Supporting Information for

# High-Performance Polyimine Vitrimers from an Aromatic Bio-Based Scaffold

Kevin A. Stewart, Jacob J. Lessard, Alexander J. Cantor, John F. Rynk, Laura S. Bailey, Brent S. Sumerlin\*

George & Josephine Butler Polymer Research Laboratory, Center of Macromolecular Science & Engineering, Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA

E-mail: <u>sumerlin@chem.ufl.edu</u>

#### **Supporting Information:**

Instrumentation Experimental Monomer and Vitrimer Synthesis and Characterization Rheology High-Temperature Studies Tensile Testing of TVn-P Reprocessability and Chemical Recycling References

Instrumentation	SI 3
Experimental	SI 4
Monomer and Vitrimer Synthesis and Characterization	SI 6
Monomer Synthesis	SI 6
Vitrimer Synthesis	SI 10
FTIR Spectroscopy	SI 11
Differential Scanning Calorimetry (DSC)	SI 14
Thermal Gravimetric Analysis (TGA)	SI 16
Rheology	SI 17
Dynamic Mechanical Analysis (DMA)	SI 17
Stress Relaxation Experiments	SI 23
Creep-Recovery Experiments	SI 24
High-Temperature Studies	SI 25
Tensile Testing of TVn-P	SI 27
Reprocessability and Chemical Recycling	SI 28
Dynamic Mechanical Analysis (DMA)	SI 28
FTIR Spectroscopy	SI 32
Hydrolytic Degradation	SI 34
References	SI 38

#### Instrumentation:

*Nuclear Magnetic Resonance (NMR) Spectroscopy.* <sup>1</sup>H NMR spectra were recorded on a Bruker 600 MHz NMR spectrometer or a Magritek 60 mHz Spinsolve Ultra spectrometer. Deuterated chloroform (CDCl<sub>3</sub>) was used as solvent, and the residual solvent signal served as a reference.

*Fourier Transform Infrared (FTIR) Spectroscopy.* Infrared spectra were acquired on a PerkinElmer Spectrum One FTIR spectrometer equipped with a PIKE MIRacle single reflection ATR accessory containing a diamond crystal sample plate. Spectra were processed using PerkinElmer Spectrum 10 software.

*Mass Spectrometry.* Mass spectrometry data were collected on an Agilent 6220 Time-of-Flight (TOF). The ionization source used was direct analysis in real time (DART) and was analyzed in positive mode. Helium was used at a 3.0 flow rate with a heater temperature of 500 °C. The sample was used as provided (dry powder).

*Thermogravimetric Analysis (TGA).* TGA experiments were collected on a TA 5500 equipped with an autosampler using a 100  $\mu$ L platinum pan. Each sample was run immediately after destruction/compression molding to limit possible moisture uptake. Ramp experiments were heated at 10 °C/min from room temperature to 650 °C under nitrogen flow. TGA experiments were recorded using TA's Thermal Advantage for Q Series software.

**Differential Scanning Calorimetry (DSC)**. DSC experiments were conducted on a TA Q2500 DSC (TA Instruments, New Castle, DE), equipped with an autosampler and refrigerated cooling system 90, using aluminum hermetic sealed pans. Ramp experiments were heated under nitrogen at 10 °C/min from -50 to 185 °C and cooled from 185 to -50 °C, with 5-min isotherms at each extreme. All DSC experiments were recorded using the Thermal Advantage for Q Series software from TA.

**Dynamic Mechanical Analysis (DMA)**. DMA experiments were collected on the TA Q800 DMA (TA Instruments, New Castle, DE). DMA experiments provided quantitative information on the viscoelastic and rheological properties of the materials by measuring the response of the vitrimers while being subjected to a 0.05% sinusoidal strain. Using a tensile clamp, each rectangular-shaped sample was heated from -30 to 200 °C at a rate of 3 °C/min. Sample dimensions were kept consistent as length x width x thickness measured approximately (20 mm x 6 mm x 1 mm). All experiments were run at a frequency of 1 Hz, and the glass transition temperature ( $T_g$ ) was taken as the peak of tan  $\delta$ . All DMA experiments were recorded using the Thermal Advantage for Q Series software from TA.

**Shear Rheology**. Shear rheology for creep recovery was performed using a TA Instruments Discovery Hybrid Rheometer (DHR-2) operating at 150 °C with a 20 mm flat-plate geometry. Creep recovery experiments were performed at 5000 Pa for 400 s, followed by 0 Pa for 200 s. Curves depicted are an average of two vitrimer discs of the same formulation.

