Supporting Information for

Creep Resistance in Doubly Crosslinked Dynamic Covalent Networks
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Materials

The following chemicals were used without purification: chloroform-d (CDCl₃, Cambridge Isotope Laboratories, 99.5%), dimethylsulfoxide-d₆ (DMSO-d₆, Cambridge Isotope Laboratories, 99.5%), methanol (MeOH, VWR, 99.8%), tert-butyl acetoacetate (VWR, ≥ 95.0%), 1,1,1-trimethylolpropane (Sigma-Aldrich, 99%), trifluoroacetic acid (TFA, Sigma-Aldrich, 99%), hexamethylenediamine (Sigma-Aldrich, 98%), xylenes (Sigma-Aldrich, 75%), hexanes (VWR, 99.5%), ethyl acetate (EtOAc, VWR, 99.5%), dichloromethane (DCM, VWR, 99.5%). Visualization of spot-on pre-coated silica gel G254 TLC plates (Merck) was achieved using the UV light (254 nm), KMnO₄ test, and ninhydrin test. Synthesized compounds were purified on silica gel column chromatographic using 100-200 mesh Silica gel.

Instrumentation

Nuclear Magnetic Resonance Spectroscopy (¹H NMR)

¹H, ¹³C, and DEPT-135 spectra were recorded using a Bruker 400 MHz and Bruker AV-400 MHz NMR Spectrometer. ¹H NMR and ¹³C NMR chemical shifts are expressed in parts per million (ppm, δ scale). CDCl₃ was referenced to CHCl₃ at δ 7.26 ppm in ¹H NMR and δ 77 ppm in ¹³C NMR. DMSO-d₆ was referenced to CHD₂SOCD₃ at δ 2.50 ppm in ¹H NMR and δ 39 ppm in ¹³C NMR. D₂O was referenced to H₂O at δ 4.79 ppm in ¹H NMR. Multiplicities are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Oscillatory Shear Rheology

Oscillatory shear rheology was performed on a TA Instruments Discovery Hybrid Rheometer (DHR-2) with a 20 mm parallel plate geometry and a gap size of 1 mm. Frequency sweeps were performed at 0.03% strain at 120, 130, 140, and 150 °C. Creep recovery experiments were conducted at a stress of 0.01 MPa for 100 seconds and 0 Pa for 100 seconds. All experiments were conducted using a TA Instruments Discovery Hybrid Rheometer (DHR-2) and TA software. Stress relaxation experiments were conducted at 0.3% strain at the desired temperatures.

Dynamic Mechanical Analysis (DMA)

DMA experiments were collected on a TA Q800 DMA (TA Instruments, New Castle, DE). DMA experiments provided quantitative information on copolymer viscoelastic and rheological properties by measuring the response of the samples as they were deformed by a 0.05% sinusoidal strain. Using a tensile clamp, each rectangular-shaped sample was heated from room temperature to 180 °C at 3 °C/min. Sample dimensions were kept consistent as length x width x thickness measured approximately (20 mm x 6 mm x 1 mm) for all samples.
All experiments were run at a frequency of 1 Hz. All DMA experiments were recorded using TA’s Thermal Advantage for Q Series software.

Thermo-gravimetric Analysis (TGA)
TGA experiments were collected on a TA Q5000 TGA, equipped with an autosampler using a 100 μL platinum pan. RAMP experiments were heated at 10 °C/min from room temperature to 600 °C under nitrogen flow (25 mL/min). All TGA experiments were recorded using TA’s Thermal Advantage for Q Series software.

Differential Scanning Calorimetry (DSC)
DSC experiments were collected on a TA Q1000 DSC equipped with an autosampler and refrigerated cooling system 90, using aluminum hermetic SI 3 sealed pans. RAMP experiments were heated at 10 °C/min from -90 to 150 °C and cooled at 10 °C/min from 150 to -90 °C, with 3 min isotherms at each extreme under nitrogen (25 mL/min). All DSC experiments were recorded using TA Thermal Advantage for Q Series software.

Melting Point
Melting points were recorded on MEL-TEMP. The heating source is an oil bath.

High-Resolution Mass Spectroscopy
High-resolution mass spectra were recorded on Agilent LC/MSD TOF mass spectrometer by electrospray ionization time-of-flight (ESI-TOF) experiments.

