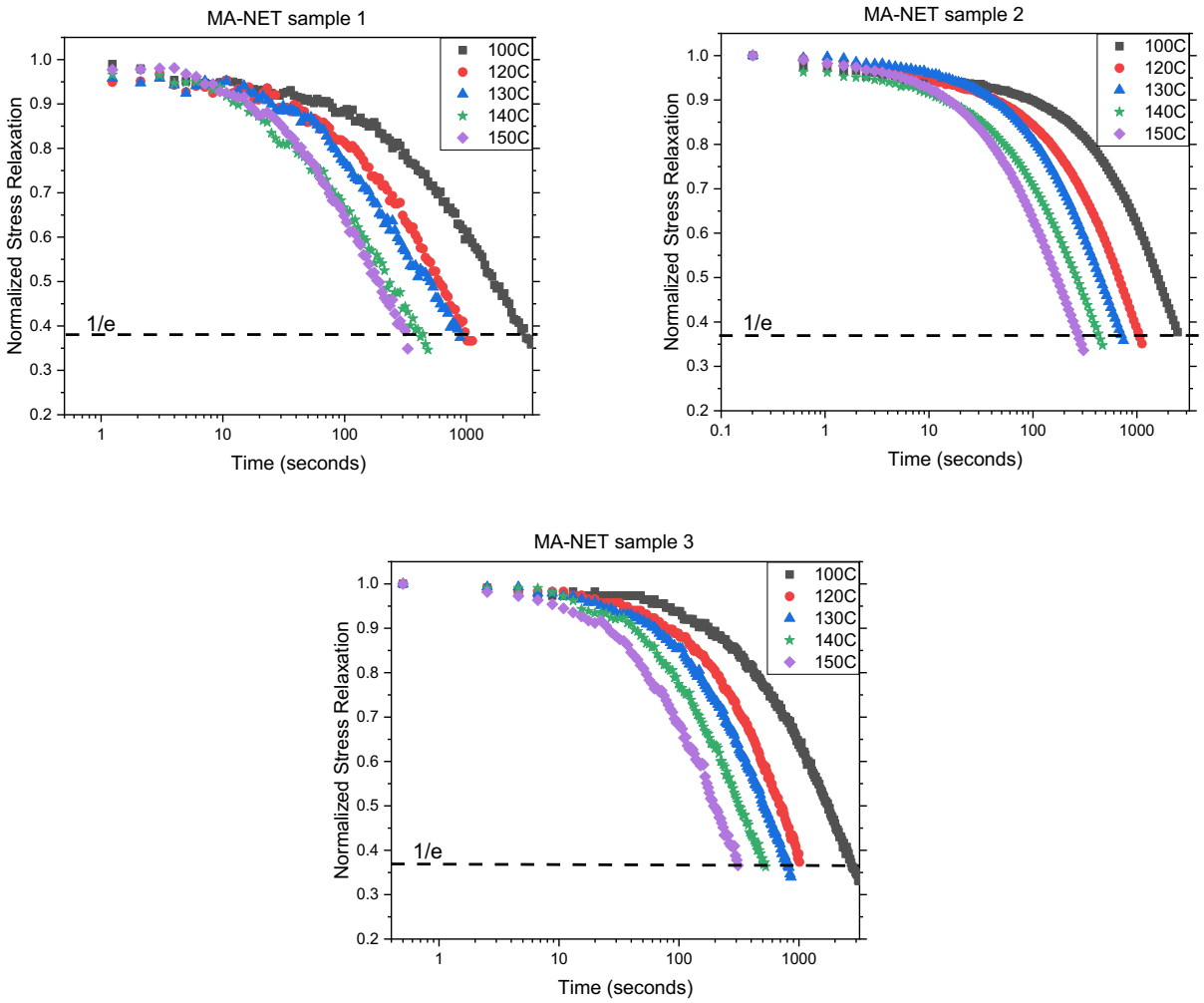


Figure S4. Normalized stress relaxation as a function of time at temperatures ranging from 100 to 150 ºC for 3 different **MA-Net** samples.

Table S7. τ values calculated for **MA-Net** at different temperatures.

Temp (°C)	τ_1	τ_2	τ_3
100	3500	2600	2800
120	1040	1070	1020
130	901	700	800
140	422	435	470
150	323	240	300

Table S8. Activation energy values calculated for 3 different **MA-Net** samples and associated errors

$E_{a,1}$ (kJ/mol)	$\sigma E_{a,1}$ (kJ/mol)	$E_{a,2}$ (kJ/mol)	$\sigma E_{a,2}$ (kJ/mol)	$E_{a,3}$ (kJ/mol)	$\sigma E_{a,3}$ (kJ/mol)	$E_{a,avg}$ (kJ/mol)	$\sigma E_{a,avg}$ (kJ/mol)
62.72	5.34	61.18	3.50	57.44	3.71	60.45	4.18

Literature flow activation energy values as a function of catalyst

To compare the effect of crosslinker variation to the effect of catalysts, we have summarized flow activation energies for literature systems below:

Table S9. Flow activation energies for literature vitrimer systems that compare catalysts.

Reference	Exchange chemistry	Catalyst	E_a (kJ/mol)
Leibler, *ACS Macro Lett.* **2012**, *1*, 789	Transesterification	PPh_3 $Zn(OAc)_2$ TBD	~40* ~90* ~140*
Bates, *ACS Macro Lett.* **2018**, *7*, 817	Transesterification	TCA MSA BSA HTFSI Triflic acid	49.6 49.7 46.4 60.2 66.7
Du Prez, *Nat. Commun.* **2017**, *8*, 14857	Vinylogous urethane exchange	None pTsOH DTBL TBD	81 ± 3 70 ± 4 31 ± 10 122 ± 19
Guan, *J. Am. Chem. Soc.* **2017**, *139*, 14881	Silyl ether exchange	None Amine (internal)	81 174
Reynaud, *Ind. Eng. Chem. Res.* **2017**, *56*, 2667	Transesterification	Dibutyltin dilaurate Dibutyltin diacetate Dibutyltin bis(acac)	121 ± 15 170 ± 21 114 ± 16
Sun, *Ind. Eng. Chem. Res.* **2019**, *58*, 5698	Transesterification	$Zn(OAc)_2$ Zn(PAM)	95 68

*Determined from graphical analysis/interpolation of Arrenhius plots.

