

## Supporting Information: Interpenetrated Triple Network Polymers: Synergies of Three Different Dynamic Bonds

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### Experimental section

#### *Materials*

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

2,2-Dimethyl-1,3-dioxolan-4-yl)methyl prop-2-enoate (protected crosslinker-Solketal acrylate) was synthesized followed a literature procedure.<sup>1,2</sup> Isopropylidene glycerol (1.4 g, 0.01 mol) and Triethyl amine (1.0 g, 0.0097 mol) was dissolved in Chloroform (50 ml). Acryloyl Chloride (1.7 g, 0.019 mol) was added to this mixture dropwise. The reaction was stirred at room temperature for 24 hrs. The product was washed seven times with water and saturated sodium chloride solution followed by addition of anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was evaporated under reduced pressure. The purity of the compound was confirmed using <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ ppm) (Figure S10)

UPyA crosslinker was synthesized as outlined in the literature method.<sup>3</sup> NMR of UPy A listed in figure S11.

#### *Synthesis of polymer incorporated with FMA –(Poly-FMA)*

Ethyl acrylate (EA) (2 g), azobis(isobutyronitrile) (AIBN) (100 mg), 1-Dodecanethiol (3% w/w), N, N dimethylformamide (DMF) (6 g) and FMA varied amounts at a time (5%, 7%, 9% w/w) were added in a round bottom flask and the solution was sonicated for 15 min to mix all the reactants. The polymerization was carried out at 65 °C for 2 h and 30 min (Monomer conversion: 83% Dispersity:2.03, Mn:10034 g/mol), as determined by NMR, CDCl<sub>3</sub> as the NMR solvent ( Figure S5, S6 and S7) and THF SEC. Then the polymer was precipitated using hexane and dried in a vacuum for 3 days.

#### *Synthesis of polymer incorporated with UPy A – (Poly-UPyA)*

Ethyl acrylate (EA) (2 g), azobis(isobutyronitrile) (AIBN) (100 mg), N, N dimethylformamide (DMF) (6 g) and UPy A crosslinker (0.1 g) were added in a round bottom flask and the solution was sonicated for 15 min to mix all the reactants. Then the polymerization was carried out at 65 °C for 24 h (Monomer conversion: 96%, Dispersity: 4.08, Mn: 27865 g/mol), as determined by NMR, CDCl<sub>3</sub> as the NMR solvent (Figure S9) and DMF SEC.

#### *Synthesis of polymer incorporated with GA-(Poly-GA)*

Ethyl acrylate (EA) (2 g), azobis(isobutyronitrile) (AIBN) (100 mg), Methanol (6 g) and Solketal acrylate crosslinker (0.1 g) were added in a round bottom flask and the solution was sonicated for 15 min to mix all the reactants. Then the polymerization was carried out at 65 °C for 24 h (Monomer conversion: 98%, Dispersity: 4.56, Mn: 30688 g/mol), as determined by NMR, CDCl<sub>3</sub> as the NMR solvent (Figure S8) and DMF SEC. Resulted polymer was treated with TFA to deprotect the ketal group followed by a literature process <sup>4</sup>. Then Poly-GA polymer was precipitated using methanol: water (1:1) mixture.

### *Synthesis of interpenetrated DNs*

#### *DN-FMA-UPY A*

Poly-UPY A (1.00 g polymer) and poly-FMA (1 g) was mixed in a vial and sonicated for 10 min. 1-[4-[[4-(2,5-dioxopyrrol-1-yl)phenyl]methyl]phenyl]pyrrole-2,5-dione (BMI) (0.05 g dissolved in methanol : DMF, 1:1, 2ml) were mixed with the polymer mixture and sonicated for 10 min. This sonicated mixture was evenly pipetted into a dogbone mold and heated at 35°C for 2 days.

