

# **Supplementary Information: Effect of Polymer Network Architecture, Enhancing Soft Materials using Orthogonal Dynamic Bonds in an Interpenetrating Network**

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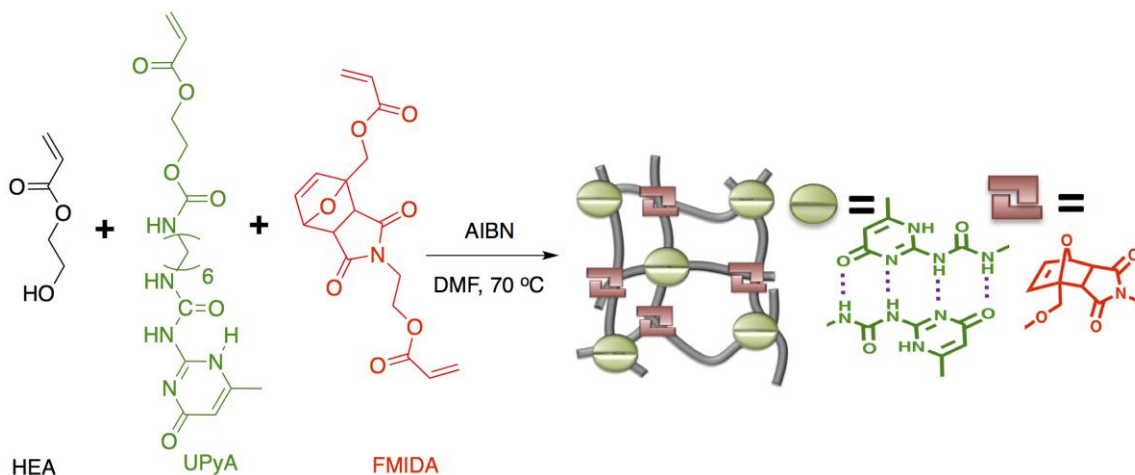
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## Experimental

### Materials

All materials were purchased from commercial suppliers unless otherwise specified. All reagents were used as received unless otherwise specified. 2-hydroxyethyl acrylate (HEA, Alfa Aesar), divinylbenzene (DVB, Aldrich), and azobis(isobutyronitrile) (AIBN, Aldrich) were used as received. 2-(((6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)hexyl)carbamoyl)oxy)ethyl acrylate (UPyA) was synthesized as outlined in the literature.<sup>1-3</sup> (2-(2-(acryloyloxy)ethyl)-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-epoxyisoindol-4-yl)methyl acrylate (FMIDA) was synthesized using procedures outlined in the literature.<sup>3,4</sup>

### Synthesis of poly(HEA)-2.5wt%UPyA-2.5wt%FMIDA single network (SN)

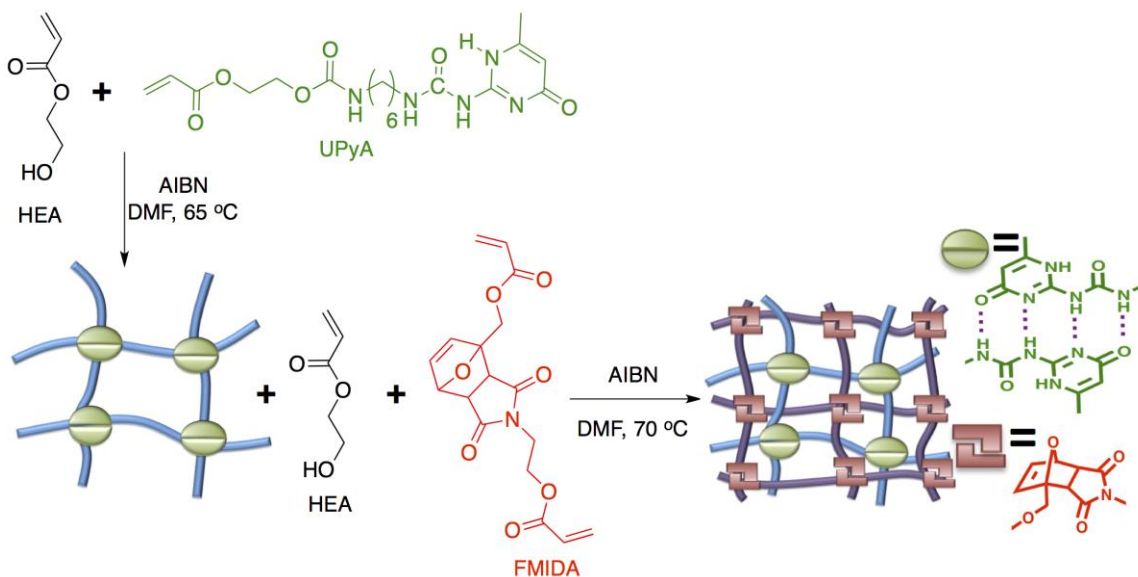


Azobis(isobutyronitrile) (AIBN) (40mg), HEA (4g), *N,N*-dimethylformamide (DMF) (8ml), UPyA (100 mg), and FMIDA (100 mg) were added to a vial. The solution was transferred to a Teflon mold for polymerization. The polymerization proceeded at 70 °C for 2 hours. The material was removed from the mold and allowed to dry at room

temperature and pressure for 3 days, followed by 16h in a vacuum oven at 35 °C.

Monomer conversion was determined by gravimetry and found to be greater than 90%.