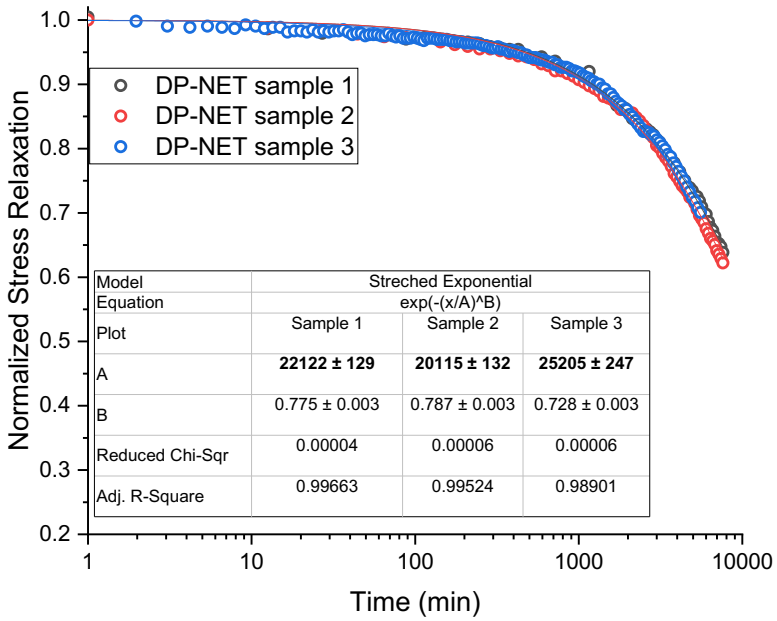
τ* Calculations for Acyclic Crosslinkers

Since the stress relaxation profiles of the acyclic crosslinked networks, **DP-Net** and **CN-Net** were extremely slow, we fitted the data using the stretched exponential function:

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

where G(t) is the relaxation modulus, $G_0(t)$ is the relaxation modulus at t=0, t is time, τ is the relaxation time and β is a fitting parameter that ranges between 0 and 1.

DP τ*:



Model	Streched Exponential		
Equation	exp(-(x/A)^B)		
Plot	Sample 1	Sample 2	Sample 3
A	**22122 ± 129**	**20115 ± 132**	**25205 ± 247**
B	0.775 ± 0.003	0.787 ± 0.003	0.728 ± 0.003
Reduced Chi-Sqr	0.00004	0.00006	0.00006
Adj. R-Square	0.99663	0.99524	0.98901

Figure S5. **DP-Net** fitted stress relaxation data for 3 different samples at 150 ºC.

CN τ*:

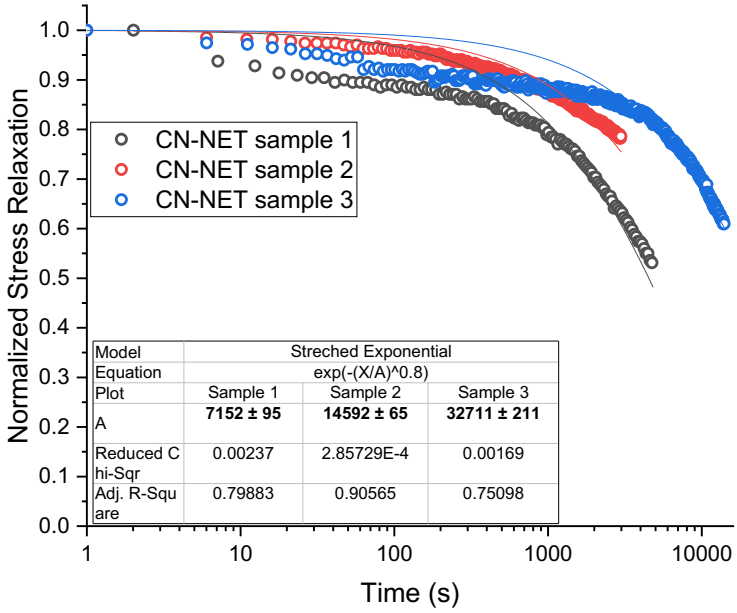


Figure S6. CN-Net fitted stress relaxation data for 3 different samples at 150 ºC.

Note: A value of 0.8 was chosen for β. This value was based on fittings from the other networks with faster cross-linkers; these values averaged ~0.8.

Plateau Modulus Calculations

A frequency sweep was performed at 3% strain, at 150 ºC, between 100 and 1 rad/s, for networks with each cross-linker (2 mol%). This enabled us to measure the rubbery plateau modulus (G_p) which is the constant storage modulus (G') between these two angular frequencies. The values were then averaged between these two frequencies and the reported error values are the calculated standard error of the mean.

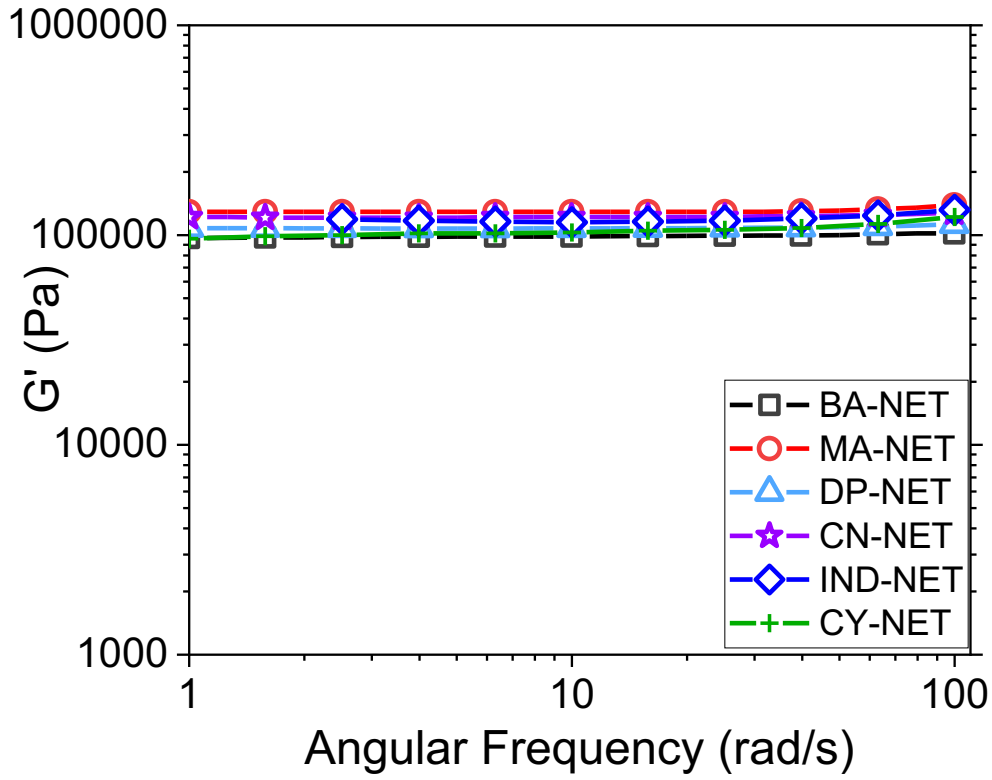


Figure S7. Storage modulus (G') of different cross-linked networks (2 mol% cross-linker) obtained from a frequency sweep between 1 and 100 rad/s at 150 ºC and 3% strain.

TGA Measurements

Thermogravimetric analysis was performed for two representative samples (**IND-Net and CY-Net**) using a Mettler Toledo TGA/DSC 3+. The TGA data for **MA-Net** were previously published by our group,[6] and demonstrated no mass loss or evolution of MeSH below 150 ºC. These analyses were performed in order to verify the thermal stability of the samples at operating temperatures, so that the 2 order of magnitude discrepancy in stress relaxation was not a function of sample degradation or residual MeSH in the networks. After the samples were gelled 5 to 6 mg of each network was placed in an aluminium pan. The sample was allowed to equilibrate at 25°C for 5 minutes which was followed by a temperature ramp of 10 °C/min (range: 25 to 350 °C) under 20 ml/min of air.