FT-IR Spectroscopy
Infrared spectra were collected on a Thermo Nicolet 5700 FT-IR spectrometer equipped with a single bounce diamond stage attenuated total reflectance (ATR) accessory.
Experimental procedures

GCBDam synthesis

Reaction conditions: i) KOH, CS₂, 1,3-dibromopropane, H₂O, rt, 6h; ii) tert-butyl (6-aminohexyl)carbamate, DIPEA, DMSO, rt, 5h; iii) TFA:DCM (50:50), 0 °C-rt, 30 min.

Compound 2: To a suspension of 1 (5.00 g, 39.3 mmol) in distilled water (20 mL) at 0 °C, KOH (5.52 g, 98.3 mmol) dissolved in distilled water (10 mL) and CS₂ (8.24 mL, 129 mmol) were added dropwise and the reaction mixture was stirred for 30 min at room temperature. Finally, 1,3-dibromopropane (4.81 mL, 47.2 mmol) was added to the above reaction mixture. The reaction mixture was stirred for 6 h at room temperature and then poured into a citric acid-containing brine solution. The resulting solid was filtered and washed with water followed by diethyl ether and dried in a P₂O₅ desiccator giving 2 (7.5 g, 78%) as a yellow solid. Note: Owing to its poor solubility in common organic solvents, 2 was carried forward for the next reactions without further purification and characterization.

Compound 3: To a suspension of 2 (5.00 g, 20.5 mmol) in DMSO, tert-butyl (6-aminohexyl)carbamate (13.8 mL, 61.6 mmol) and DIPEA (10.7 mL, 61.6 mmol) were added and stirred at room temperature for 6 h. After completion of the reaction, the reaction mixture was poured into a citric acid-containing brine solution. The resultant solid was filtered, washed with water, diethyl ether, and dried in a P₂O₅ desiccator. The residue obtained was purified by column chromatography (eluent: 3% MeOH/DCM, Rf: 0.5) to afford 3 (7.3 g, 62%) as a white solid: mp: 195-200 °C; ¹H NMR (500 MHz, CDCl₃) δ: 11.10 (bs, 2H), 8.48 (bs, 2H), 4.84 (bs, 2H), 4.84 (bs, 2H), 3.41-3.40 (m, 4H), 3.10-3.07 (m, 4H), 1.67-1.62 (m, 4H), 1.52-1.46 (m, 4H), 1.42 (bs, 21H), 1.37-1.34 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.7, 163.4, 156.1, 154.4, 82.4, 78.9, 45.0, 40.3, 30.0, 29.9, 28.3, 26.3; HRMS (ESI) calculated [M+H]^+ for C₂₇H₅₀N₇O₆: 568. 3817, found 568.3809 [M+H]^+.

Compound 4 (GCBDam): The Boc-protected compound 3 was subjected to deprotection by using TFA: DCM (1:1) mixture for 30 min at 0 °C. After completion of the reaction, the mixture was stripped of solvent and co-
evaporated with DCM (3 times). Further, diethyl ether (Et₂O) was added to the reaction mixture, and the resultant solid was washed thrice with Et₂O by decantation and dried under vacuum giving 4, (GCBDam) in quantitative yield, as a white solid: mp: 205-210 °C; ¹H NMR (500 MHz, D₂O) δ: 3.27-3.26 (m, 4H), 2.94-2.92 (m, 4H), 1.63-1.59 (m, 6H), 1.52 (bs, 2H), 1.38 (bs, 4H), 1.27(bs, 4H); ¹³C NMR (125 MHz, D₂O) δ: 163.3-162.5 (residual TFA signal), 161.5, 158.6, 151.5, 119.8-112.9 (residual TFA signal), 83.2, 44.5, 42.2, 39.3, 28.9, 26.5, 25.5, 25.1; HRMS (ESI) calculated [M+H]⁺ for C₁₇H₃₄N₇O₂: 368.2768, found 368.2758 [M+H]⁺.

Figure S1. ¹H NMR spectrum of compound 3.
Figure S2. $^{13}$C NMR spectrum of compound 3.

Figure S3. DEPT-135 NMR spectrum of compound 3.
Figure S4. HRMS-ESI of compound 3.

Figure S5. $^1$H NMR spectrum of GCBDam.
Figure S6. $^{13}$C NMR spectrum of GCBDam.