#### *DN-FMA-GA*

Poly-GA (1g polymer) and poly-FMA (1.00 g) was mixed in a vial and sonicated for 10 min. 1-[4-[[4-(2,5-dioxopyrrol-1-yl)phenyl]methyl]phenyl]pyrrole-2,5-dione (BMI) (0.05 g dissolved in methanol : DMF, 1:1, 2ml ) and Phenylidiboronic acid ( 0.02 g in methanol, 0.5ml ) were mixed with the polymer mixture and sonicated for 10 min. This sonicated mixture was evenly pipetted into a dogbone mold and heated at 35°C for 2 days.

#### *DN-GA-UPY A*

Poly-GA (1g polymer) and poly-UPY A (1.00 g) was mixed in a vial and sonicated for 10 min. Phenylidiboronic acid (0.02 g in methanol, 0.5ml) were mixed with the polymer mixture and sonicated for 10 min. This sonicated mixture was evenly pipetted into a dogbone mold and heated at 35°C for 2 days.

### *Synthesis of interpenetrated TNs*

Poly-FMA (1 g), Poly-UPY A (1 g) and Poly-GA (1.00 g) was mixed in a vial and sonicated for 10 min. 1-[4-[[4-(2,5-dioxopyrrol-1-yl)phenyl]methyl]phenyl]pyrrole-2,5-dione (BMI) (0.05 g dissolved in methanol : DMF, 1:1, 2ml) and Phenylidiboronic acid ( 0.02 g in methanol, 0.5ml) were mixed with the polymer mixture and sonicated for 10 min. This sonicated mixture was evenly pipetted into a dogbone mold and heated at 35°C for 2 days.

### *Nuclear Magnetic Resonance (NMR)*

NMR data were collected on a 400 MHz and 500 MHz Bruker Avance NMR spectrometer.

### *Size Exclusion Chromatography (SEC) using THF as the Eluent*

Size exclusion chromatography (SEC) was performed using an Agilent SEC system which consisted of an autosampler, an Agilent 1260 isocratic pump, 1 × Agilent MixedB-guard and 2 × Agilent Mixed-B analytical columns and an Agilent 1260 refractive index (RI) detector. The eluent was tetrahydrofuran set to a flow rate of 1 mL/min. The GPC was calibrated with poly(methyl methacrylate) standards of known molecular weights in the range 617,000 to 1,010. Samples were filtered using a 200 nm PTFE filter prior to injection.

### *Size Exclusion Chromatography (SEC) using DMF as the Eluent*

Size exclusion chromatography (SEC) was accomplished using Agilent 1260 SEC system equipped with an auto-sampler, an Agilent 1260 isocratic pump, Agilent 1 guard and 2 analytical PolarGel-M columns, degasser and Agilent 1260 refractive index (RI detector). DMF was used as the eluent at 50 °C with a flow rate of 1 mL/min. All the samples were filtered before the injection to instrument. The system was calibrated with PMMA standards in the molecular weight range of 617,000 to 1,010. Samples were filtered using a 200 nm PTFE filter prior to injection.

### *Tensile testing*

Elastomeric properties of the materials were characterized by an Instron 3344 universal testing system with a 100N load cell. Extensions of the dog bone samples were increased at a rate of 5 mm/s.

### *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°C for 24hr. Samples were tested by performing tensile tests.

### *Stress relaxation*

An Instron Model 3344 universal testing system equipped with a 100 N load cell was used to analyze stress relaxation. For all materials, the extension was increased at a rate of 0.5 mm/s. The strain was maintained at 20 % of initial length of the sample. Relaxation times were determined by fitting a stretch exponential function of the form below with  $t = 0$  at the peak:<sup>5</sup>

$$\sigma(t) = \sigma_{\infty} + (\sigma_0 - \sigma_{\infty})e^{-\left(\frac{t}{\tau}\right)^{\beta}} \quad (S1)$$

where  $\sigma_{\text{peak}}$  is the stress at the peak  $\sigma_{\infty}$  is the asymptotic stress at infinite time,  $\tau$  is the relaxation time and  $\beta$  is the powerlaw in the stretch exponential.