Figure S8 shows that no mass loss was observed in either sample until temperatures much higher than 150°C (the maximum operating temperature).

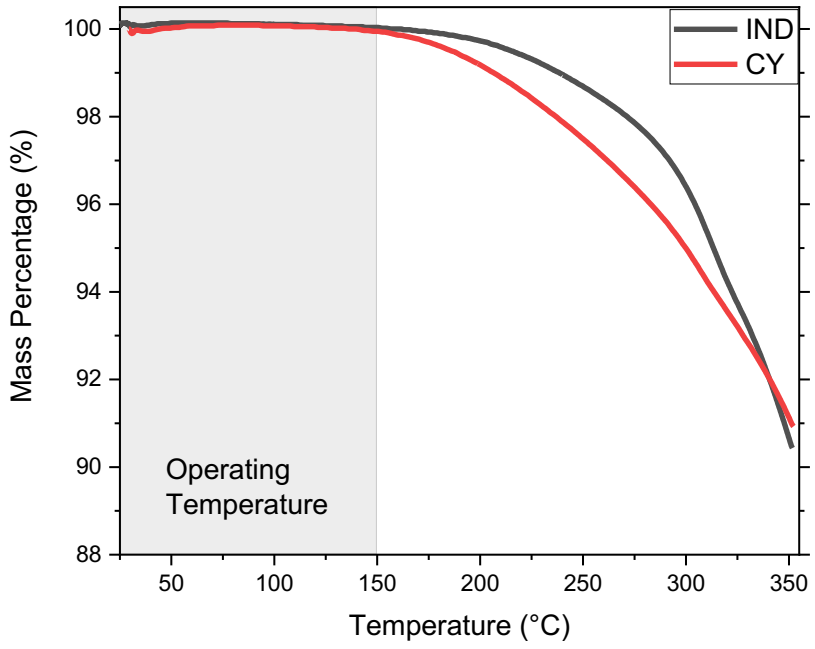


Figure S8. TGA curves of 2 mol% IND-NET and CY-NET.

Gel Fraction Measurements

Four representative gels (2 mol% cross-linker) spanning 3 to 4 orders of magnitude differences in stress relaxation (**BA-Net**, **MA-Net**, **IND-Net** and **CN-Net**) were placed in toluene at 25°C. After 48 hours, the samples were removed and placed in a convection oven at 130°C for 8 hours. The mass of the samples before and after were compared and used to calculate the gel fraction as shown in Table S10. All samples had gel fractions ranging between 81 and 90%, supporting the claim that the cross-link density of the samples are the same and that differences in stress relaxation is not due to differences in cross-linking density.

Table S10. Gel fraction study for various networks at 2 mol% cross-linking (IND, MA, BA and CN).

	Mass Before (mg)	Mass After (mg)	Gel Fraction (%)
IND-Net	24.0	21.8	90.8
CN-Net	32.5	28.9	88.9
MA-Net	38.0	30.8	81.1
BA-Net	37.8	31.2	82.5

T_v Calculations

The vitrimer glass transition temperature (T_v) can be calculated by using the Maxwell equation:

$$\eta = G_p \tau^*$$

where η is the viscosity, G_p is the plateau modulus and τ^* is the characteristic relaxation time. T_v occurs when the Network reaches a viscosity of 10^{12} Pa•s. Using the equation above, τ^* was calculated to be around 10^7 s for all samples since they possess similar G_p values. The Arrhenius relationship from equation 1 in the main was then extrapolated to $\tau^* = 10^7$ s to find T_v for each cross-linked Network. Table S9 summarizes the intercept and estimated T_v values with associated standard errors.

Table S11. Y-intercept from Arrhenius plot and freezing transition temperature for cyclic cross-linker vitrimer samples.

	BA-Net	**MA-Net**	**IND-Net**	**CY-Net**
$\ln(\tau_0)$ (s)	-13.4	-12.0	-14.3	-15.7
$\ln(\tau_0)$ Error	1.2	1.0	1.5	0.7
T_v (K)	245	252	263	233
T_v Error	11	10	13	5

While all the T_v values are below room temperature, it should be noted that we do not see any noticeable creep at room temperature, as shown below in Figure S9. The results indicate that the Arrhenius argument may not be valid over all temperature ranges. Thus, calculating the true T_v value may require more rigour.

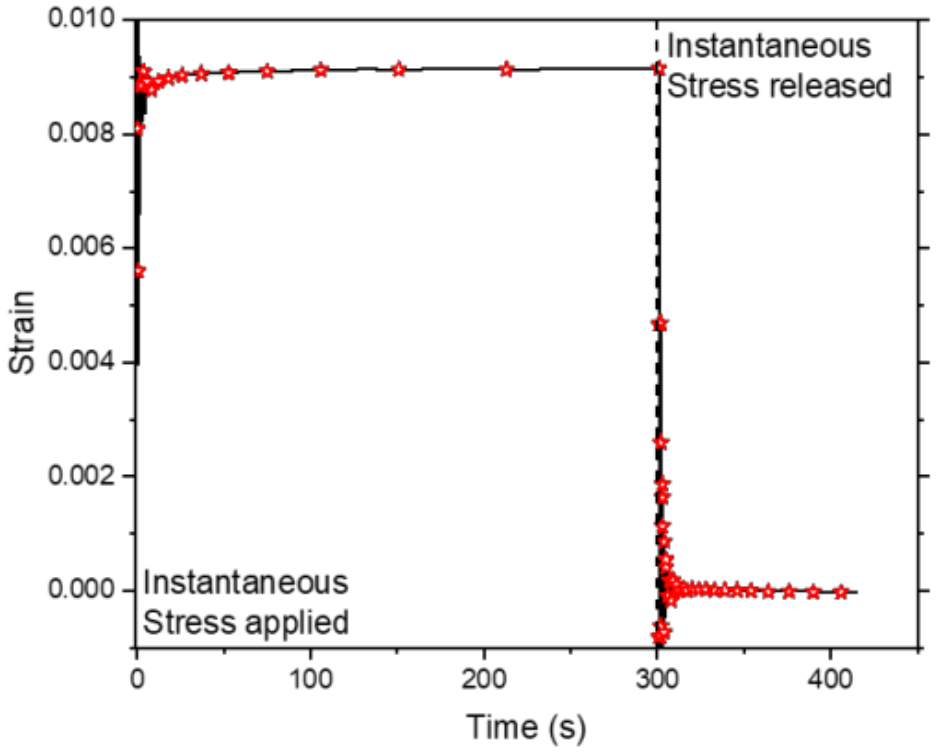


Figure S9. Creep experiment for **MA-NET** (2 mol%) performed at room temperature. The plot shows full recovery of strain.