Figure S7. DEPT-135 NMR spectrum of GCBDam.
Figure S8. HRMS-ESI of GCBDam.

Trifluoroacetic acid salt of hexamethylenediamine synthesis (HexDam.2TFA)

![HRMS-ESI of GCBDam](image)

Scheme S2. Synthesis of HexDam.2TFA.

Hexamethylenediamine (HexDam) (1.21 g, 10.4 mmol) was dissolved in DCM (4 mL) and excess trifluoroacetic acid (TFA) (1.59 mL, 20.8 mmol) was added dropwise into the solution. The solution was stirred at room temperature for 3 h. The resulting mixture was dried under vacuum using a rotary evaporator to eliminate excess trifluoroacetic acid. Finally, the trifluoroacetic acid salt of hexamethylenediamine was dried in a vacuum oven at 40 °C overnight.
Crosslinker synthesis

Scheme S3. Synthesis of trimethylolpropane triacetoacetate (TMPTAc).

1,1,1-Trimethylolpropane (5.00 g, 37.3 mmol), tert-butyl acetoacetate (19.7 mL, 119 mmol), and xylenes (10 mL) were heated overnight in a flask equipped with a distillation column, still head, and thermometers in the base and head of the system. The system was brought to 100 °C under an N₂ atmosphere, and the tert-butanol (t-BuOH) byproduct was collected once the temperature in the still head reached 75-90 °C (bp t-BuOH = 82 °C). The reaction mixture was dried under a vacuum using a rotary evaporator to eliminate trace tert-butanol. The
remaining crude product mixture of trimethylolpropane triacetoacetate (TMPTAc) was purified by column chromatography using 1:4 EtOAc and Hexanes.

**Figure S10.** A) $^1$H NMR; B) $^{13}$C NMR spectra of TMPTAc.$^3$
Synthesis of vitrimers

Single networks (SNs)

Scheme S4. Synthesis of SNs.

TMPTAc (0.500 g, 1.29 mmol) was loaded into a petri dish and dissolved in MeOH (3 mL). In separate vials, HexDam (0.286 g, 2.46 mmol) and HexDam.2TFA (0.044 g, 0.130 mmol) were diluted with MeOH (2 mL). The amine solutions were added to the petri dish, and the solution was evaporated at room temperature under an inert atmosphere. The resulting film was further cured at 70-80 °C for up to 4 h under reduced pressure to yield a yellow film. The film was ground up and compression molded at 150 °C for up to 2 h under an inert atmosphere, yielding a transparent material.

Doubly crosslinked networks (DNs)

TMPTAc (0.500 g, 1.29 mmol) was loaded into a mold and dissolved in MeOH (3 mL). In separate vials, HexDam (0.286 g, 2.46 mmol) and GCBDam (0.073 g, 0.130 mmol) were diluted with MeOH (2 mL). The amine solutions were added to the mold, and the solution was evaporated at room temperature under an inert atmosphere. The resulting film was further cured at 70-80 °C for up to 4 h under reduced pressure to yield a yellow film. The film was ground up and compression molded at 150 °C for up to 1.5-2 h under an inert atmosphere, yielding a transparent material.

Gel swelling study

SNs and DNs were heated in THF (50 mg/mL) at 50 °C in a sealed vial 18 h. Final masses were then obtained after gravity filtration, followed by further drying under reduced pressure for 18 h. Recovered mass percentages (i.e., gel fractions) were then calculated for each sample.

Table S1. Gel fraction study of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Gel fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN&lt;sub&gt;5%&lt;/sub&gt;</td>
<td>80.16%</td>
</tr>
<tr>
<td>DN&lt;sub&gt;5%&lt;/sub&gt;</td>
<td>79.45%</td>
</tr>
<tr>
<td>SN&lt;sub&gt;10%&lt;/sub&gt;</td>
<td>72.77%</td>
</tr>
<tr>
<td>DN&lt;sub&gt;10%&lt;/sub&gt;</td>
<td>72.56%</td>
</tr>
</tbody>
</table>
Figure S11. A) Molds to prepare rectangular-shaped sample; B) Film formed at 90 °C under vacuum after curing; C) shredded sample in compression mold; D) rectangular-shaped sample for DMA after compression molding.

