Supporting Information

Catalyst-Free Vitrimers from Vinyl Polymers

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Materials and Instrumentation:

Materials:

All chemicals were used as received unless otherwise noted. Azobisisobutyronitrile (AIBN, Sigma, 98%) was recrystallized from ethanol and dried in vacuo prior to use. Methyl methacrylate (MMA, Aldrich, 99%) and (2-acetoacetoxy)ethyl methacrylate (AAEMA, Aldrich, 95%) were passed through a column of basic alumina to remove inhibitors and/or acidic impurities prior to polymerization. 1,4-Dioxane (ACS, Fisher) was passed through a column of basic alumina to remove possible formed peroxides prior to polymerization. Tetrahydrofuran (THF, ACS) was purchased from VWR. Acetonitrile (HPLC), hexanes (ACS), ethyl acetate (ACS), N,N-dimethylformamide (DMF, ACS), acetone (ACS), lithium chloride (LiCl, ACS), and ethanol (100%) were purchased from Fisher Scientific. Tristriaminoethyl amine (TREN, 97%) was purchased from Alfa Aesar. N,N-dimethylacetamide (DMAc, ACS) was purchased from Millipore Sigma. 4-Cyan-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]petanoic acid (CDP, RAFT CTA) was synthesized from previous literature.

Instrumentation:

**Nuclear Magnetic Resonance (NMR) Spectroscopy.** $^1$H NMR spectra were recorded on an Inova 500 spectrometer. $^1$H NMR chemical shifts in DMSO-$d_6$ were referenced to CHD$_2$SOCD$_3$ (2.50 ppm).

**Gel Permeation Chromatography (GPC).** GPC was performed in DMAc with 50 mM LiCl at 50 ºC and a flow rate of 1.0 mL/min (Agilent isocratic pump, degasser, and autosampler; columns: Viscogel I-series 5 μm guard + two Viscogel I-series G3078 mixed bed columns, molecular weight range 0–20 × 10$^3$ and 0–100 × 10$^4$ g/mol). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm, a Wyatt miniDAWN Treos light scattering detector operating at 659 nm, and a Viscotek VE 3210 UV/vis detector. Absolute molecular weights and molecular weight distributions were calculated using the Wyatt ASTRA software.

*Note: Figure S22 & S24: detection consisted of Wyatt DSP refractive index detector and a Wyatt DAWN EOS light scattering detector operating at 690 nm adding ~1.5 min to time; therefore, the elution times cannot be compared with other traces.*

**UV-Vis Spectroscopy.** All measurements were taken using a Molecular Devices SpectraMax M2 Multimode Microplate Reader at 25 ºC. Absorbance measurements were conducted with 200 μL of sample on clear 96-well polystyrene microplates (Greiner Bio-One).

**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.

**Thermal Gravimetric Analysis (TGA).** TGA experiments were collected on a TA Q5000 TGA, equipped with an autosampler using a 100 μL platinum pan. Each sample was heated to 110 ºC isotherm for 30 min prior to each run to remove any possible moisture or residual solvent. RAMP experiments were heated at 10 ºC/min from room temperature to 600 ºC under nitrogen flow (25 mL/min). Isothermal experiments were heated under nitrogen flow (25 mL/min) at 20 ºC/min from room temperature to 160 ºC, and once at target temperature the experiment was recorded. 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
sealed pans. RAMP experiments were heated at 5 °C/min from 0 to 200 °C and cooled at 5 °C/min from 200 to 0 °C, with 5-min isotherms at each extreme under nitrogen (25 mL/min). All DSC experiments were recorded using TA Thermal Advantage for Q Series software.

**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 by measuring the response of the vitrimers as they are deformed by a 0.05% sinusoidal strain. Using a tensile clamp, each rectangular-shaped sample heated from room temperature to 180 °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) for all samples. All experiments were run at a frequency of 1 Hz and the glass transition temperature ($T_g$) was taken as the peak of tan δ. All DMA experiments were recorded using TA’s Thermal Advantage for Q Series software.