Time-Cross-linker Superposition

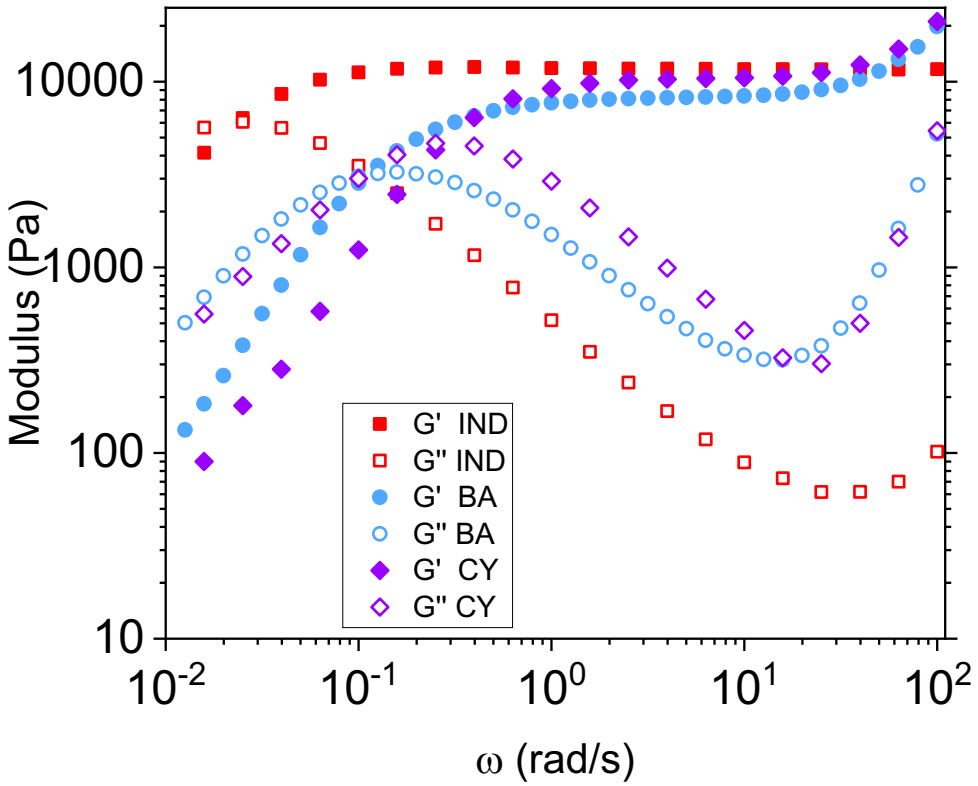


Figure S10. Frequency sweep data for **IND-Net**, **BA-Net**, and **CY-Net** at 1.25 mol% crosslinking at a temperature 150 ºC and 3% strain.

Note: The high-frequency data for **BA** and **CY** between 10 and 100 rad/s were not included in the superposition. This is because higher frequency values are not expected to follow ideal Maxwell behavior, and will not superimpose.

Mixed Cross-linker Networks

The shape of the curves for the mixed systems indicate additional complexity in the relaxation modes of the mixed cross-linkers. Therefore, the normalized stress relaxation data were fit to the Kohlrausch-Williams-Watts (KWW) model, which is a stretched exponential function:

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

The fitting parameter, β, can range between 0 and 1 where a value of 1 means that it is an ideal Maxwell material with a single relaxation mode. The further away β is from 1, the less ideal a Maxwell material the polymer is and the more relaxation modes it contains. The β value of **BA/MA-Net** (0.83 ± 0.1) was similar to those of **CY-Net**, **BA-Net**, and **MA-Net** at (0.94 ± 0.01), (0.83 ± 0.01), and (0.86± 0.01), respectively, which are all close to 1, consistent with a single relaxation mode. The **BA/DP-Net** and **CY/MA-Net** samples had a much lower β value at (0.54 ± 0.01) and (0.55 ± 0.01), respectively, indicating a deviation from ideal Maxwell behavior, as shown in Figure S11. The stress relaxation profiles of the **BA/MA-Net** samples at 100 to 140 ºC are shown in Figure S12. The calculated flow activation energy (derived from the 1/e of τ values) is 68 ± 2 kJ/mol.

The continuous relaxation spectrum was extracted from the relaxation modulus as a function of time (G(t) vs t) using Python via an algorithm developed for the PyReSpect program.[7,8] The input parameters used were unchanged from the default file provided with the program.

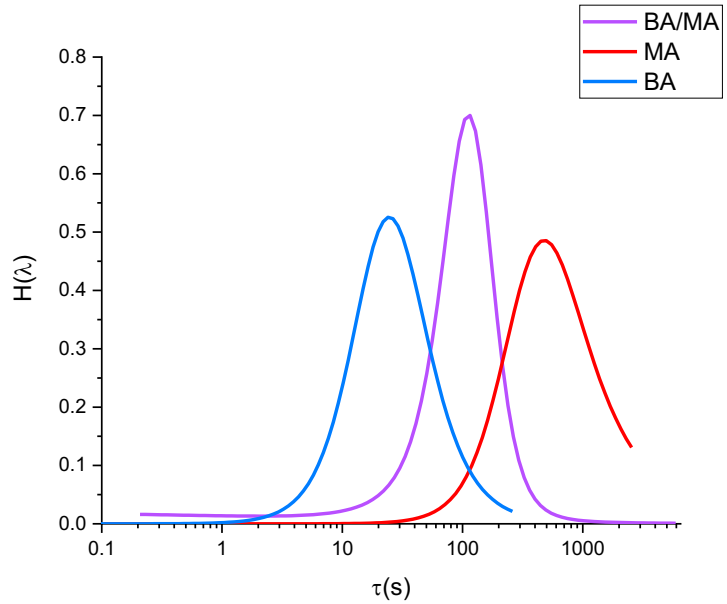


Figure S11. Continuous relaxation (infinity) spectra for 2 mol% samples of **BA-Net, MA-Net** and the mixed 1:**1 BA/MA-Net** at 140°C showing a single relaxation mode for all samples.