Figure S12. IR spectra of A) DN₅% and SN₅%; B) DN₁₀% and SN₁₀%.
Thermogravimetric analysis (TGA)

Figure S13. Comparison of TGA for A) DN5% and SN5%; B) DN10% and SN10%.

Isothermal Study

Figure S14. Isothermal TGA analysis at 150°C for A) DN5% and SN5%; B) DN10% and SN10%.
Rheology experiments

Frequency sweeps

**Figure S15.** Frequency sweeps of A) SN$5\%$ and B) DN$5\%$ over the temperature range 120-150 °C.

**Figure S16.** Comparison of the frequency sweeps of SN$5\%$ and DN$5\%$ at A) 120 °C; B) 130 °C; C) 140 °C; D) 150 °C.
Figure S17. Frequency sweeps of A) SN_{10\%} and B) DN_{10\%} over the temperature range 120-150 °C.

Figure S18. Comparison of the frequency sweeps of SN_{10\%} and DN_{10\%} at A) 120 °C; B) 130 °C; C) 140 °C; D) 150 °C.
Creep-recovery experiments

**Figure S19.** Comparison of the creep-recovery experiments of SN\(_{5\%}\) and SN\(_{10\%}\) at A) 120 °C; B) 130 °C; C) 140 °C; D) 150 °C.

**Table S2.** Recovery strain\% of the samples SN\(_{5\%}\) and SN\(_{10\%}\)

<table>
<thead>
<tr>
<th>Sample - Temperature</th>
<th>Recovery strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN(_{5%})-120 °C</td>
<td>2.1 %</td>
</tr>
<tr>
<td>SN(_{5%})-130 °C</td>
<td>3.8 %</td>
</tr>
<tr>
<td>SN(_{5%})-140 °C</td>
<td>7.1 %</td>
</tr>
<tr>
<td>SN(_{5%})-150 °C</td>
<td>12.6 %</td>
</tr>
<tr>
<td>SN(_{10%})-120 °C</td>
<td>17.7 %</td>
</tr>
<tr>
<td>SN(_{10%})-130 °C</td>
<td>34.8 %</td>
</tr>
<tr>
<td>SN(_{10%})-140 °C</td>
<td>63.8 %</td>
</tr>
<tr>
<td>SN(_{10%})-150 °C</td>
<td>107.5 %</td>
</tr>
</tbody>
</table>
Figure S20. Comparison of the creep-recovery experiments of DN$_{5\%}$ and DN$_{10\%}$ at A) 120 °C; B) 130 °C; C) 140 °C; D) 150 °C.

Table S3. Recovery strain% of the samples DN$_{5\%}$ and DN$_{10\%}$

<table>
<thead>
<tr>
<th>Sample - Temperature</th>
<th>Recovery strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>DN$_{5%}$-120 °C</td>
<td>1.1 %</td>
</tr>
<tr>
<td>DN$_{5%}$-130 °C</td>
<td>2.2 %</td>
</tr>
<tr>
<td>DN$_{5%}$-140 °C</td>
<td>4.2 %</td>
</tr>
<tr>
<td>DN$_{5%}$-150 °C</td>
<td>8.4 %</td>
</tr>
<tr>
<td>DN$_{10%}$-120 °C</td>
<td>10.3 %</td>
</tr>
<tr>
<td>DN$_{10%}$-130 °C</td>
<td>20.7 %</td>
</tr>
<tr>
<td>DN$_{10%}$-140 °C</td>
<td>41.5 %</td>
</tr>
<tr>
<td>DN$_{10%}$-150 °C</td>
<td>72.3 %</td>
</tr>
</tbody>
</table>
Stress relaxation

**Figure S21.** Comparison of the stress-relaxation experiments of SN$_{5\%}$ and SN$_{10\%}$ at A) 120 °C; B) 130 °C; C) 140 °C; D) 150 °C; E) 160 °C.
Figure S22. Comparison of the stress-relaxation experiments of DN$_{5\%}$ and DN$_{10\%}$ at A) 120 °C; B) 130 °C; C) 140 °C; D) 150 °C; E) 160 °C.
Figure S23. Triplicates of raw data for A) SN$_{10\%}$; B) DN$_{10\%}$; C) SN$_{5\%}$; D) DN$_{5\%}$. 
Arrhenius relation (calculation of activation energy using a single Maxwell model)

The characteristic relaxation time ($\tau$) is the normalized stress relaxation at $1/e$, assuming a single Maxwell element as seen in literature examples.

$$\tau = \text{time at } (1/e) = \text{time at 0.37 normalized modulus}$$

$$\ln(\tau) = \frac{E_a}{RT} + \ln(\tau_0) \quad \cdots \quad (1)^4, 5$$

![Image of stress relaxation curves for different samples and temperatures.]