#### *Fracture energy test*

Fracture energy test was performed using an Instron 3344 universal testing system equipped with a 100 N load cell at room temperature. Two groups of samples were analyzed as “notched” and “unnotched”. Unnotched materials were tested using tensile test. Notched samples were cut half-way through their width before being loaded onto the Instron. Then samples were tested using the same tensile method. The stress-strain data of the uncut samples up to the average strain at break for the cut samples were integrated to calculate the Fracture energy.

#### *Dynamic Mechanical Analysis (DMA)-Frequency sweep experiment*

TA instrument Q800 with a tension clamp was used to conduct Temperature Sweep dynamic mechanical analysis (DMA) using Isothermal temperature/frequency sweep test. Frequency was ranged from 0.1- 150 Hz at a constant temperature of 35 °C. Samples were hold five minutes to equilibrate at 35 °C and then data was collected with a strain of 0.01%, a preload force of 0.01 N.

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

Creep and Creep Recovery test were carried out on a TA instrument Q800 equipped with a film tension clamp. Samples were equilibrated five minutes at 35 °C before applying stress. Temperature was held constant at 35 °C. The experiment was carried out with a stress of 0.005MPa 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.

#### *Infrared (IR) Spectroscopy*

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

## Supplementary Data

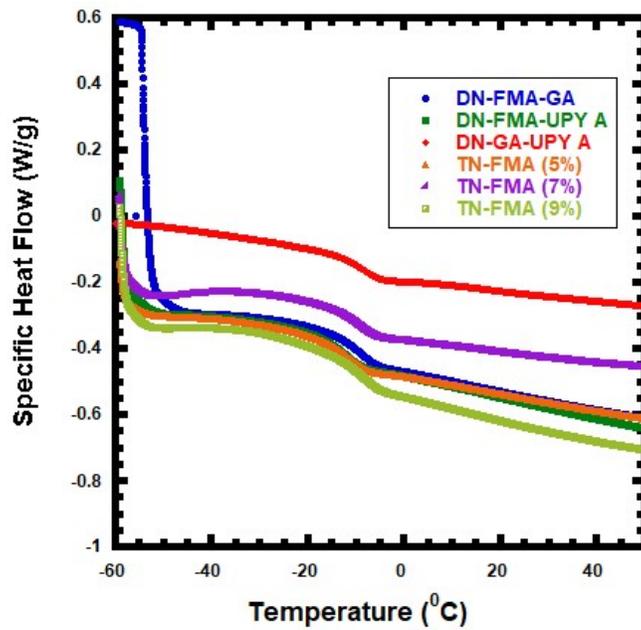


Figure S1: DSC curves of DNs and TNs

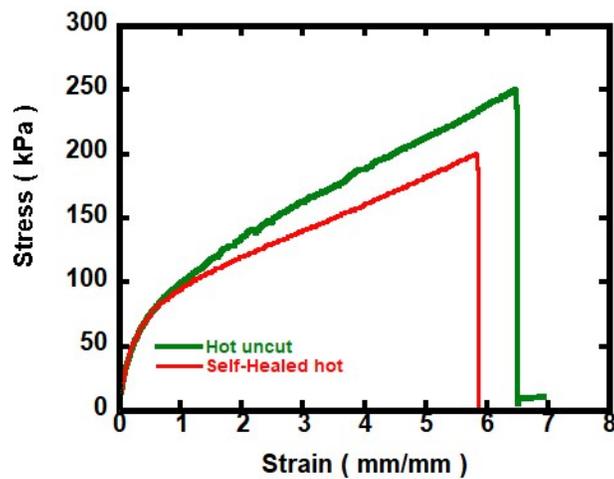


Figure S2: Self-healing results of DN-FMA-GA

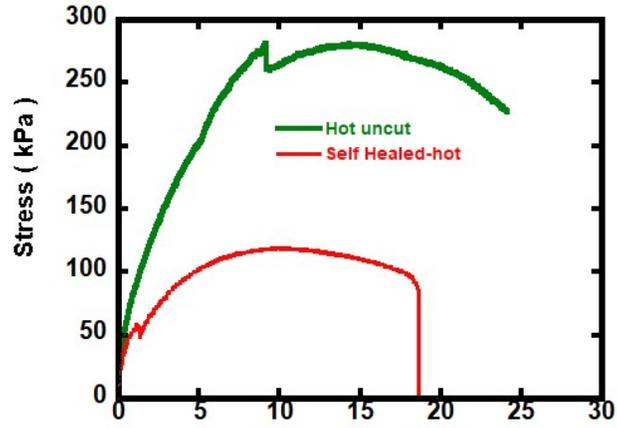


Figure S3: Self-healing results of DN-FMA-UPY A

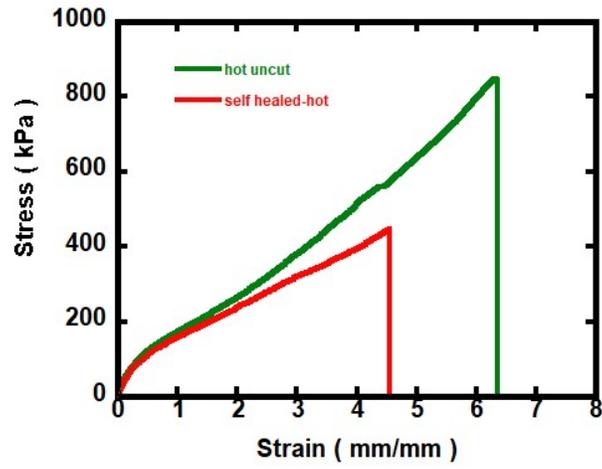


Figure S4: Self-healing results of DN-GA-UPY A

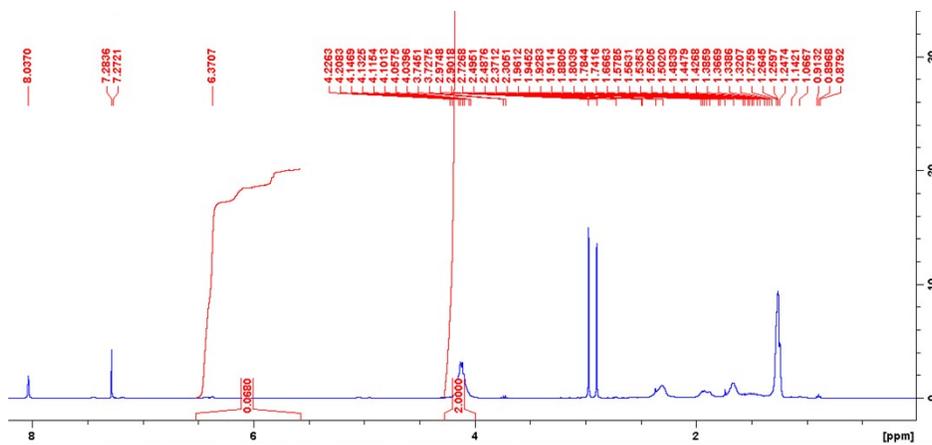


Figure S5:  $^1\text{H}$  NMR of Poly-FMA(5%)

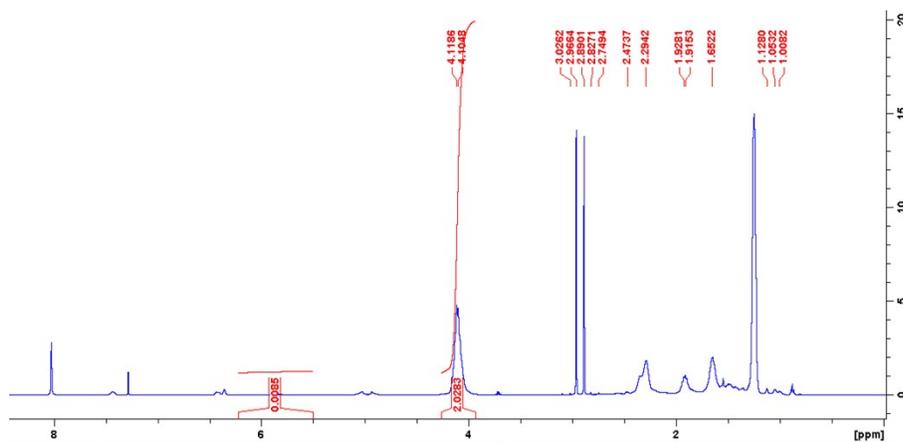


Figure S6:  $^1\text{H}$  NMR of Poly-FMA(7%)