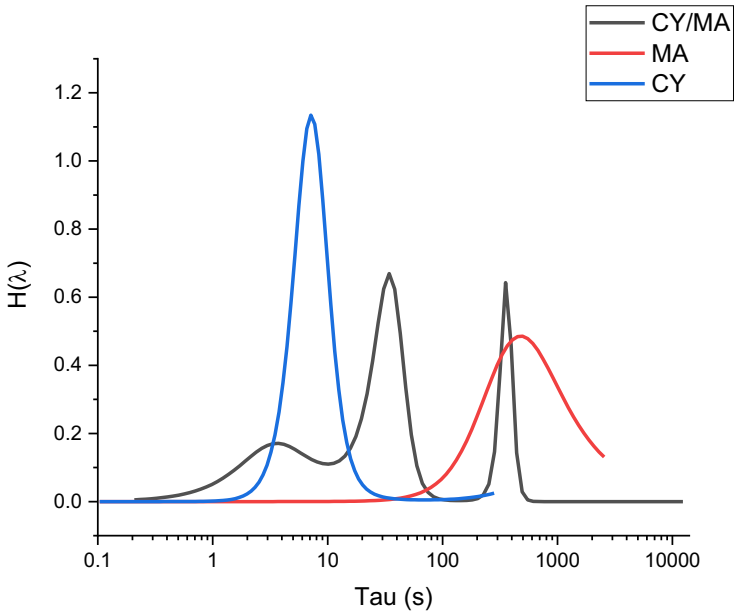
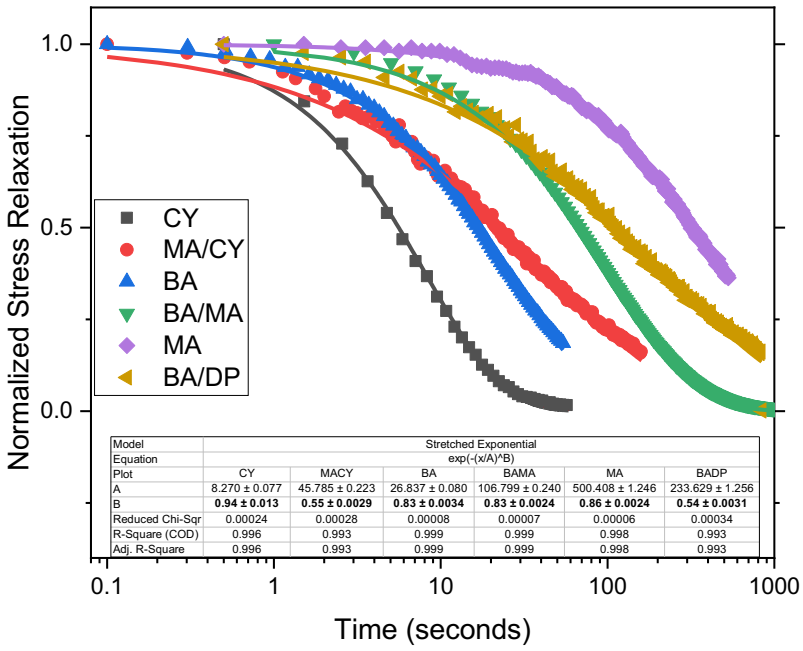


Figure S12. Continuous relaxation (infinity) spectra for 2 mol% samples of **MA-Net**, **CY-Net** and the mixed **1:1 CY/MA-Net** at 140°C showing a single relaxation mode for **MA-Net** and **CY-Net,** but multiple relaxation modes for **CY/MA-Net**.



Model	Stretched Exponential					
Equation	exp(-(x/A)^B)					
Plot	CY	MACY	BA	BAMA	MA	BADP
A	8.270 ± 0.077	45.785 ± 0.223	26.837 ± 0.080	106.799 ± 0.240	500.408 ± 1.246	233.629 ± 1.256
B	**0.94 ± 0.013**	**0.55 ± 0.0029**	**0.83 ± 0.0034**	**0.83 ± 0.0024**	**0.86 ± 0.0024**	**0.54 ± 0.0031**
Reduced Chi-Sqr	0.00024	0.00028	0.00008	0.00007	0.00006	0.00034
R-Square (COD)	0.996	0.993	0.999	0.999	0.998	0.993
Adj. R-Square	0.996	0.993	0.999	0.999	0.998	0.993

Figure S13. Stretched exponential fitting for different cross-linked networks at 140 ºC. Subset shows fitting to stretched exponential function.

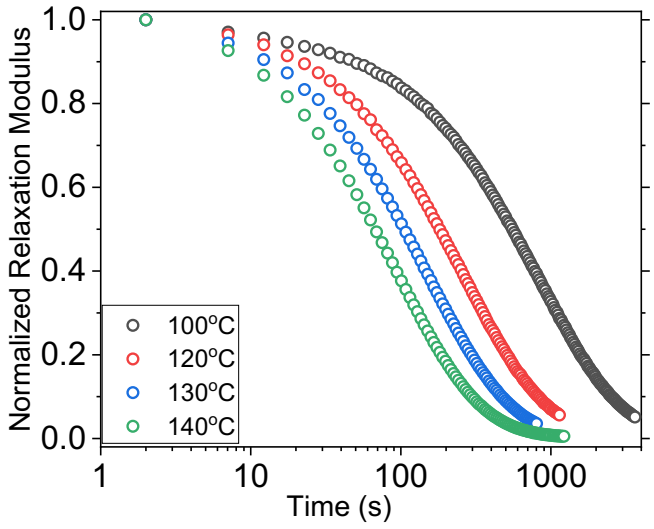


Figure S14. Stress relaxation profiles for the **MA/BA-Net** samples at temperatures ranging from 100 to 140 ºC.

Computational Calculation Details

Calculations were performed using the TURBOMOLE[9–11] software package on Northwestern University's Quest computational cluster.

Table S12. Computed enthalpy, entropy and Gibbs free energy of the transition states and Gibbs free energy of the intermediate.

	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol K)	$\Delta G^{\ddagger}$ (kJ/mol)	ΔG_{int} (kJ/mol)
CY	28	-285	112	99
BA	80	-226	147	131
MA	69	-276	152	135
IND	69	-268	149	108
DP	-	-	-	130
CN	-	-	-	156

Note: In the following illustrations, most hydrogens have been removed for clarity.

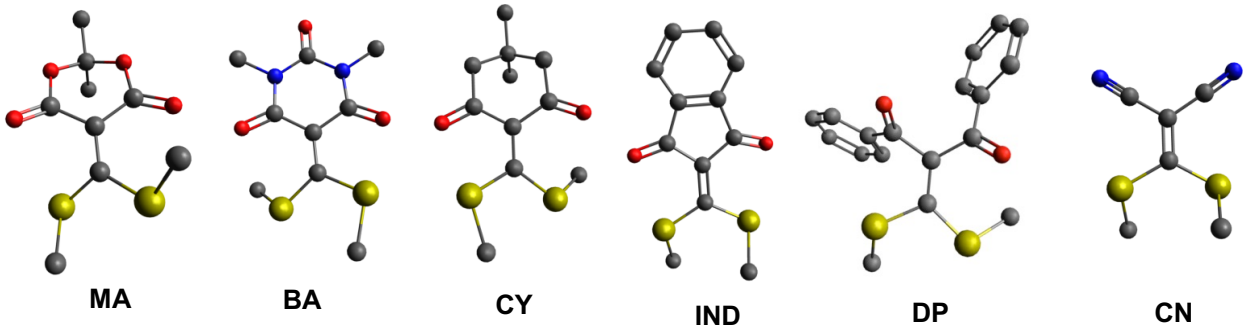


Figure S15. Optimized cross-linker structures.

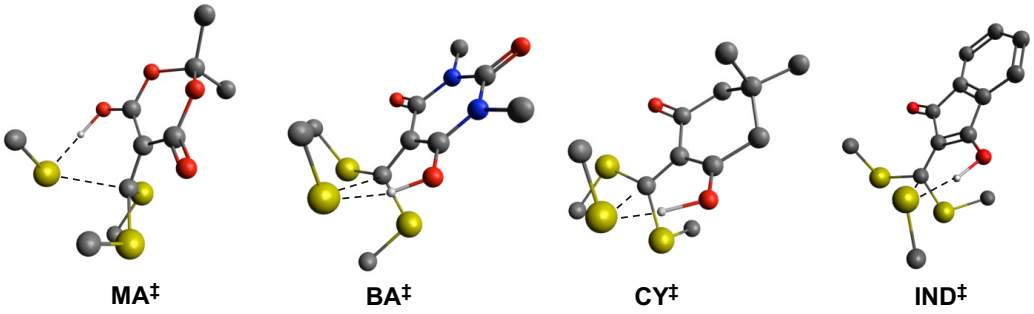


Figure S16. Optimized transition structures of the cyclic cross-linkers.