**Rheology.** Shear rheology was performed on a TA Instruments Discovery Hybrid Rheometer (DHR-2) operating at 95 - 150 °C with a 20 mm parallel-plate geometry. Stress Relaxation experiments were conducted at 1% strain at the desired temperatures. Creep-recovery experiments were conducted at a stress of 5000 Pa for 1500 seconds and 0 Pa for 1500 seconds. All experiments were conducted using a TA Instruments Discovery Hybrid Rheometer (DHR-2) and TA software.
Polymer Synthesis:

Synthetic Procedures:

Prepolymer Synthesis

MMA (5.03 mL, 47.2 mmol), AAEMA (1.00 mL, 5.24 mmol), CDP (0.2350 g, 0.5822 mmol), AIBN (0.0048 g, 0.029 mmol) were added to a Schleck flask containing 1,4-dioxane (46 mL). The solution was sparged with argon prior to being heated at 70 °C for 14-16 h. The solution was precipitated into hexanes resulting in a yellow powder (4.4624 g). The powder was dissolved in ethyl acetate (50 mL) prior to the addition of AIBN (0.4780 g, 2.912 mmol), under argon. The solution was heated at 70 °C for 7 h and precipitated from hexanes yielding a white powder (3.4181 g).

*Note: End-group removal is important to protect the terminal methacrylate unit from amidation*

Synthesis of PMMA control

MMA (2.13 mL, 20.0 mmol), CDP (0.090 g, 0.222 mmol), AIBN (3.6 mg, 0.022 mmol) were added to a Schleck flask containing 1,4-dioxane (20 mL). The solution was sparged with argon prior to being heated at 70 °C for 16 h. The solution was precipitated into hexanes, resulting in a yellow powder. The powder was dissolved in ethyl acetate (20 mL) prior to the addition of AIBN (0.1823 g, 1.110 mmol) under argon. The solution was heated at 70 °C for 7 h and precipitated from hexanes yielding a white powder (1.6112 g).
Polymerization vs time:

![Graph showing polymerization vs time](image)

**Figure S1.** GPC chromatograms from kinetic study.

**Figure S2.** Mole fraction of AAEMA to MMA collected by NMR spectroscopy.
$^1$H NMR Spectroscopy:

10% AAEMA prior to end-group removal

Figure S3. $^1$H NMR spectrum of P(MMA-co-AAEMA) prior to end group removal.

10% AAEMA after end-group removal

Figure S4. $^1$H NMR spectrum of P(MMA-co-AAEMA) post end group removal.

Calculation of AAEMA incorporation:

$A_x$ is the area under the resonance where “x” equals the corresponding signal in SI Figure 2

% AAEMA = $\left(\frac{A_e}{(A_{c+d} - 2 + A_e)}\right) \times 100\%$

% AAEMA = $\left[3 / (29.43 - 2 + 3)\right] \times 100\% = 9.9\%$ AAEMA incorporated into polymer backbone
Gel Permeation Chromatography (GPC):

\[ M_n = 8.6 \text{ kg/mol} \]
\[ M_w = 8.8 \text{ kg/mol} \]
\[ D = 1.02 \]

**Figure S5.** GPC chromatogram of P(MMA-co-AAEMA) prior to end group removal (molecular weights were determined by MALS assuming 100% mass recovery).

\[ M_n = 9.7 \text{ kg/mol} \]
\[ M_w = 10.4 \text{ kg/mol} \]
\[ D = 1.07 \]

**Figure S6.** GPC chromatogram of P(MMA-co-AAEMA) post end group removal (molecular weights were determined by MALS assuming 100% mass recovery).
Ultraviolet-Visible (UV-Vis) Spectroscopy:

Figure S7. UV-vis spectroscopy before (blue) and after (orange) end-group removal
Vitrimer Synthesis and Characterization:

Synthetic Procedures:

Prepolymer (10 mol% AAEMA incorporated, 0.50 g, 0.44 mmol AAEMA units) was loaded into a mold and dissolved in THF (3 mL). In a separate vial, TREN (34 μL, 0.22 mmol) was diluted with THF (2 mL). The TREN solution was added to the mold, and the solution was evaporated at room temperature, under inert atmosphere. The resulting film was further cured at 70-80 °C for up to 24 h under reduced pressure to yield a yellow, transparent film. The film was ground up and compression molded at 160 °C for up to 6 h under reduced pressure or inert atmosphere, yielding a transparent material.