*Synthesis of poly(HEA)-2.5wt%UPyA-2.5wt%FMIDA interpenetrating network (IPN)*



Azobis(isobutyronitrile) (AIBN) (20mg), HEA (2g), *N,N*-dimethylformamide (DMF) (8ml), and UPyA (100 mg) were added to a vial. The solution was heated at 65 °C for 16h to polymerize, giving a viscous liquid of poly(HEA) with pendant UPy units. The conversion of this first network was found to be greater than 90% as determined by nuclear magnetic resonance (NMR). Azobis(isobutyronitrile) (AIBN) (20mg), HEA (2g), and FMIDA (100 mg) were added to the vial. The solution was transferred to a Teflon mold for polymerization of the second network. The polymerization proceeded at 70 °C for 2 hours. The material was removed from the mold and allowed to dry at room temperature and pressure for 3 days, followed by 16h in a vacuum oven at 35 °C. Monomer conversion was determined by gravimetry and found to be greater than 90%.

### *Synthesis of poly(HEA)-2 wt%DVB single network (DVB)*

Azobis(isobutyronitrile) (AIBN) (40mg), HEA (4g), *N,N*-dimethylformamide (DMF) (8ml), and divinylbenzene (DVB) (96 mg) were placed in a vial. The solution was transferred to a Teflon mold for polymerization. The polymerization proceed at 70°C for 90 minutes. The material was removed for the mold and allowed to dry at room temperature and pressure for 3 days, followed by 16h in a vacuum oven at 35°C.

## **Methods and Techniques**

### *Analytical Methods*

Infrared (IR) spectroscopy was performed on a Perkin Elmer Spectrum 100 Spectrometer scanning from 4000 to 700 wavenumbers. All nuclear magnetic resonance (NMR) spectra were collected on a Bruker 300 MHz or 500 MHz spectrometer.

### *Differential Scanning Calorimetry (DSC)*

Differential scanning calorimetry was performed on a TA instruments Q20 system using a heat cool heat cycle over the range -40 °C to 160 °C. Heating rates were 10 °C per minute and only data from the second heating cycle was collected on a single sample of SN and a single sample of IPN. The glass transition temperature was found by determining the inflection point after 5 pt smoothing. Uncertainty in glass transition temperature was determined as half the width at 95% of the minimum of the derivative of heat flow with respect to temperature.

### *Tensile Testing*

Materials were tested for tensile strength using an Instron Model 3344 universal testing system equipped with a 100 N load cell at ambient temperature. The extension was increased at a rate of 1 mm/s. All samples were measured until failure. Uncut peak stress

and strain at break data were determined as the mean and standard deviation of 5 replicates.

#### *Young's Modulus Calculation*

The tensile response of the material was modeled using an incompressible Ogden hyperelastic constitutive law (Eq. S1):

$$S = \frac{2G}{a} \left( \lambda^{a-1} - \lambda^{-1-(a/2)} \right) \quad \text{Eq. S1}$$

where  $\sigma$  is engineering stress,  $G$  is the shear modulus,  $\alpha$  is the strain hardening exponent, and  $\lambda$  is the stretch ratio.<sup>5</sup>  $G$  and  $\alpha$  were found for each sample by fitting Eq. S1 to the experimental stress-strain data, and the elastic modulus ( $E$ ) was found from Eq. S2:

$$E = 2G(1 + \nu) \quad \text{Eq. S2}$$

where  $\nu$  represents Poisson's ratio (taken as 0.5 for an incompressible material). Mean Young's modulus and strain hardening exponents are given in the table below using 5 specimens in the averaging procedure.

**Table S1:** Mean Young's modulus and strain hardening exponents for the IPN and SN data.

Sample	E (kPa)	$\alpha$ (Dimensionless)
SN	200±30	1.93±0.06
IPN	80±20	2.8±0.2

#### *Fracture Toughness Determination*

An Instron Model 3344 universal testing system equipped with a 100 N load cell was used to analyze fracture toughness at ambient temperature. Each test consisted of a pristine sample and a sample that was notched horizontally to the midpoint of the

sample.<sup>6</sup> For each notched sample, the extension was increased at a rate of 1 mm/s until the sample broke. Similarly, the pristine sample was subjected to extension at a rate of 1 mm/s until at least the extension needed to break the notched sample. The fracture energy was determined using the following formula (Eq. S3) applied to the pristine sample:

$$G = H \int_1^{\lambda_c} \sigma d\lambda \quad \text{Eq. S3}$$

Where  $H$  is the original height of the material before tensile testing,  $\sigma$  is the stress,  $\lambda$  is the stretch ratio and  $\lambda_c$  is critical stretch ratio at which the notched sample broke. At least two notched and two unnotched specimens were tested for fracture toughness determinations for each material studied, DVB, SN and IPN.

#### *Loading-Unloading Experiments*

Materials were tested for tensile strength using an Instron Model 3344 universal testing system equipped with a 100 N load cell at ambient temperature. The extension was increased at a rate of 0.5 mm/s until a strain of 1 was achieved followed by a decrease of extension at a rate of 0.5 mm/s until a strain of 0 was achieved. Mean energy dissipated and standard deviation was determined using 2 replicates.

The proportion of energy dissipated was determined as the hysteresis ( $H$ ) between loading and unloading curves using the following equation (Eq. S4)<sup>7</sup>:

$$H = \frac{\int_0^1 \sigma_{\text{loading}} d\varepsilon - \int_0^1 \sigma_{\text{unloading}} d\varepsilon}{\int_0^1 \sigma_{\text{loading}} d\varepsilon} \quad \text{Eq. S4}$$

where  $\sigma_{\text{loading}}$  is the stress on the loading cycle (where strain is increasing),  $\sigma_{\text{unloading}}$  is the stress on the unloading cycle (where strain is decreasing), and  $\varepsilon$  is the strain.