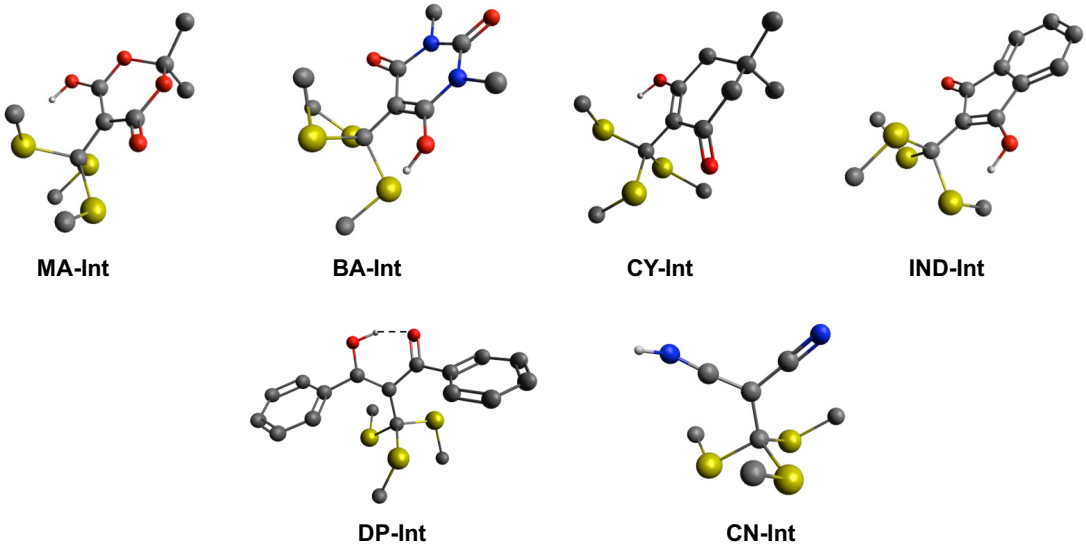


Figure S17. Optimized intermediate state structures of the cross-linkers.

Coordinates for Starting Materials

Methanethiol (MeSH)

C -0.503674 0.022160 -0.016976
S 1.202205 0.711745 0.035028
H -1.175048 0.878592 -0.047906
H -0.719429 -0.562325 0.875229
H -0.658457 -0.578968 -0.910744
H 1.854403 -0.471203 0.065368

MA

C -2.393586 -0.584150 0.054062
O -1.465124 -1.658882 0.235787
C -0.126535 -1.432231 0.080145
O 0.612375 -2.381461 0.078254
C 0.294787 -0.003803 0.063142
C 1.541250 0.362733 -0.428572
S 2.509273 1.732851 0.060287
C 2.250806 1.917867 1.865723
S 2.163774 -0.522238 -1.817244
C 3.994108 -0.432001 -1.711091
C -0.645553 1.005695 0.583928
O -0.392612 2.153967 0.858357
O -1.933779 0.577620 0.755289
C -2.580241 -0.277832 -1.429308
C -3.677751 -1.010909 0.735474
H 1.428036 2.597487 2.056996
H 2.047591 0.942190 2.302689
H 3.193872 2.305323 2.249350
H 4.373439 0.546097 -1.991202
H 4.323515 -0.702271 -0.710676
H 4.342912 -1.178750 -2.423977
H -2.941697 -1.168863 -1.942985
H -1.643202 0.032730 -1.892691
H -3.308751 0.524239 -1.549308
H -4.064654 -1.912518 0.261483
H -4.419149 -0.215858 0.658158
H -3.482901 -1.216933 1.787128

BA

C -2.491302 0.270576 0.764615
O -3.606528 0.589342 1.128290
N -1.789375 -0.760627 1.377707

C -0.483357 -1.146337 1.054656
O 0.018803 -2.101878 1.630304
C 0.225418 -0.341556 0.054158
C 1.569900 -0.605379 -0.204687
S 2.300381 -2.124997 0.335183
C 4.024341 -2.054671 -0.296260
S 2.683555 0.474661 -1.038637
C 2.161107 2.188895 -0.667940
C -0.554226 0.606539 -0.753161
O -0.167201 1.137355 -1.783726
N -1.854621 0.884212 -0.311737
C -2.620488 1.858449 -1.099638
C -2.470033 -1.484022 2.460083
H 4.582820 -1.227096 0.135062
H 4.070218 -2.019134 -1.382844
H 4.446740 -2.999154 0.047437
H 1.722493 2.234030 0.327231
H 1.458935 2.545483 -1.413357
H 3.087925 2.761521 -0.684100
H -2.085459 2.806173 -1.137064
H -3.584336 1.987957 -0.620447
H -2.746403 1.494557 -2.118678
H -2.090613 -2.500340 2.481085
H -3.538357 -1.465587 2.271492
H -2.270238 -1.009075 3.422473

IND

C 4.418690 -0.654993 -0.934195
C 4.549885 -0.097478 0.342208
C 3.428272 0.287175 1.074745
C 2.181971 0.102977 0.494695
C 2.051044 -0.459858 -0.773059
C 3.162773 -0.841277 -1.509169
C 0.605737 -0.528846 -1.147031
O 0.176274 -0.911653 -2.219155
C -0.156767 0.011110 0.011263
C -1.520011 0.125024 0.101000
S -2.517301 -0.437302 -1.258812
C -4.072170 -1.035262 -0.477853
S -2.225170 0.829541 1.573259
C -3.741997 1.694276 0.991862
C 0.829406 0.405491 1.053892
O 0.613465 0.842514 2.168706
H 5.308155 -0.945029 -1.480605
H 5.538910 0.035886 0.763949
H 3.516249 0.719191 2.063813

H 3.048215 -1.271268 -2.496422
H -4.359028 -1.906442 -1.064961
H -4.866212 -0.294774 -0.523569
H -3.890162 -1.339847 0.550094
H -3.640751 1.981998 -0.052036
H -3.801058 2.590965 1.606956
H -4.638218 1.097778 1.140324

CY

C -2.137027 -0.677686 0.159334
C -1.925972 0.009329 -1.194554
C -0.521567 0.524934 -1.472430
O -0.372532 1.349358 -2.367044
C 0.613310 0.014223 -0.680751
C 1.871571 0.605376 -0.827662
S 2.204945 1.655183 -2.212505
C 3.959216 2.164845 -1.991824
S 3.226999 0.432911 0.282052
C 2.548092 0.118958 1.949750
C 0.403136 -1.225120 0.096694
O 1.317310 -1.921230 0.518080
C -1.024686 -1.723519 0.298307
C -3.506158 -1.373194 0.180372
C -2.081490 0.344861 1.308534
H -2.602925 0.855347 -1.334666
H -2.152568 -0.698785 -2.001103
H 4.647879 1.323396 -2.037854
H 4.108047 2.726069 -1.071957
H 4.133535 2.815333 -2.849067
H 2.418129 -0.944756 2.118136
H 1.602014 0.642998 2.069718
H 3.289310 0.544371 2.625799
H -1.178579 -2.519358 -0.440774
H -1.045774 -2.211272 1.275659
H -3.668523 -1.888549 1.130935
H -4.314566 -0.648548 0.051392
H -3.587746 -2.112939 -0.620396
H -2.204668 -0.152545 2.274041
H -2.883192 1.080660 1.206734
H -1.135521 0.889445 1.330449

