Supplementary Information: Dynamic Covalent Chemistry for Architecture Changing Interpenetrated and Single Networks

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Experimental section

Materials

The required materials were purchased from commercial suppliers and used without any purification unless otherwise specified.

2-((1-(2-(acryloyloxy)ethyl)-2,5-dioxopyrrolidin-3-yl) thio)ethyl acrylate (TMMDA) was synthesized according to the literature. [1] The purity of the compound was confirmed using ^{1}H-NMR (^{1}H NMR 300 MHz, DMSO-d6, δ ppm)

Synthesis of single network crosslinked by TMMDA

2-Hydroxyethyl acrylate (HEA) (5 g), azobis(isobutyronitrile) (AIBN) (50 mg), N,N dimethylformamide (DMF) (10 g) and TMMDA crosslinker (0.1 g, 2%) were added in a vial and the solution was sonicated for 15 min to mix all the reactants. Then the mixture was evenly pipetted into a Teflon mold for the polymerization. The polymerization was carried out at 65 °C for 2h. Then materials were taken out from the mold and allowed to dry for 3 days at room temperature followed by vacuum drying for one day at 40 °C. Conversion was calculated using mass difference between initial monomer weight and the final material, giving a conversion of over 99%.

Synthesis of Interpenetrating Network crosslinked by TMMDA

2-Hydroxyethyl acrylate (HEA) (5 g), azobis(isobutyronitrile) (AIBN) (50 mg), N, N dimethylformamide (DMF) (10 g) and TMMDA crosslinker (0.1 g, 2%) were added in a vial and the solution was sonicated for 15 min to mix all the reactants. Then the mixture was evenly pipetted into two Teflon molds for the polymerization. A 15 min sonicated mixture of 2-Hydroxyethyl acrylate (HEA) (5 g), V-70 (50 mg), N,N dimethylformamide (DMF) (5 g) and TMMDA crosslinker (0.1 g, 2%) was evenly transferred to the existing polymer and covered with a glass plate for 24h to ensure the polymer was completely swelled with the second network mixture. Then the polymerization was carried out at 35 °C for 6h. Materials were removed from the mold and allowed to solvent to evaporate for 3 days followed by drying under vacuum for one day. Conversion was calculated using mass difference between initial monomer weight and the final material, giving a final conversion of 94%.

Tensile testing

An Instron 3344 universal testing system with a 100N load cell was used to characterize the elastomeric properties of the material. Extensions of the dog bone samples were increased at a rate of 0.5 mm/s. All data were collected until material broke.

Self-healing procedure

Materials were cut into half using a sharp blade. Then two pieces were gently pressed from fingers for few seconds. Materials were healed at 90^{o}C for different time points (1hr, 4hr, 16hr, 24hr). Samples were tested by performing tensile tests.

Infrared Spectroscopy

Infrared (IR) spectroscopy was performed on a PerkinElmer Spectrum one FT-IR Spectrometer.

Calculation of average molecular weight between cross-links (M_c)

Average Molecular weight between crosslinks (M_c) was calculated from equation 1.[2] Average storage modulus (E) at low frequency (0.1Hz-0.01Hz) was taken to calculate G according to the equation 2. In here we assumed that the density of the polymer is equal to polyHEA (1.29 g/mL) [3] and the material is incompressible.

$$G = \frac{E}{3} \qquad \text{Eq 1}$$

$$G = \frac{\rho RT}{M_c} \qquad \text{Eq 2}$$

Dynamic Mechanical Analysis (DMA)-Temperature sweep experiment

TA instrument Q800 equipped with a tension clamp was used to carry out the Temperature Sweep dynamic mechanical analysis (DMA) using temperature ramp/ frequency sweep test. The temperature ranged from 30 °C to 180 °C with a rate of 10 °C/minute at a constant frequency of 1Hz. Before the test, samples were pre-equilibrated at 30 °C for 1minute. 1% of strain with a preload force of 0.01 N was used to run the experiment.

Dynamic Mechanical Analysis (DMA)-Frequency sweep experiment

TA instrument Q800 equipped with a tension clamp was used to carry out the Temperature Sweep dynamic mechanical analysis (DMA) using Isothermal temperature/frequency sweep test. Frequency was ranged from 0.01- 150 Hz at a constant temperature of 30 °C. Samples were hold one minute to equilibrate at 30 °C. Data was collected with a strain of 1%, a preload force of 0.01 N.