### *Stress Relaxation Experiments*

An Instron Model 3344 universal testing system equipped with a 100 N load cell was used to analyze stress relaxation at ambient temperature. For all materials, the extension was increased at a rate of 0.5 mm/s until a strain of  $\epsilon = 1$  mm/mm was achieved. The strain was maintained at 100% while the stress was measured over time.

### *Creep Experiments*

An Instron Model 3344 universal testing system equipped with a 100 N load cell was used to analyze the extent of creep under constant load at ambient temperature. All materials were extended at the rate of 0.25 mm/s until a stress of 50 kPa was achieved. The stress was maintained at 50 kPa while the strain was measured over time.

### *Creep Recovery Experiment*

To determine creep recovery, a sample was stretched to twice the original length (tensile strain of 1) and fixed in this configuration for 48 h. After the 48 h had passed the tensile strain was released and the sample length was measured and compared with the original length as a function of time.

### *Rheology*

A TA Instruments Discovery HR-1 rheometer with a 20 mm crosshatched plate geometry was used for rheological frequency sweeps at an applied strain of 1%. The storage and loss moduli were determined at 25 °C.

### *Cutting and Healing Procedures*

Materials were cut with a razor blade. Cut samples were completely cut through the thickness of the sample. The two sections were placed in contact by gentle pressure from

the fingers for several seconds. Materials were heated at 100 °C for different times ranging from 1h to 4h.

#### *Reshaping Materials*

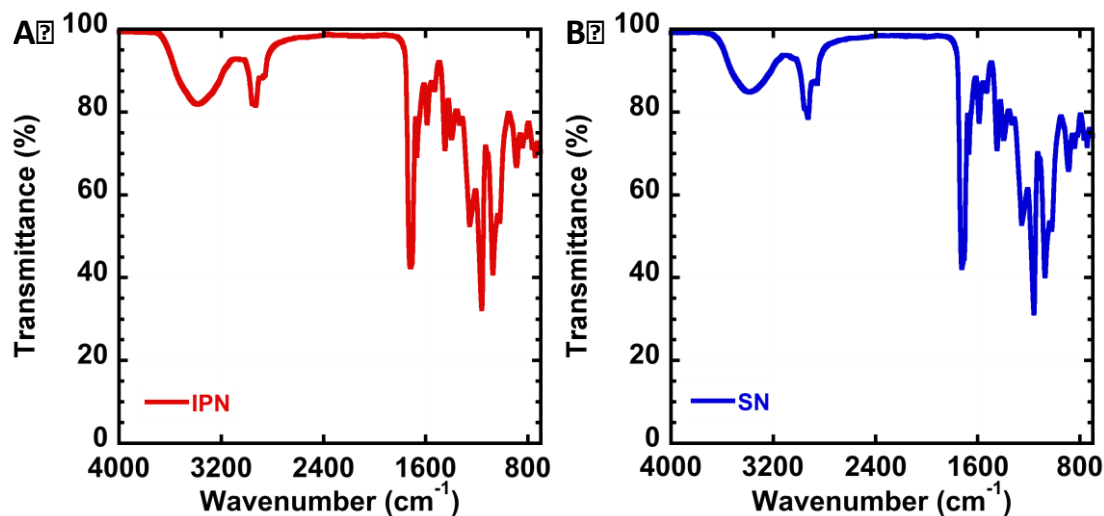
A series of IPN and SN dogbone shaped material were twisted by 360° and fixed in this configuration. The materials were heated at 100°C for 1 hour, 2 hours, or 4 hours. After heating, the sample was released and allowed to relax. The angle between the two ends of the polymer was determined for each sample 1h after being removed from the oven.

#### *Swelling Ratio Determination*

Small samples of IPN and SN samples were placed in glass vials. Samples were immersed with a large excess of solvent. Three solvents were studied: water, acetone, and hexanes. At specified periods, the samples were taken out of solution, blotted to remove excess solvent and weight. This process was repeated until the mass of the polymer + solvent increased by less than 5%. Two samples were used for determining mean swelling ratios.