Shear rheology for stress relaxation was performed using an Anton-Paar MCR-702 rheometer operating at 180 to 145 °C with a 20 mm flat-plate geometry (part 45950). Stress relaxation experiments were conducted at 0.3% strain at the desired temperature. All experiments were performed using the Anton software. All samples were allowed to equilibrate at temperature prior to each run.

**Tensile Testing.** Tensile testing of the Priamine crosslinked vitrimer was performed on an Instron 5969 operating with a 50kN load cell. The experiments were conducted at a strain rate of 5.0 mm/min, and specimens were pulled until failure. All experiments were recorded using software from Instron, and the curves were generated using Matlab software.

## Experimental:

*Materials*. (Per-)Pentafluoropyridine (PFP, Synquest Laboratories, 99%), vanillin (Millipore Sigma, 99+%), cesium carbonate ( $Cs_2CO_3$ , Millipore Sigma, 99%), potassium carbonate ( $K_2CO_3$ , Fisher, Reagent grade), *N*,*N*-dimethylformamide (DMF, Fisher, ACS grade), Dichloromethane (DCM, Fisher, ACS grade), and hexanes (DCM, Fisher, ACS grade) were purchased and used as received. Xylylene diamine (XDA, 99%), hexamethylenediamine (HMDA, 98%), and 1,12-diaminododecane (DADD, 98%) were all purchased from Millipore Sigma and used as received.

Synthesis of Tris(vanillyl)-3,5-difluoropyridine (TVnFP) with Cesium Carbonate. Perfluoropyridine (PFP, 5.49 mL, 50.0 mmol, 1.00 equiv) was added to a 250 mL RBF containing 185 mL of DMF. A stir bar was added, and vanillin (24.2 g, 160 mmol, 3.20 equiv) was added to the RBF with stirring. After 10 min, cesium carbonate (52.1 g, 160 mmol, 3.20 equiv) was added to the RBF while stirring. The solution was allowed to stir at room temperature for 15 minutes, capped, and then placed in an oil bath at 80 °C. The reaction was monitored by <sup>19</sup>F NMR spectroscopy, showing full conversion to the trisubstituted product after 8 h. The reaction was removed from heat and cooled to room temperature. The solution was then filtered into 500 mL of cold DI water, resulting in an off-white precipitate and milky solution. The product solution was extracted with DCM (4 x 100 mL). The organic layers were combined, dried, and rotary evaporated to dryness. The slightly yellow solid was recrystallized in a DCM/hexanes mixture. The recrystallized product was filtered and dried, vielding a pale-vellow solid. The filtrate was concentrated in vacuo, and a second crop was recrystallized (24.4 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.95 (s, 1H), 9.80 (s, 2H), 7.52 (s, 1H), 7.48 (d, 1H), 7.28 – 7.25 (d, 4H), 7.20 (d, 1H), 7.05 (d, 2H), 4.00 (s, 3H), 3.25 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ190.75, 190.66, 151.98, 150.44, 149.85, 143.76, 143.61, 136.84, 134.44, 133.81, 125.08, 124.48, 122.18, 117.46, 111.24, 110.50, 56.34, 55.94; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 400 MHz): δ -158.

**Synthesis of TVnFP with Potassium Carbonate.** Perfluoropyridine (PFP, 5.49 mL, 50.0 mmol, 1.00 equiv) was added to a 250 mL RBF containing 185 mL of DMF. A stir bar was added, and vanillin (24.2 g, 160 mmol, 3.20 equiv) was added to the RBF with stirring. After 10 min, potassium carbonate (22.1 g, 160 mmol, 3.20 equiv) was added to the RBF while stirring. The solution was allowed to stir at room temperature for 15 minutes, capped, and then placed in an oil bath at 80 °C. The reaction was monitored by <sup>19</sup>F NMR spectroscopy, showing full conversion to the trisubstituted product after 14 h. The reaction was removed from heat and cooled to room temperature. The solution. The organic layers were combined, dried, and rotary evaporated to dryness. The slightly yellow solid was recrystallized in a DCM/hexanes mixture. The recrystallized product was filtered and dried, yielding a pale-yellow solid (17.7 g, 62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.95 (s, 1H), 9.80 (s, 2H), 7.52 (s, 1H), 7.48 (d, 1H), 7.28 – 7.25 (d, 4H), 7.20 (d, 1H), 7.05 (d, 2H), 4.00 (s, 3H), 3.25 (s, 6H); <sup>13</sup>F NMR (CDCl<sub>3</sub>, 400 MHz): δ -158.