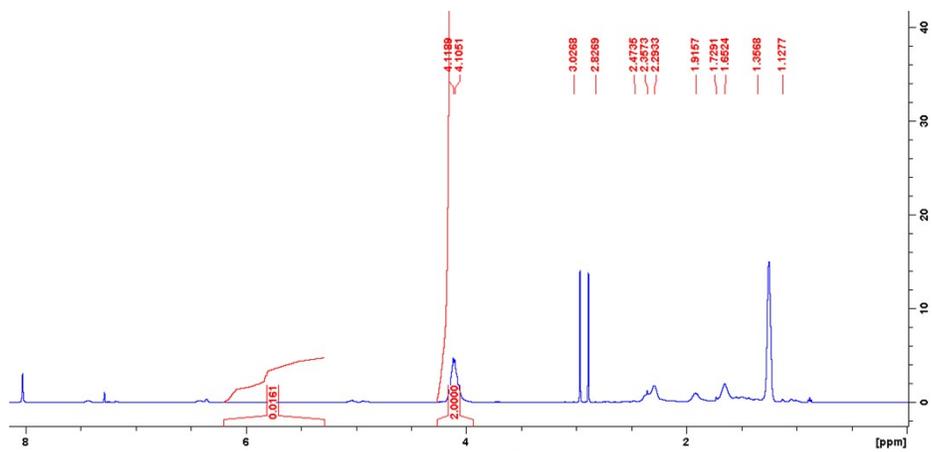


Figure S7:  $^1\text{H}$  NMR of Poly-FMA(9%)