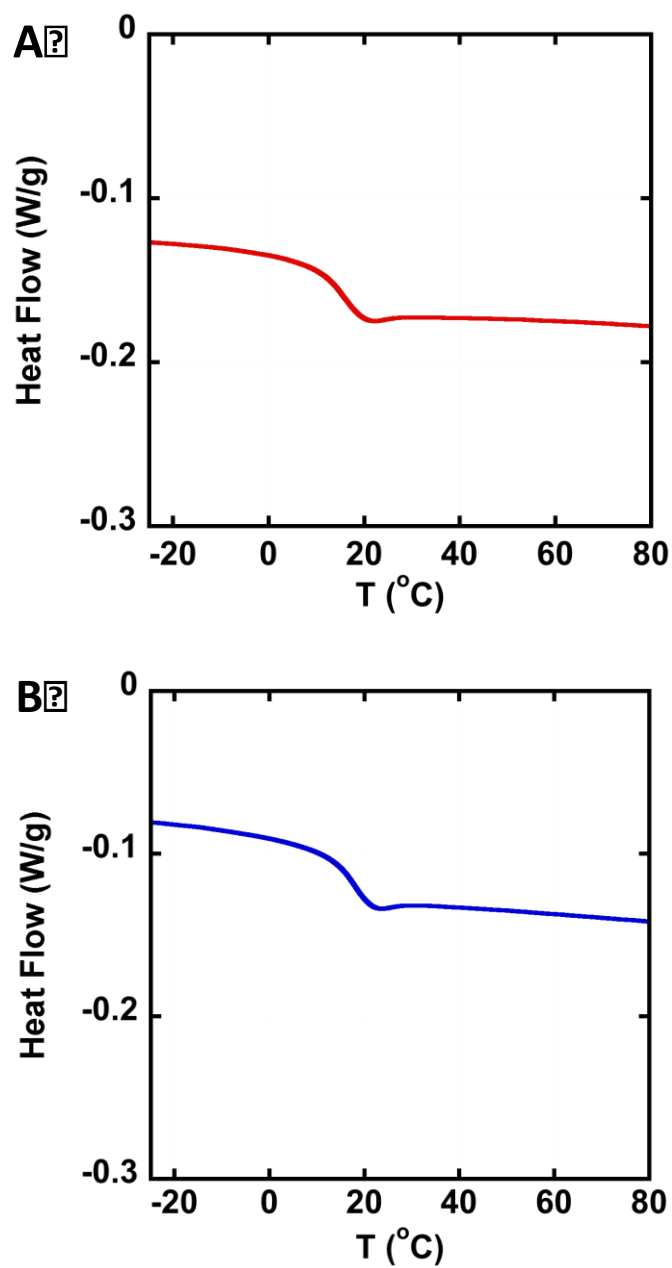
## Supplementary Data



**Figure S1:** Infrared spectra for the poly(HEA) IPN (A) and SN (B) materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA.

**Table S2:** Proposed assignments of the major infrared (IR) bands of poly(HEA) IPN and SN materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA.<sup>8</sup>

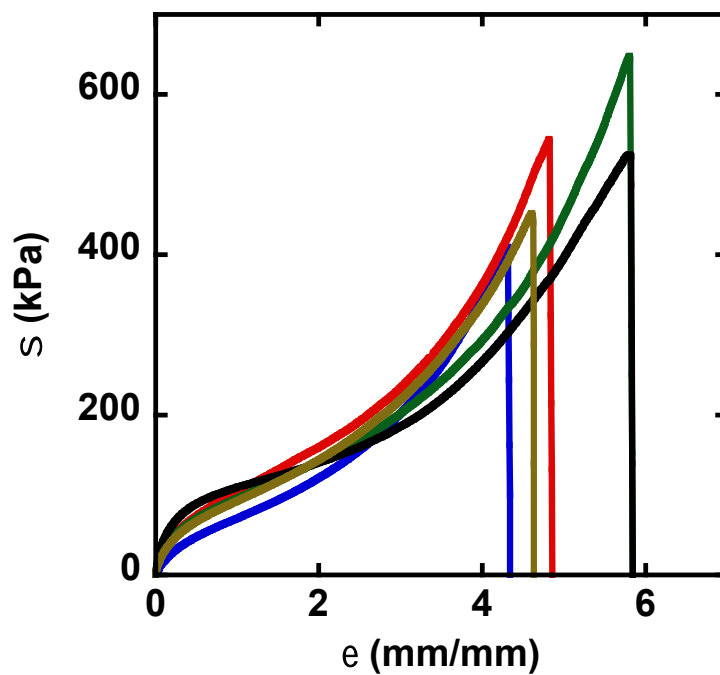
Peak (cm <sup>-1</sup> )	Proposed Assignment	Reference
3400	O-H stretch	9,10
2950	C-H stretch	9
1720	C=O stretch	9,10
1450	CH <sub>2</sub> bend	9,10
1400	CH <sub>2</sub> rock and twist	10
1250	O-H bend	9
1160	C-O ester stretch	9,10
1070	C-O-C stretch	10
890	O-CH <sub>2</sub> -CH <sub>2</sub> rocking	11



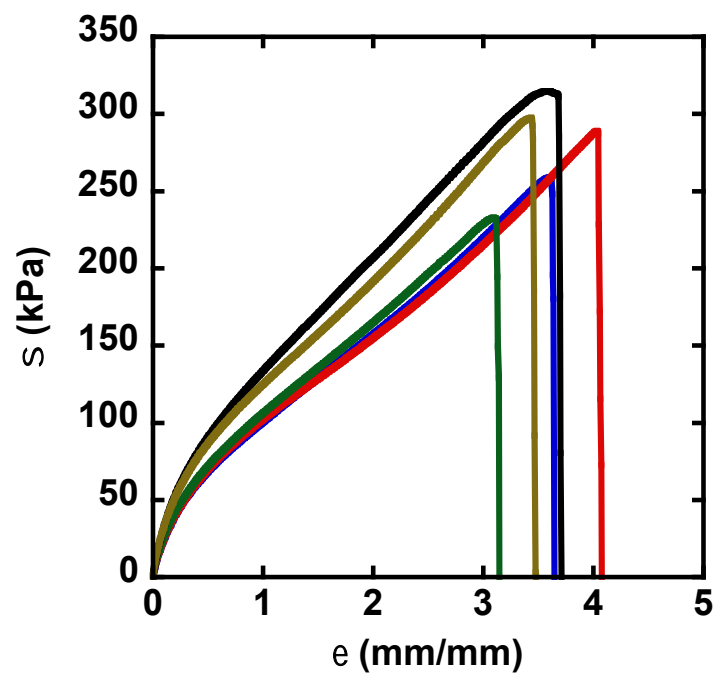
**Figure S2:** Differential scanning calorimetry heating cycle data for the poly(HEA) IPN (A) and SN (B) materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA.