Dynamic Mechanical Analysis (DMA)-Creep and Creep Recovery Methods

Creep and Creep Recovery test were performed on a TA instrument Q800 equipped with a film tension clamp. Samples were equilibrated one minute at 30 °C before applying stress. Temperature was held constant at 30 °C. The experiment was carried out with a stress of 0.01MPa with a preload force of 0.001N. Stress were applied for 60 minutes and then allowed to recover for 120 minutes.

Differential Scanning Calorimetry (DSC)

All glass transition temperatures (T_g) were obtained using a TA instrument Q20 DSC. The data was obtained in a heat cool heat cycle ranging from -40 °C to 160 °C with 10 °C/min heating rate. Data from second heating cycle was used to plot the curve.

Swelling Experiment

The gels were dried by placing them in the vacuum for 3 days. Both cold and heated samples were weighted and then immersed in excess water for 2 days at room temperature. Samples were weighted and the swelling ratio was calculated as the equation3: m_S and m_D are the weights of the swollen and dry gels respectively.

$$\frac{m_S - m_D}{m_D} \times 100 = \ swelling\ ratio \qquad \text{Eq 3}$$

Supplemental Data

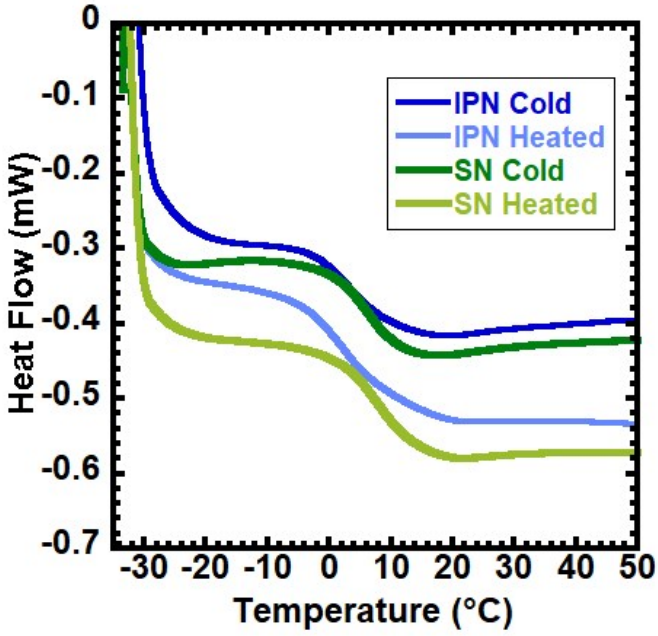

Figure S1: DSC curves of IPN and SN cold and heated samples.