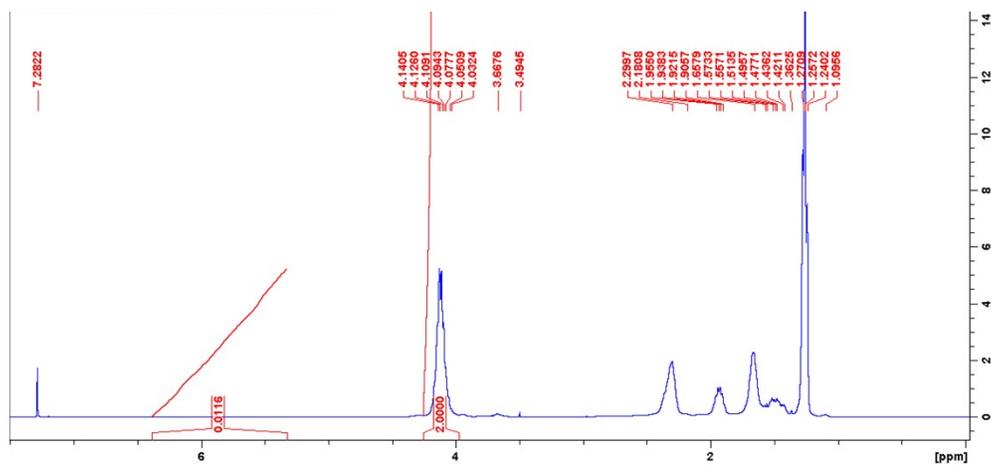
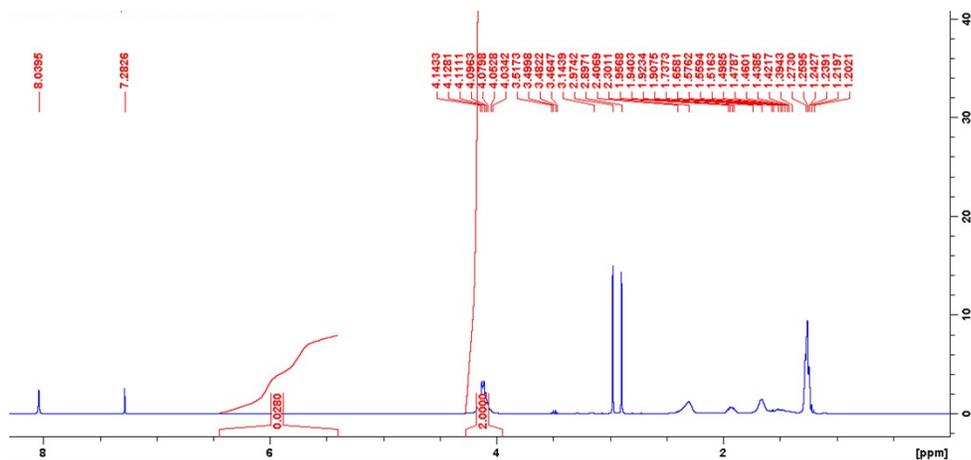
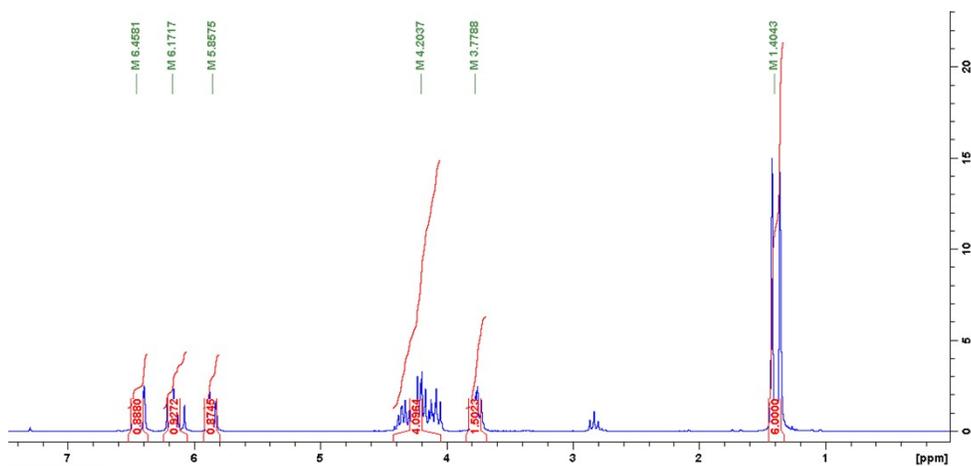


Figure S8:  $^1\text{H}$  NMR of Poly-GA



**Figure S9:**  $^1\text{H}$  NMR of *Poly-UPY A*



**Figure S10:**  $^1\text{H}$  NMR of (2,2-dimethyl-1,3-dioxolan) methyl acrylate (protected crosslinker-Solketal acrylate)