**Table S3:** Swelling ratio data for the poly(HEA) IPN and SN materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA.

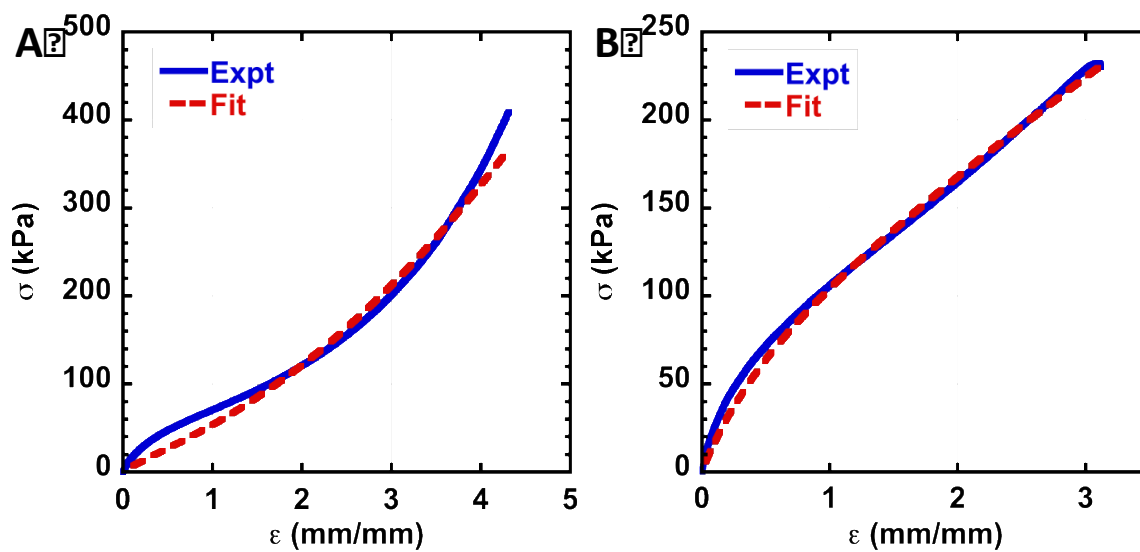
Sample	Swelling Ratio (H <sub>2</sub> O)	Swelling Ratio (acetone)	Swelling Ratio (Hexanes)
IPN	4.2±0.2	1.32±0.04	1.0
SN	4.70±0.09	1.37±0.01	1.0



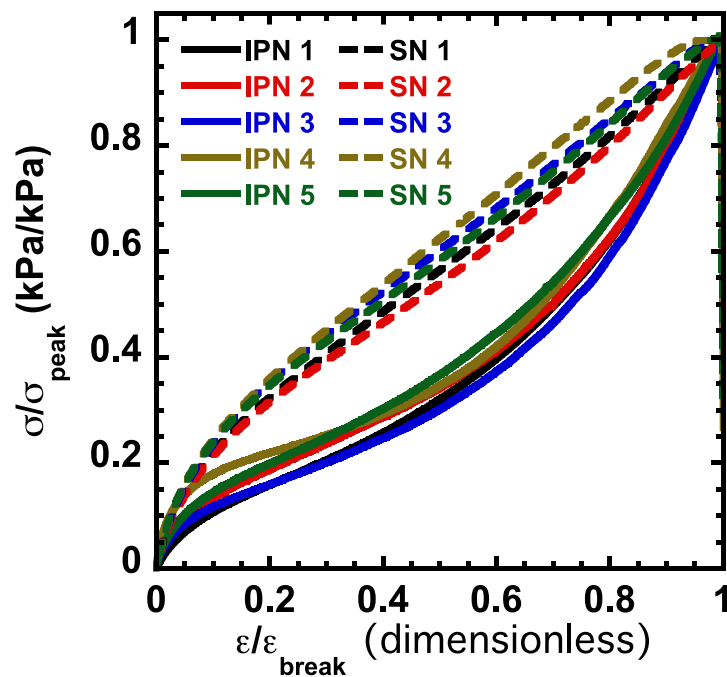
**Figure S3:** Typical stress strain data for the poly(HEA) IPN material crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA.



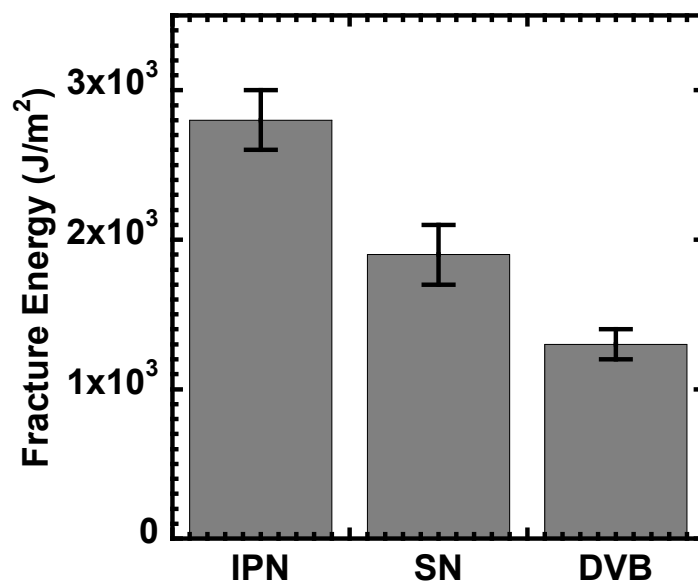
**Figure S4:** Typical stress strain data for the poly(HEA) SN material crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA.