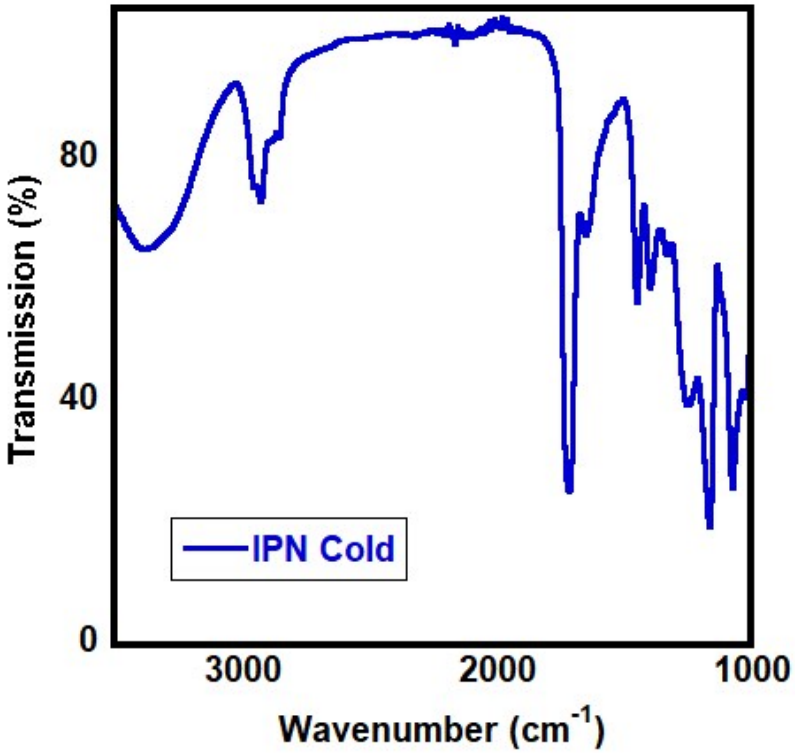

Figure S2: IR of cold IPN

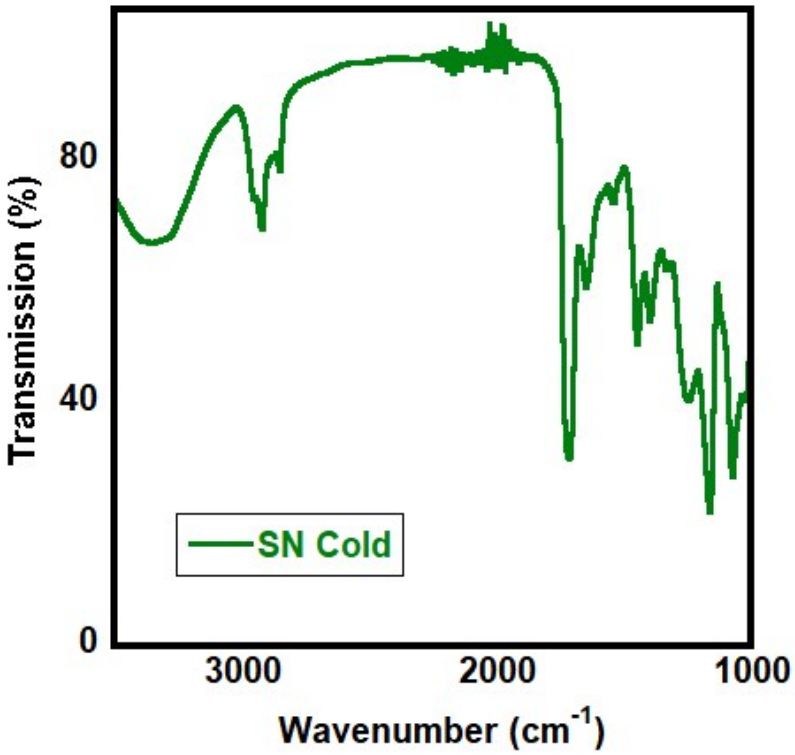

Figure S3: IR of cold SN

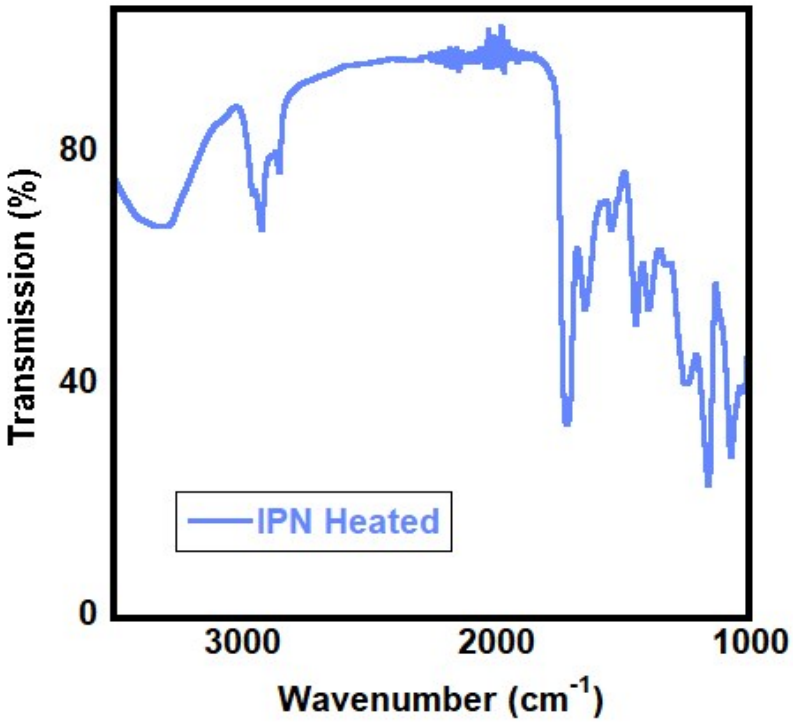

Figure S4: IR of heated IPN

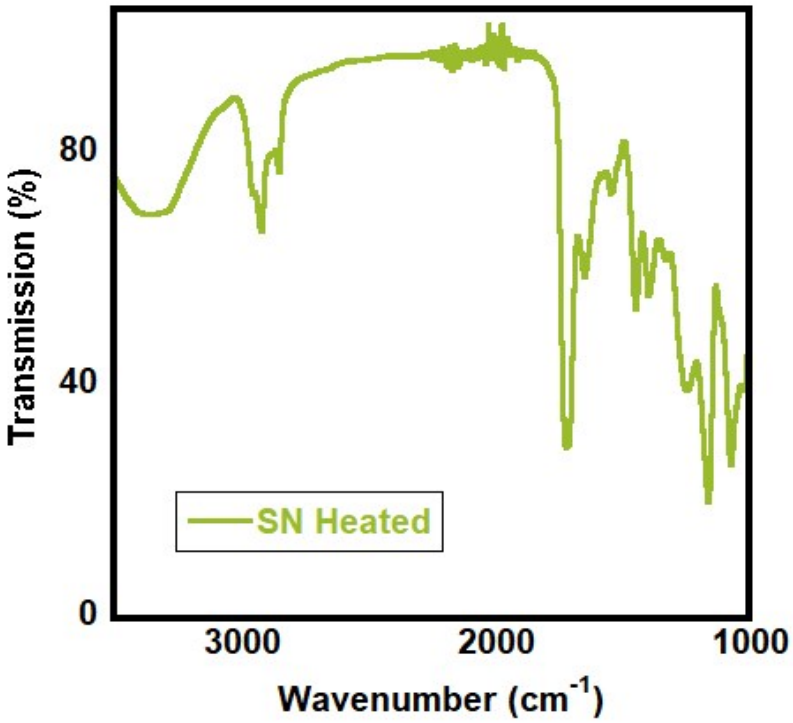

Figure S5: IR of heated SN

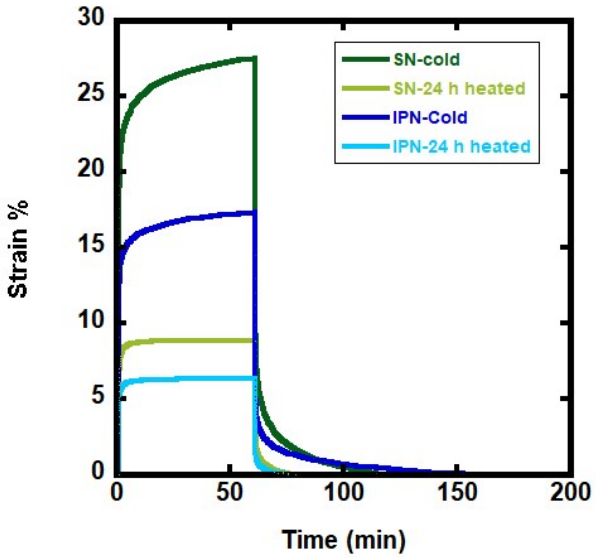

Figure S6. Creep and creep recovery experiment for both SN and IPN samples. Samples heated at 90 °C for 24 h denoted as 'heated' and unheated samples were denoted as 'cold'.

References

(1) Chakma, P.; Possarle, L. H. R.; Digby, Z. A.; Zhang, B.; Sparks, J. L.; Konkolewicz, D. Dual Stimuli Responsive Self-Healing and Malleable Materials Based on Dynamic Thiol-Michael Chemistry. *Polym. Chem.* **2017**, *8* (42), 6534–6543.

(2) Treloar, L. R. G. The Elasticity and Related Properties of Rubbers. *Reports Prog. Phys.* **1973**, *36* (7), 755–826. https://doi.org/10.1088/0034-4885/36/7/001.

(3) Andreopoulos, A. G. Acrylate) Networks. **1989**, *10* (February 1988).