**Synthesis of TVnFP Vitrimer with m-Xylylene Diamine (TVn-X).** TVnFP (1.000 g, 1.77 mmol, 1.00 equiv) was loaded into a Petri dish and dissolved in DCM (8 mL). In a separate vial, XDA (0.350 mL, 2.65 mmol, 1.50 equiv) was diluted with 2 mL of DCM. The XDA solution was added to the Petri dish, and the solvent was partially evaporated at room temperature. The resulting organogel was further cured and allowed to foam at 85 °C for 5 h under vacuum yielding a vitrimer

foam. The resulting foam was ground and compression molded at 170 °C under reduced pressure, yielding a yellow, highly transparent material.

**Synthesis of TVnFP Vitrimer with Hexamethylenediamine (TVn-H).** TVnFP (1.00 g, 1.77 mmol, 1.00 equiv) was loaded into a Petri dish and dissolved in DCM (8 mL). In a separate vial, XDA (0.346 mL, 2.65 mmol, 1.50 equiv) was diluted with 2 mL of DCM. The HMDA solution was added to the Petri dish, and the solvent evaporated at room temperature. The resulting vitrimer film was further cured at 85 °C for 5 h under vacuum yielding a tough vitrimer film. The resulting film was cut with scissors into small shards and compression molded at 150 °C under reduced pressure, yielding a yellow, highly transparent material.

**Synthesis of TVnFP Vitrimer with Diaminododecane (TVn-D).** TVnFP (1.00 g, 1.77 mmol, 1.00 equiv) was loaded into a Petri dish and dissolved in DCM (6 mL). In a separate vial, DADD (0.531 g, 2.65 mmol, 1.50 equiv) was diluted with 2 mL of DCM and heated with a heat gun until DADD was solubilized. The DADD solution was rapidly added to the Petri dish. An additional 2 mL of DCM was added to the DADD vial, heated, and added to the Petri dish. Then, the solvent was evaporated at room temperature. The resulting film was further cured at 85 °C for 5 h under vacuum yielding a tough vitrimer film. The resulting film was cut with scissors into small shards and compression molded at 150 °C under reduced pressure, yielding a yellow, highly transparent material.

**Synthesis of TVnFP Vitrimer with Priamine 1074 (TVn-P).** TVnFP (3.00 g, 5.31 mmol, 1.00 equiv) was loaded into a large Petri dish and dissolved in DCM (20 mL). In a separate vial, Priamine 1071 (4.26 g, 7.96 mmol, 1.50 equiv) was diluted with 7 mL of DCM. The Priamine solution was added dropwise to the Petri dish. An additional 3 mL of DCM was added to the Priamine vial and added to the Petri dish. Then, the solvent was evaporated at room temperature. The resulting film was further cured at 85 °C for 5 h under vacuum yielding a flexible, stretchable vitrimer film. The resulting film was cut with scissors into small shards and compression molded at 150 °C under reduced pressure, yielding a yellow, highly transparent material.

Monomer and Vitrimer Synthesis and Characterization



Figure S1: Stacked <sup>1</sup>F NMR spectra of Tris(vanillyl)-3,5-difluoropyridine (TVnFP) synthesis at 1, 3, and 8 h. Pentafluoropyridine (PFP) for references (top).



Figure S2: <sup>1</sup>H NMR spectrum of Tris(vanillyI)-3,5-difluoropyridine (TVnFP).



Figure S3: <sup>19</sup>F NMR spectrum of Tris(vanillyI)-3,5-difluoropyridine (TVnFP).



Figure S4: <sup>13</sup>C NMR spectrum of Tris(vanillyI)-3,5-difluoropyridine (TVnFP).



Figure S5: Direct analysis in real time (DART) mass spectrometry of Tris(vanillyl)-3,5-difluoropyridine (TVnFP).



Figure S6: (A) Scheme for vitrimer formation with TVnFP and *m*-xylyenediamine (X); (B) TVnFP powder in petri dish before and (C) after addition of diamine solution; (D) organogel formation after 1 hour at room temperature; (E) Foamed vitrimer after curing under vacuum at 85 °C.