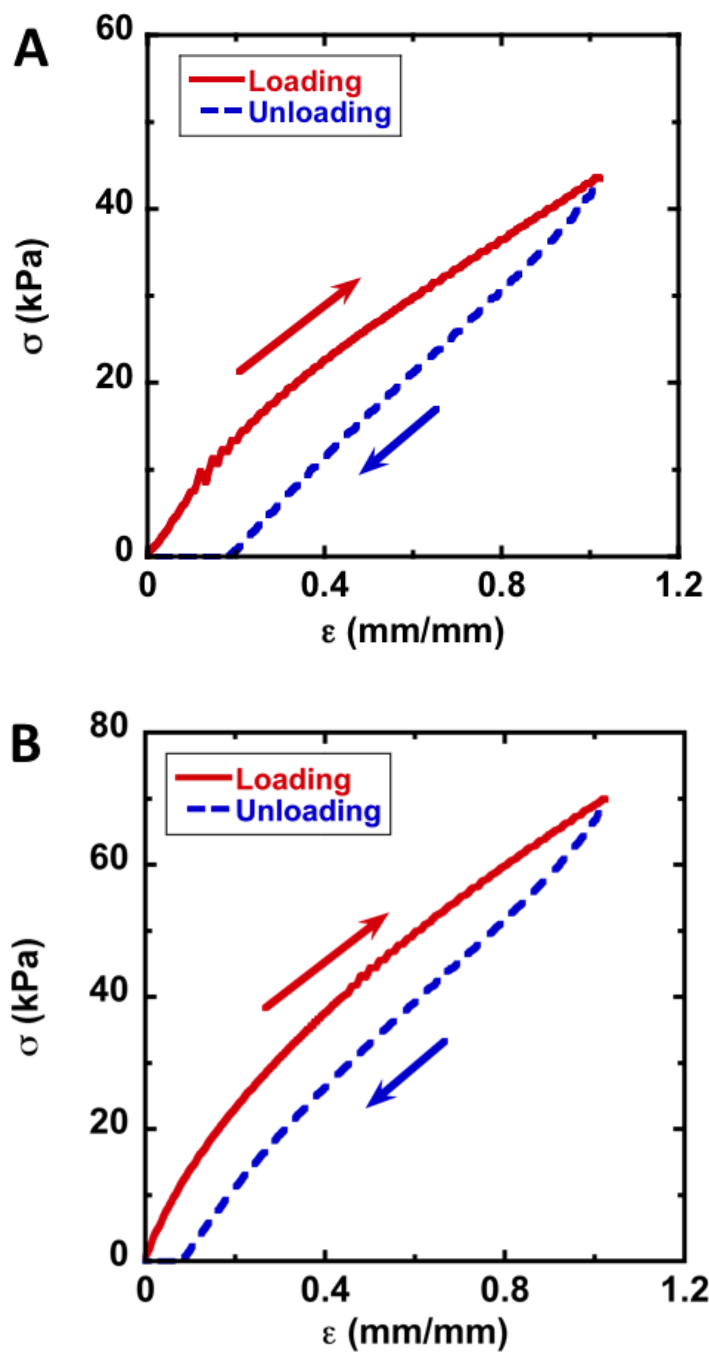
**Figure S5:** Typical fit of the Ogden Model to stress strain data for a typical IPN (A) and a typical SN (B) material.



**Figure S6:** Normalized stress-strain data showing the characteristic behavior of both the SN and IPN materials.



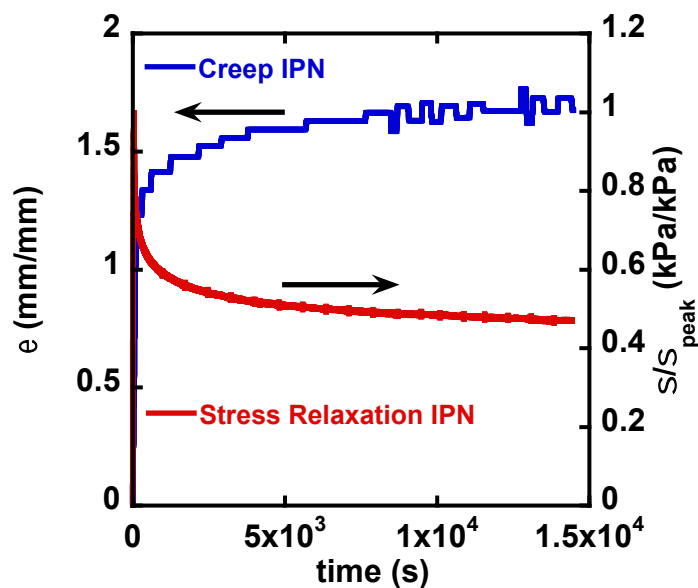
**Figure S7:** Fracture energy data for the poly(HEA) crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA IPN and SN materials, and poly(HEA) crosslinked with 2 wt% DVB.