DP

C -0.093560 0.512709 1.200522
C 0.581750 1.668777 1.462988
S -0.021320 3.320416 1.566699
C -1.535799 3.392346 0.545408
S 2.289041 1.539490 1.974923
C 3.181676 2.827319 1.014505
C -1.577839 0.376307 1.395225
O -2.167855 1.072797 2.205533
C -2.344976 -0.633820 0.597207
C -3.534235 -1.135501 1.137419
C -4.314399 -2.024442 0.412596
C -3.928818 -2.406574 -0.871304
C -2.756771 -1.899724 -1.422796
C -1.963629 -1.024768 -0.688116
C 0.654408 -0.784635 1.000487
O 0.399239 -1.731767 1.722498
C 1.641823 -0.932973 -0.123020
C 1.714618 -0.037719 -1.194445
C 2.608293 -0.256074 -2.237064
C 3.445051 -1.368129 -2.216357
C 3.376957 -2.266666 -1.153527
C 2.476107 -2.055257 -0.119119
H -1.639066 4.437251 0.255541
H -1.420612 2.777805 -0.346421
H -2.397685 3.062704 1.119472
H 3.085482 2.637089 -0.052697
H 4.225393 2.719888 1.308441
H 2.835134 3.826032 1.261414
H -3.828630 -0.818212 2.129113
H -5.225145 -2.420546 0.845322
H -4.541318 -3.096696 -1.439309
H -2.456812 -2.187813 -2.423001
H -1.055393 -0.636499 -1.129870
H 1.066536 0.829226 -1.216842
H 2.649706 0.438760 -3.067464
H 4.144409 -1.536583 -3.026628
H 4.025720 -3.134166 -1.134689
H 2.402620 -2.750051 0.707156

CN

C -1.676032 -0.932852 -0.393242
C -0.499317 -0.278430 -0.139939
S -0.396690 1.457578 -0.477499

C 0.428706 2.117782 1.026185
S 0.866578 -1.197863 0.513507
C 2.279664 -0.610597 -0.504654
C -2.884400 -0.237159 -0.706384
N -3.881054 0.285636 -0.962381
C -1.779241 -2.357804 -0.362219
N -1.905703 -3.504950 -0.347523
H 1.419529 1.695449 1.168558
H -0.190466 1.936976 1.901449
H 0.510522 3.189766 0.851509
H 2.117483 -0.864030 -1.549468
H 3.142429 -1.156793 -0.125611
H 2.448192 0.457190 -0.395190

Coordinates for Intermediates

MA-INT

C 2.761339 -0.177829 -0.508366
O 2.093109 1.028273 -0.837597
C 0.777626 1.213012 -0.443067
O 0.316612 2.315846 -0.586322
C 0.070771 0.007529 -0.007719
C 0.630946 -1.186726 -0.410449
O 0.026673 -2.356804 -0.490366
O 1.885818 -1.293458 -0.836676
C -1.283727 0.037822 0.677275
S -1.804878 1.638815 1.454358
C -2.637170 2.614139 0.151316
S -1.082926 -1.068374 2.185649
C -2.787352 -1.265656 2.832193
S -2.630277 -0.743673 -0.411985
C -2.253757 -0.094134 -2.087798
C 3.947699 -0.298454 -1.441046
C 3.151345 -0.231653 0.964652
H -0.942342 -2.230690 -0.358753
H -3.470181 2.055602 -0.273390
H -1.925953 2.935435 -0.604472
H -3.033771 3.484453 0.675961
H -2.665854 -1.734972 3.808546
H -3.259845 -0.293242 2.949737
H -3.385989 -1.912713 2.194351
H -1.270231 -0.414220 -2.425019
H -3.014813 -0.524635 -2.738499
H -2.322049 0.989488 -2.116164
H 3.608878 -0.261798 -2.475511
H 4.467388 -1.240195 -1.264826
H 4.633755 0.528635 -1.262490
H 3.812800 0.606650 1.183399
H 3.679238 -1.162794 1.172035
H 2.282262 -0.164897 1.616839

BA-INT

C -2.880851 0.478514 0.361484
O -4.050529 0.769659 0.527813
N -2.307340 0.414431 -0.913946
C -1.008501 0.016605 -1.118376
O -0.701805 0.025681 -2.413544
C -0.154123 -0.311414 -0.082170

C -0.628817 -0.029898 1.263992
O 0.071089 0.026835 2.262384
N -2.017495 0.213189 1.400843
C -2.557617 0.362099 2.757449
C 1.285667 -0.751433 -0.316501
S 2.067247 -1.798381 1.028191
C 2.969394 -0.664199 2.141052
S 1.246874 -2.023653 -1.717121
C 2.997964 -2.154126 -2.232846
S 2.377094 0.674649 -0.875159
C 1.736170 2.093288 0.091192
C -3.165535 0.724174 -2.067951
H 0.135066 -0.483997 -2.555430
H -2.601966 1.414487 3.043183
H -1.899568 -0.164394 3.440341
H -3.562082 -0.050673 2.779369
H 3.613683 -1.316825 2.731964
H 2.282165 -0.124066 2.784166
H 3.593172 0.011294 1.557592
H 3.611781 -2.361926 -1.358901
H 3.030420 -3.001720 -2.916829
H 3.333807 -1.255407 -2.744018
H 0.729044 2.360819 -0.221497
H 1.758318 1.890647 1.158809
H 2.412177 2.916820 -0.139458
H -3.278756 -0.154584 -2.701353
H -4.129248 1.024560 -1.672515
H -2.728606 1.530056 -2.654608

IND-INT

C 4.575021 -0.267587 0.308600
C 4.276386 -0.363301 1.663526
C 2.946744 -0.319805 2.110577
C 1.955844 -0.184406 1.164359
C 2.255514 -0.089258 -0.193566
C 3.559410 -0.124213 -0.648080
C 0.976909 0.060589 -0.914557
C -0.099246 0.049180 -0.055950
C 0.457764 -0.108528 1.319055
O -0.121094 -0.164772 2.384131
C -1.543952 0.071750 -0.475352
S -1.879473 -1.628448 -1.173060
C -3.619077 -1.535258 -1.751586
S -1.806665 1.269146 -1.917344
C -1.276246 2.882936 -1.217922
S -2.802750 0.626832 0.780757

C -3.025012 -0.780025 1.935842
O 1.010446 0.200842 -2.230354
H 5.608506 -0.303801 -0.013783
H 5.080339 -0.472602 2.381257
H 2.700937 -0.389877 3.163106
H 3.790637 -0.047411 -1.702784
H -3.957758 -2.567033 -1.842594
H -4.225022 -1.012863 -1.013199
H -3.693421 -1.037985 -2.715745
H -1.285371 3.582461 -2.053546
H -0.269374 2.815908 -0.809897
H -1.973101 3.215948 -0.453064
H -3.989700 -0.599633 2.411058
H -2.227061 -0.805660 2.669220
H -3.065420 -1.714145 1.377735
H 0.103286 0.442941 -2.542384