Figure S7: Subsequent diamines used in remaining vitrimer formulations.



Figure S8: Vitrimer films of (A) TVn-H, (B) TVn-D, and (C) TVn-P after curing under vacuum at 85 °C.



Figure S9: Petri dish and vitrimer film of TVn-P (left) for scale. Smaller petri dish (right) used for the synthesis of TVn-X, -H, and -D.



Figure S10: Overlayed FT-IR spectra of TVnFP monomer and processed TVn-X vitrimer.



Figure S11: Overlayed FT-IR spectra of TVnFP monomer and processed TVn-H vitrimer.



Figure S12: Overlayed FT-IR spectra of TVnFP monomer and processed TVn-D vitrimer.



Figure S13: Overlayed FT-IR spectra of TVnFP monomer and processed TVn-P vitrimer.



Figure S14: Overlayed FT-IR spectra of TVnFP monomer and all processed vitrimers



Figure S15: DSC thermogram of TVn-X vitrimer.



Figure S16: DSC thermogram of TVn-H vitrimer.



Figure S17: DSC thermogram of TVn-D vitrimer.



Figure S18: DSC thermogram of TVn-P vitrimer.



Figure S19: TGA thermogram (N<sub>2</sub>) of TVn-H vitrimer.

Sample	T <sub>g, DSC</sub> (°C)	<i>T</i> <sub>g, DMA</sub> (°C)	T <sub>d, 5% mass loss</sub> (°C)	T <sub>d, 10% mass loss</sub> (°C)	Char Yield at 650 °C (N <sub>2</sub> ) (%)	Biomass Content (wt %)
TVn-X	147	160	339	391	68	44
TVn-H	89	90	301	335	55	47
TVn-D	66	80	344	371	36	37
TVn-P	9	37	366	392	15	94

Table S1: Selected properties of polyimine vitrimers.

## <u>Rheology</u>



Figure S20: DMA storage modulus (E') trace of processed TVn-X vitrimer.



Figure S21: DMA loss modulus (*E*") trace of processed TVn-X vitrimer.



Figure S22: DMA  $tan(\delta)$  trace of processed TVn-X vitrimer.



Figure S23: DMA storage modulus (E') trace of processed TVn-H vitrimer.



Figure S24: DMA loss modulus (*E*") trace of processed TVn-H vitrimer.



Figure S25: DMA tan( $\delta$ ) trace of processed TVn-H vitrimer.



Figure S26: DMA storage modulus (E') trace of processed TVn-D vitrimer.



Figure S27: DMA loss modulus (E") trace of processed TVn-D vitrimer.



Figure S28: DMA tan( $\delta$ ) trace of processed TVn-D vitrimer.



Figure S29: DMA storage modulus (*E*') trace of processed TVn-P vitrimer.



Figure S30: DMA loss modulus (*E*") trace of processed TVn-P vitrimer.



Figure S31: DMA tan( $\delta$ ) trace of processed TVn-P vitrimer.

- Arrhenius Relation (calculation of Activation Energy using single Maxwell model):

The normalized stress relaxation at 1/*e* is the characteristic relaxation time ( $\tau$ ), assuming a single Maxwell element as seen in literature examples.<sup>1-4</sup>

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

$$\ln(\tau) = E_a/RT + \ln(\tau_o)$$

Equation S1: Arrhenius relation of the characteristic relaxation time used to calculate the energy of activation for viscous flow.



Figure S32: Normalized stress relaxation (0.3% strain) traces for (A) TVn-X, (B) TVn-H, (C), TVn-D, and (D) TVn-P at varying temperatures.



Figure S33: Creep-recovery experiments for TVn-P at varying temperatures at a constant force of 5000 Pa.

Table S2: Creep-recovery values for polyimine vitrimers at 150 °C at a constant force of 5000 Pa.

Sample	Maximum Strain (%)	Recovery (%)
TVn-X	4.14	20.5
TVn-H	9.80	24.0
TVn-D	14.8	10.8
TVn-P	66.1	2.10



Figure S34: (A) High-temperature (red line) DMA thermogram of TVn-X vitrimer overlayed with initial lower temperature experiment (black). (B) High-temperature DSC thermogram of TVn-X vitrimer showing exotherm in cycle 1.