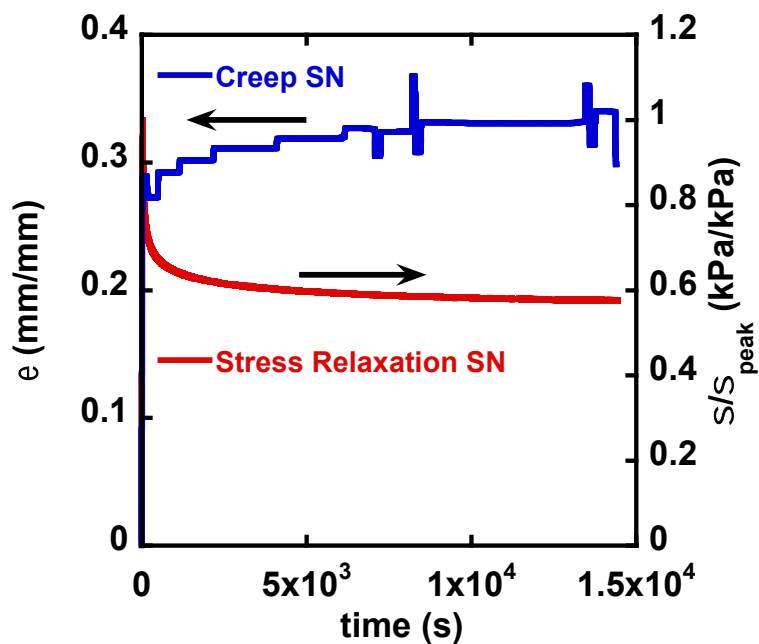
**Figure S8:** Typical loading-unloading curves for poly(HEA) crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA in an IPN (A) and SN (B) architecture. In these experiments a strain rate of 0.5 mm/s was used.

**Table S4:** Hysteresis of IPN and SN materials determined during loading-unloading experiments

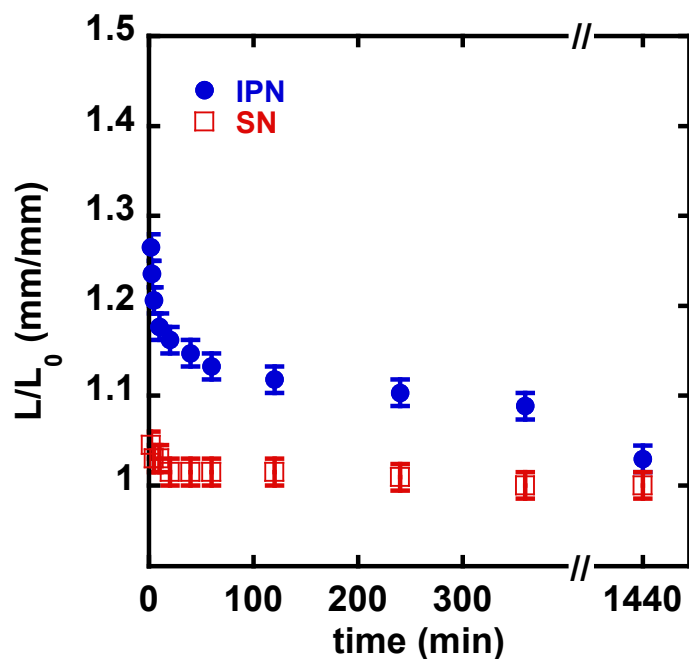
Sample	Energy		H (%)
	Loading	Unloading	
	(J/m <sup>3</sup> )	(J/m <sup>3</sup> )	
IPN	25.3±0.9	17.1±0.9	32±1
SN	43.2±0.2	33.9±0.5	22±1



**Figure S9:** Creep and stress relaxation data for the poly(HEA) IPN material crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA. Creep experiment was performed under a stress of  $\sigma = 50$  kPa, while the stress relaxation experiment was performed at a strain of  $\epsilon = 1$  mm/mm.

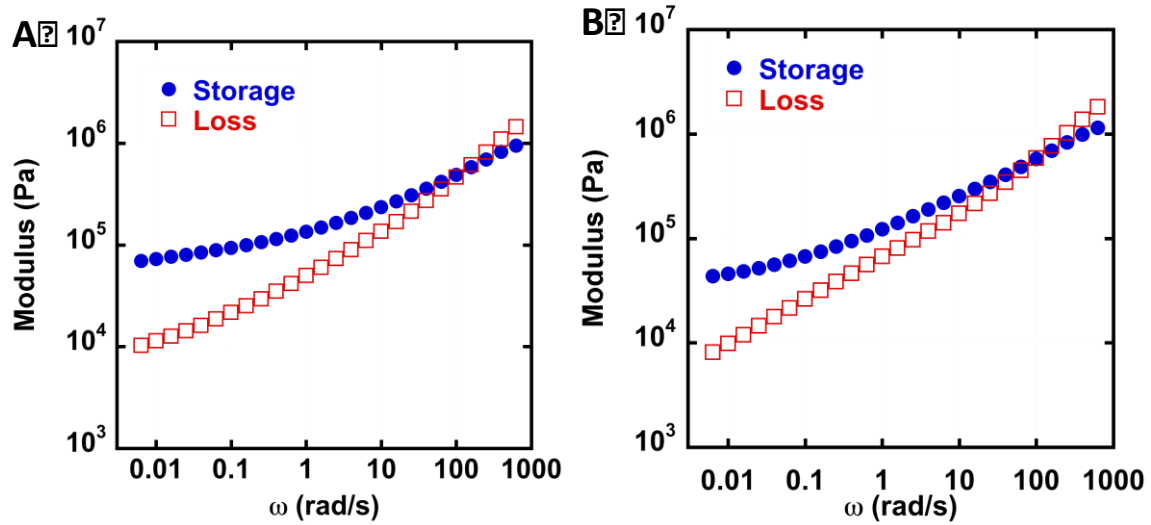


**Figure S10:** Creep and stress relaxation data for the poly(HEA) SN material crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA. Creep experiment was performed under a stress of  $\sigma = 50$  kPa, while the stress relaxation experiment was performed at a strain of  $\epsilon = 1$  mm/mm.