**Figure S24.** Normalized stress relaxation curves fitted to three phase exponential decay for A) SN$_{5\%}$ and DN$_{5\%}$; B) SN$_{10\%}$ and DN$_{10\%}$.

![Image of lnT vs. 1000/T plots for different samples and temperatures.]

**Figure S25.** Calculation of activation energies of flow from stress relaxation A) DN$_{5\%}$ and SN$_{5\%}$; B) DN$_{10\%}$ and SN$_{10\%}$. 
Figure S26. Activation energy of flow calculated from creep-recovery experiment following previous report A) DN$_{5\%}$ and SN$_{5\%}$; B) DN$_{10\%}$ and SN$_{10\%}$.$^{6,7}$
Reprocessing analysis

![Image of sample and molded samples](image)

**Figure S27.** A) Sample before analysis; B) Shredded samples after analysis in a mold; C) Compression molded samples.

After analysis of the sample, the material was shredded into small pieces. The shredded sample was compression molded at 150 °C under an inert atmosphere for 2 h to yield the reprocessed sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E'(175 , ^\circ C) )</th>
<th>( T_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN(_{10%})</td>
<td>0.401 MPa</td>
<td>87 °C</td>
</tr>
<tr>
<td>DN(_{10%})</td>
<td>0.399 MPa</td>
<td>126 °C</td>
</tr>
<tr>
<td>SN(_{5%})</td>
<td>8.31 MPa</td>
<td>100 °C</td>
</tr>
<tr>
<td>SN(_{5%})_Recycle 1</td>
<td>9.13 MPa</td>
<td>113 °C</td>
</tr>
<tr>
<td>SN(_{5%})_Recycle 2</td>
<td>6.3 MPa</td>
<td>100 °C</td>
</tr>
<tr>
<td>SN(_{5%})_Recycle 3</td>
<td>5.14 MPa</td>
<td>99 °C</td>
</tr>
<tr>
<td>SN(_{5%})_Recycle 5</td>
<td>6.28 MPa</td>
<td>100 °C</td>
</tr>
<tr>
<td>DN(_{5%})</td>
<td>8.82 MPa</td>
<td>122 °C</td>
</tr>
<tr>
<td>DN(_{5%})_Recycle 1</td>
<td>6.68 MPa</td>
<td>114 °C</td>
</tr>
<tr>
<td>DN(_{5%})_Recycle 2</td>
<td>6.48 MPa</td>
<td>114 °C</td>
</tr>
<tr>
<td>DN(_{5%})_Recycle 3</td>
<td>6.75 MPa</td>
<td>104 °C</td>
</tr>
<tr>
<td>DN(_{5%})_Recycle 4</td>
<td>8.21 MPa</td>
<td>107 °C</td>
</tr>
<tr>
<td>DN(_{5%})_Recycle 5</td>
<td>7.91 MPa</td>
<td>114 °C</td>
</tr>
</tbody>
</table>
DMA for reprocessing samples

**Figure S28.** Temperature ramp by DMA for DN$_{5\%}$ over five recycling cycles.

**Figure S29.** Temperature ramp by DMA for SN$_{5\%}$ over five recycling cycles.
DSC thermograms

Figure S30. DSC thermograms of DN$_{5\%}$ over five reprocessing cycles.

Figure S31. DSC thermograms of SN$_{5\%}$ over five reprocessing cycles.
FT-IR spectroscopy

Figure S32. FT-IR spectra of DN5% over five reprocessing cycles.

Figure S33. FT-IR spectra of SN5% over five reprocessing cycles.
Chemical degradation studies

Butyl amine (1 mL) was added into the vial containing networks (20-30 mg) and MeOH (2 mL). The solution was heated at (50 °C) overnight to obtain a clear solution.

Figure S34. Images of chemical degradation studies.

References