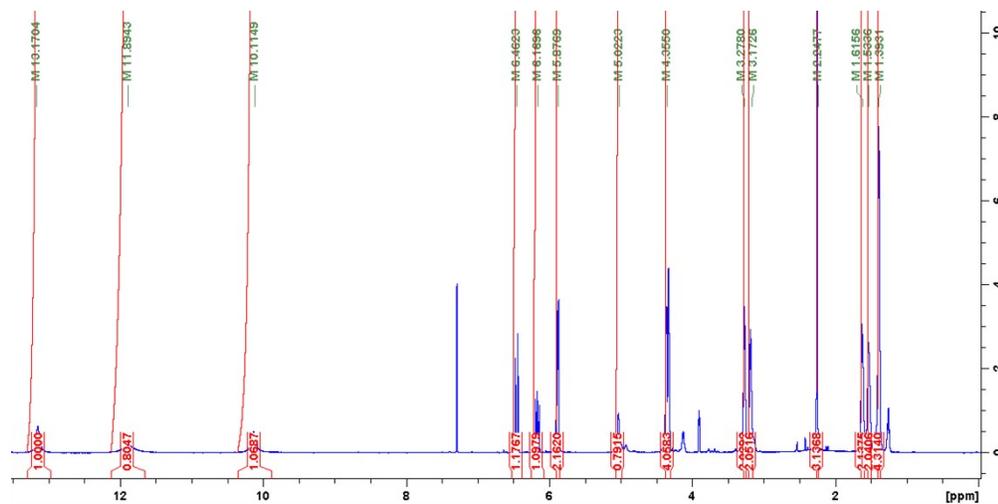


Figure S11:  $^1\text{H}$  NMR of UPyA crosslinker in  $\text{CDCl}_3$

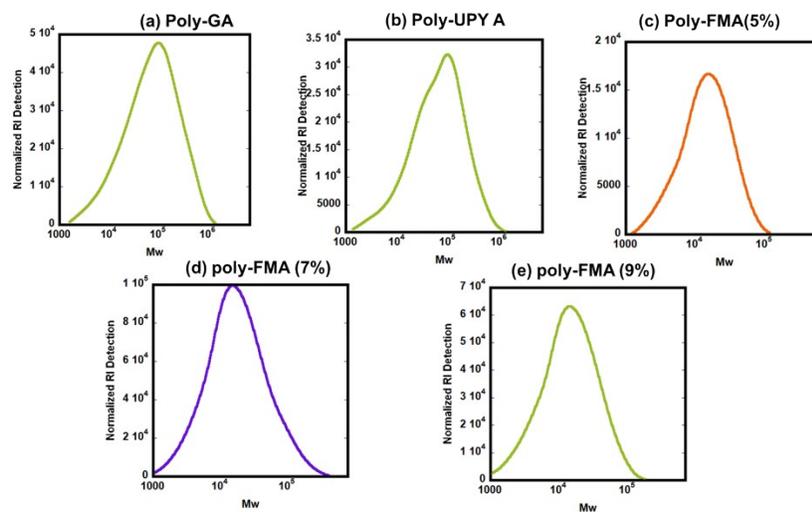
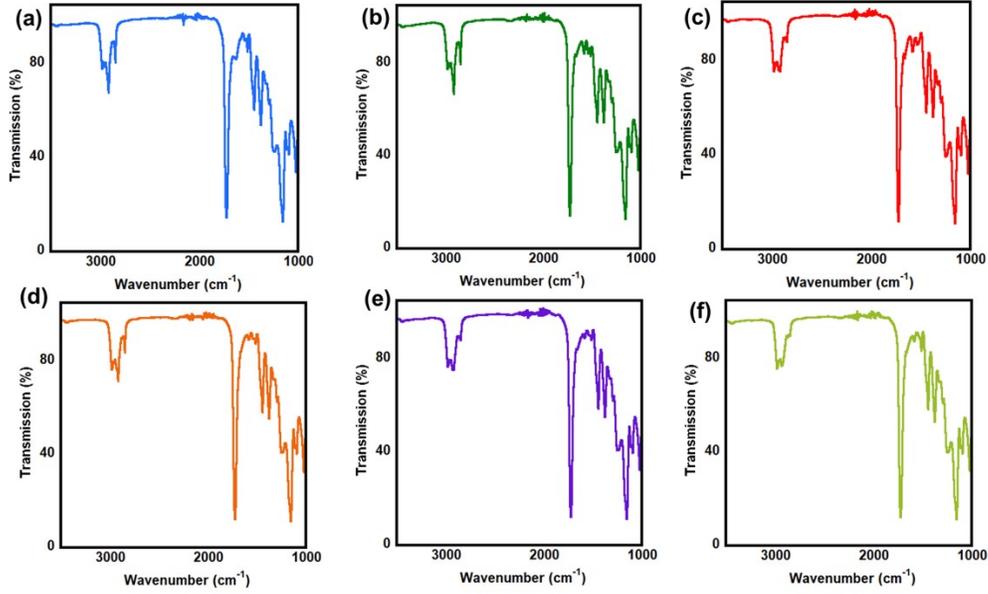
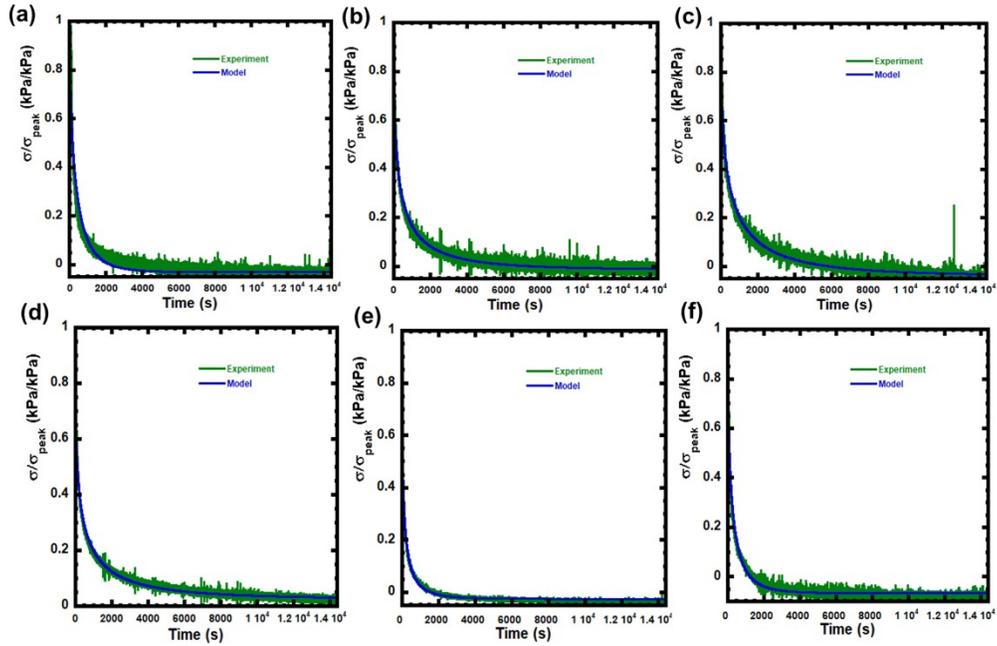