Figure S35: (A) High-temperature (red line) DMA thermogram of TVn-H vitrimer overlayed with initial lower temperature experiment (black). High-temperature specimen reprocessed from vitrimer scraps from initial processing. (B) High-temperature DSC thermogram of TVn-H vitrimer showing slight exotherms in cycles 1-3.



Figure S36: (A) High-temperature (red line) DMA thermogram of TVn-D vitrimer overlayed with initial lower temperature experiment (black). High-temperature specimen reprocessed from vitrimer scraps from initial processing. (B) High-temperature DSC thermogram of TVn-D vitrimer showing no apparent exotherms.



Figure S37: (A) High-temperature (red line) DMA thermogram of TVn-P vitrimer overlayed with initial lower temperature experiment (black). High-temperature specimen was a virgin sample. (B) High-temperature DSC thermogram of TVn-P vitrimer showing no apparent exotherms.



Figure S38: Tensile specimens of TVn-P vitrimer.



Figure S39: Tensile testing of TVn-P vitrimer dogbone specimens. Samples were pulled at a strain rate of 5.0 mm/min until failure. Sample 2 showed clear yielding early due to a defect in cross-sectional area.



Figure S40: Overlayed DMA storage moduli (E') traces of (A) TVn-X, (B) TVn-H, (C) TVn-D, and (D) TVn-P vitrimer samples after each reprocess cycle.



Figure S41: Overlayed DMA loss moduli (E") traces of (A) TVn-X, (B) TVn-H, (C) TVn-D, and (D) TVn-P vitrimer samples after each reprocess cycle.



Figure S42: Overlayed DMA  $tan(\delta)$  traces of (A) TVn-X, (B) TVn-H, (C) TVn-D, and (D) TVn-P vitrimer samples after each reprocess cycle.



Figure S43: Pictures of vitrimer bars of (A) TVn-X, (B) TVn-H, (C) TVn-D, and (D) TVn-P vitrimer samples after each reprocessing cycle.



Figure S44: Overlayed FT-IR spectra of TVn-X processed vitrimer with reprocessed sample.



Figure S45: Overlayed FT-IR spectra of TVn-H processed vitrimer with the second and fifth reprocessed samples.



Figure S46: Overlayed FT-IR spectra of TVn-D processed vitrimer with the second and fifth reprocessed samples.



Figure S47: Overlayed FT-IR spectra of TVn-P processed vitrimer with the second and fifth reprocessed samples.



Figure S48: Vitrimer hydrolytic recycling: TVn-X, -H, and -D immersed in 5 mL of 0.1M HCl before (A) and after (B) 48 h at room temperature, followed by heating at 60 °C for 2 h (C). TVn-H shows significant degradation before heating, whereas TVn-X and TVn-D show no significant degradation at room temperature. After heating for 2 h, the degraded samples were filtered, washed with copious amounts of DI water, and dried under vacuum at 60 °C overnight.



Figure S49: TVn-P samples before (A) and after (B) immersion in 10 mL of 0.1M HCl. (C) Sample following 48 h at room temperature. (D) Degraded sample after charging an additional 10 mL of DI water and heating at 60 °C for 2 h. Degraded sample was gravity filtered, dissolved in DCM, and dried with magnesium sulfate. The organic solution was then filtered in cold hexanes. The resultant precipitate was vacuum filtered and allowed to dry overnight under reduced pressure.



Figure S50: <sup>1</sup>H-NMR spectra of recycled TVnFP monomer from each vitrimer network following hydrolytic recycling overlayed with virgin TVnFP monomer. Inset images of harvested samples and virgin TVnFP.



Figure S51: <sup>19</sup>F-NMR spectra of recycled TVnFP monomer from each vitrimer network following hydrolytic recycling overlayed with virgin TVnFP monomer.

## References:

(1) Goodwin, J. W.; Hughes, R. W., *Rheology for Chemists: An Introduction*. Royal Society of Chemistry: 2008; p 95–100

(2) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L., Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334*, 965–968

(3) Ishibashi, J. S. A.; Kalow, J. A., Vitrimeric Silicone Elastomers Enabled by Dynamic Meldrum's Acid-Derived Crosslinks. *ACS Macro Lett.* **2018**, *7*, 482–486.

(4) Ogden, W. A.; Guan, Z., Recyclable, Strong, and Highly Malleable Thermosets Based on Boroxine Networks. *J. Am. Chem. Soc.* **2018**, *140*, 6217–6220.