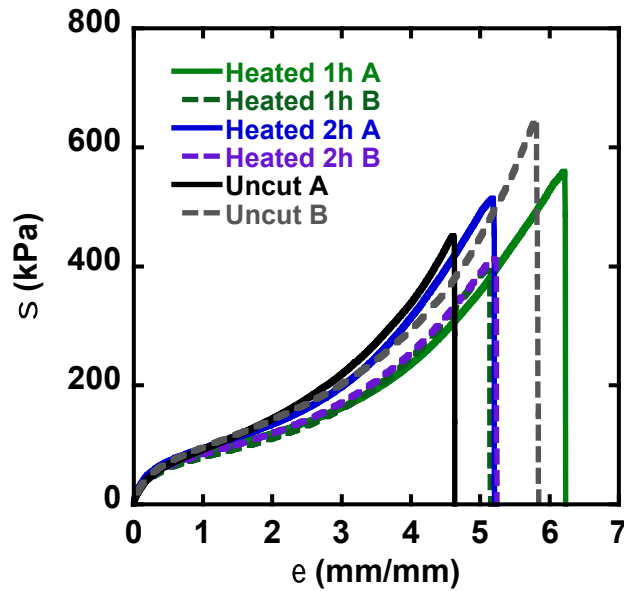




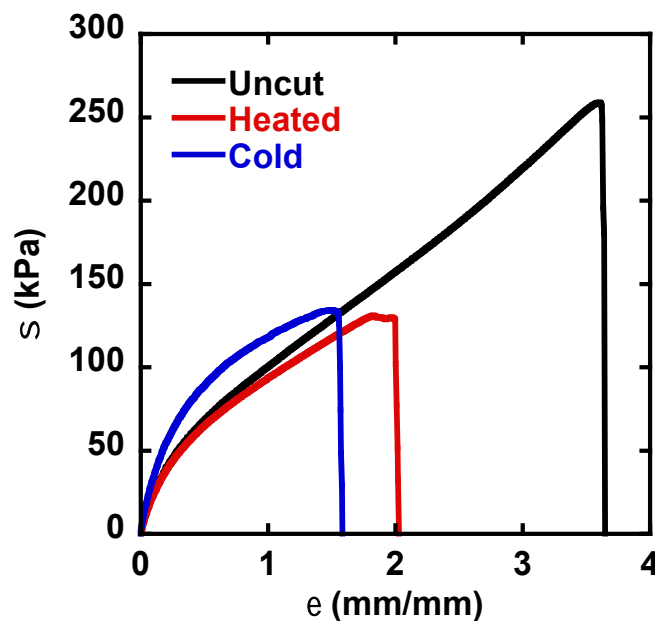
**Figure S11:** Creep recovery for the poly(HEA) IPN and SN materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA. Samples were placed under a strain of  $\varepsilon = 1$  mm/mm for 48 h, and the length (L) relative to the sample length before strain ( $L_0$ ) was measured as a function of time.



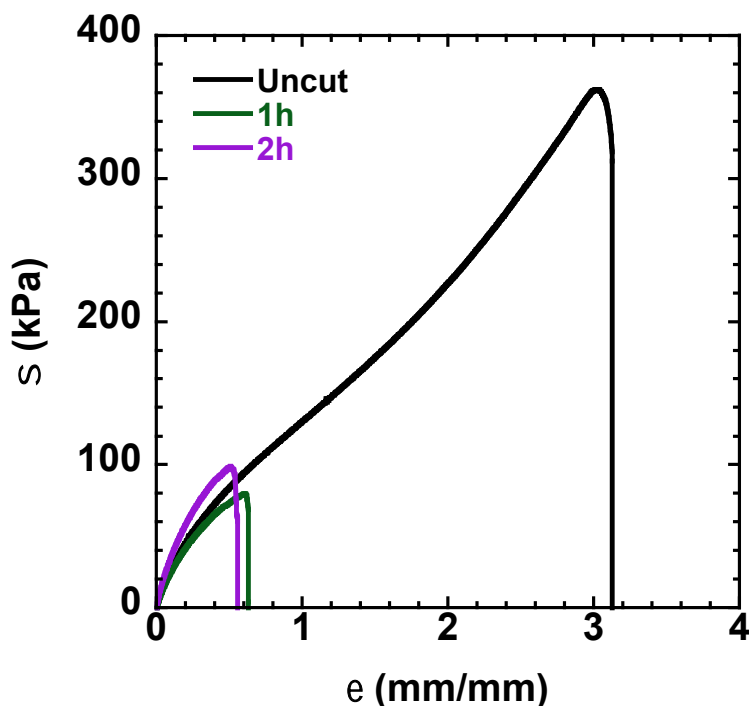
**Figure S12:** Rheology data at 25 °C for poly(HEA) IPN (A) and SN (B) materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA at 25 °C.



**Figure S13:** Stress-Strain data for poly(HEA) IPN materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA after being cut and healed for 1 h and 2 h at 100 °C, compared to uncut samples.



**Figure S14:** Stress-Strain data for poly(HEA) SN materials crosslinked with 2.5 wt% UPyA and 2.5 wt% FMIDA after being cut and healed for 2 h at 100 °C, or for 4h 40 min at room temperature compared to uncut samples.



**Figure S15:** Stress-Strain data for poly(HEA) materials crosslinked with 2 wt% DVB after being cut and healed for 1 h or 2 h at 100 °C compared to a typical uncut sample.

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