Figure S12: GPC traces of Polymers



**Figure S13:** IR spectra of Polymers. (a) DN-FMA-GA (b) DN-FMA-UPY A (c) DN-GA-UPY A (d) TN-FMA (5%) (e) TN-FMA (7%) (f) TN-FMA (9%)



**Figure S14:** Stress relaxation curves fit with a model. (a) DN-FMA-GA (b) DN-FMA-UPY A (c) DN-GA-UPY A (d) TN-FMA (5%) (e) TN-FMA (7%) (f) TN-FMA (9%)

	<i>DN-FMA-UPYA</i>	<i>DN-FMA-GA</i>	<i>DN-GA-UPYA</i>	<i>TN-FMA (5%)</i>	<i>TN-FMA (7%)</i>	<i>TN-FMA (9%)</i>
$\tau$	292.92	337.92	446.98	258.85	95.01	218.75
$\beta$	0.4457	0.6622	0.4566	0.40	0.47	0.59

**Table S1:** Stress relaxation parameters using equation S1, in all cases  $\sigma_{\infty}$  were essentially 0.

### References:

- 1 G. Robert-Nicoud, R. Evans, C.-D. Vo, C. J. Cadman and N. Tirelli, *Polymer Chemistry*, 2013, **4**, 3458–3470.
- 2 H. Mori, A. Hirao and S. Nakahama, *Macromolecules*, 1994, **27**, 35–39.
- 3 B. Zhang, Z. A. Digby, J. A. Flum, E. M. Foster, J. L. Sparks and D. Konkolewicz, *Polymer Chemistry*, 2015, **6**, 7368–7372.
- 4 Y. Zhen, S. Wan, Y. Liu, H. Yan, R. Shi and C. Wang, *Macromolecular Chemistry and Physics*, 2005, **206**, 607–612.
- 5 A. Lukichev, *Physics Letters A*, 2019, **383**, 2983–2987.