CY-INT

C 2.590871 -0.247878 -0.627329
C 2.351692 -0.360387 0.883255
C 0.904059 -0.656582 1.247787
O 0.671609 -1.489088 2.110626
C -0.160221 0.090428 0.543011
C 0.213443 0.745184 -0.605735
O -0.601304 1.433148 -1.408185
C 1.617670 0.816661 -1.145793
C -1.619039 0.007677 1.007469
S -1.775046 -0.580346 2.778482
C -3.556626 -0.284913 3.096408
S -2.516404 1.666379 0.830218
C -1.425993 2.772070 1.798808
S -2.661780 -1.044367 -0.162464
C -1.858171 -2.674304 0.045277
C 2.332998 -1.598815 -1.317434
C 4.035450 0.189210 -0.905004
H 2.628028 0.585989 1.364612
H 2.960189 -1.146288 1.332534
H -1.475540 1.573055 -0.969583
H 1.996607 1.816507 -0.897903
H 1.544378 0.788582 -2.236239
H -4.161234 -0.701433 2.292176
H -3.758795 -0.833218 4.017384
H -3.794070 0.766744 3.237461
H -1.280736 2.354661 2.793999
H -0.466650 2.917329 1.306187
H -1.951401 3.723845 1.868210

H -2.521538 -3.393502 -0.434149
H -1.760581 -2.905793 1.104208
H -0.883917 -2.699558 -0.438125
H 2.527721 -1.525335 -2.390170
H 1.302245 -1.934612 -1.189515
H 2.987443 -2.372027 -0.908269
H 4.743468 -0.560693 -0.543901
H 4.266750 1.136104 -0.409911
H 4.206026 0.319094 -1.977280

DP-INT

C 0.109152 0.305758 0.820237
C -0.290138 -0.817911 -0.147908
S -0.732118 -0.157065 -1.860130
C -0.108296 -1.336131 -3.107737
S 1.026980 -2.108530 -0.399237
C 1.345197 -2.692642 1.289715
S -1.771104 -1.637727 0.650061
C -2.311098 -2.823246 -0.607778
C -0.896483 0.978498 1.678486
O -0.605613 1.327896 2.837013
C -2.241150 1.416980 1.191951
C -2.404822 2.032178 -0.047581
C -3.640333 2.556775 -0.412980
C -4.722269 2.459731 0.451575
C -4.560764 1.857935 1.698473
C -3.325376 1.357225 2.073522
C 1.424814 0.692116 1.066161
O 1.758134 1.340368 2.176683
C 2.613094 0.544836 0.189233
C 3.834436 0.184274 0.768462
C 4.984342 0.109017 -0.004241
C 4.938281 0.432440 -1.356505
C 3.735888 0.833812 -1.929028
C 2.578677 0.885755 -1.164166
H 0.977663 -1.375082 -3.125830
H -0.466854 -0.922009 -4.050365
H -0.518186 -2.333455 -2.979370
H 0.414733 -2.972558 1.778101
H 1.976697 -3.572239 1.171262
H 1.875115 -1.949974 1.882329
H -1.524861 -3.539337 -0.838390
H -3.159109 -3.344550 -0.166004
H -2.637613 -2.302533 -1.506014

H -1.563601 2.129736 -0.717918

H -3.752505 3.043673 -1.372938
H -5.685750 2.859763 0.163107
H -5.399208 1.788840 2.379399
H -3.187474 0.907103 3.046755
H 0.934618 1.380969 2.749379
H 3.875925 -0.038564 1.825323
H 5.919383 -0.189823 0.451395
H 5.837229 0.384238 -1.957366
H 3.699070 1.110841 -2.974622
H 1.645194 1.192619 -1.612412

CN-INT

N 2.397195 -1.155143 1.746449
C 1.485698 -0.592760 1.312475
C 0.340829 0.088979 0.809617
C -0.334343 0.807462 1.698976
N -0.827648 1.571359 2.494769
C -0.157145 -0.122819 -0.610958
S 1.021850 0.378519 -1.958594
C 2.585601 -0.529266 -1.630836
S -0.573365 -1.905223 -0.939047
C -1.514686 -2.406868 0.554246
S -1.714416 0.836157 -0.952056
C -1.227721 2.609697 -0.832890
H -1.563825 1.252681 3.122587
H 3.157022 -0.084299 -0.821550
H 2.388951 -1.579445 -1.428027
H 3.144352 -0.443507 -2.563005
H -2.398969 -1.787151 0.689291
H -1.827034 -3.432638 0.357390
H -0.889631 -2.392536 1.445134
H -2.086411 3.152239 -1.229162
H -0.360451 2.810491 -1.456619
H -1.045751 2.923970 0.191810

Coordinates for Transition States

MA‡

C 3.108457 -0.020478 0.174429
O 2.496207 1.256466 0.220067
C 1.138581 1.351910 0.473248
O 0.726685 2.412407 0.869871
C 0.360962 0.149173 0.169477
C 1.011969 -0.871307 -0.569287
O 0.433363 -1.799180 -1.219814
O 2.335567 -0.883044 -0.704810
C -1.013877 -0.018283 0.595757
S -2.051084 1.264367 1.204547
C -2.114525 2.525717 -0.110431
S -1.273561 -1.545502 1.487248
C -3.095486 -1.736687 1.589978
S -2.151692 -0.732238 -1.677379
C -1.448196 0.342562 -2.995038
C 4.453817 0.154809 -0.497220
C 3.206566 -0.651591 1.559215
H -0.658003 -1.534550 -1.408061
H -2.488330 2.056692 -1.018148
H -1.141251 2.985741 -0.249627
H -2.831193 3.265350 0.245966
H -3.265932 -2.800113 1.754156
H -3.508544 -1.162013 2.413981
H -3.544620 -1.431292 0.647369
H -0.589405 0.900065 -2.613711
H -1.118197 -0.272518 -3.831703
H -2.200820 1.048307 -3.343211
H 4.319454 0.604412 -1.480220
H 4.943096 -0.812500 -0.608280
H 5.080593 0.807559 0.109533
H 3.802475 -0.004682 2.203069
H 3.690944 -1.625527 1.487218
H 2.224384 -0.781228 2.012558

BA‡

C -3.091056 -0.085886 -0.119890
O -4.296561 -0.103420 -0.269819
N -2.209409 -0.109869 -1.211300
C -0.848078 -0.136554 -1.069908
O -0.197157 -0.099666 -2.184749
C -0.246591 -0.153875 0.206825
C -1.104950 0.022542 1.375633

O -0.718049 0.159911 2.524435
N -2.499386 -0.011537 1.122746
C -3.421072 0.064078 2.264602
C 1.163397 -0.475513 0.350261
S 2.135543 -0.156732 1.769701
C 1.893308 1.611558 2.129577
S 1.611661 -2.011223 -0.436619
C 3.446931 -2.021266 -0.453668
S 2.240296 1.178275 -1.471185
C 1.336974 2.781267 -1.407950
C -2.783919 -0.079704 -2.565218
H 0.828449 0.294506 -2.032210
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