*Note: If the dried solution cast film was cured at temperatures over 80 °C (ex. 160 °C) or in rare instances at 80 °C foams were formed rather than transparent films (Figure S8).*

Figure S8. Foam formed at 160 °C under vacuum during curing post solution cast.
Table S1. Initial vitrimer study for various AAEMA incorporation

| Percent AAEMA | $M_n$ (kg/mol) | $D$ | $T_g$ ($^\circ$C, DMA) | Before Rx1 | Rx1 |
|---------------|---------------|-----|-----------------------|------------|-----|
| 10%           | 8.14          | 1.09| 110                   |            |     |
| 15%           | 12.4          | 1.19| 105                   |            |     |
| 20%           | 10.6          | 1.10| 117                   |            |     |

TGA:

Figure S9. Temperature Ramp TGA experiment of P(MMA-co-AAEMA) vitrimer and values for PMMA standard (12.6 kg/mol).
Isothermal TGA:

Figure S10. Isothermal TGA experiment of P(MMA-co-AAEMA) vitrimer at 160 °C.

FT-IR Spectroscopy:

Figure S11. FT-IR spectra of prepolymer (bottom) and crosslinked, processed sample (top) (enlarged from Figure 4).
Figure S12. FT-IR spectroscopy of prepolymer (bottom) and crosslinked, processed sample (top) showing relevant stretching peaks (enlarged from Figure 4).
Reprocessing and Analysis:

Reprocessing Procedures:

Figure S13. After processing cycle and being ground with a motor and pestle (left, processed). After being compression molded at 160 °C under reduced pressure (middle and right, reprocessed x1). After analysis, the material was ground using a motor and pestle into small shards or a powder. The sample was compression molded at 160 °C under reduced pressure or inert atmosphere for up to 4 h to yield the reprocessed sample.

Figure S14. A. After DMA temperature sweep (reprocessed x1) B. Ground up vitrimer from “A” (reprocessed x1) C. Ground up vitrimer from “A” in compression mold (reprocessed x1) D. Reprocessed vitrimer after compression molding at 160 °C under reduced pressure (reprocessed x2).
Figure S15. Processed and reprocessed (x1) vitrimer on image.

FT-IR:

Figure S16. FT-IR spectra of (re)processed vitrimers over 6 compression cycles.
Figure S17. FT-IR spectroscopy of processed and reprocessed vitrimer over 6 compression cycles showing relevant stretching peaks (enlarged from Figure 4).
Figure S18. DSC thermograms of (re)processed vitrimers over 6 compression cycles.
Gel Fraction:

To examine gel fractions of the vitrimer networks, processed and reprocessed samples were weighed and subsequently immersed in THF (50 mg/mL) for 18 h in a sealed vial. Final masses were then obtained after gravity filtration, followed by further drying under reduced pressure for 48 h. Recovered mass percentages (i.e., gel fractions) were then calculated for each sample and revealed high gel fractions (>0.99). The samples were then heated at 160 °C showing an average 97 wt% retained across (re)process cycles.

Figure S19. Gel fractions of (re)processed vitrimer networks after vacuum for 18 h at room temperature.

Figure S20. Gel fractions of (re)processed vitrimer networks after vacuum for an additional 6 h at 160 °C.
Rheology:

- DMA Temperature Sweep:

![Diagram showing DMA Temperature Sweep]

**Figure S21.** Rubbery plateau used to calculate molecular weight between crosslinks ($M_x$) over reprocess cycles.

The molecular weight between crosslinks ($M_x$) was calculated using the tensile storage modulus ($E'$) from the rubbery plateau.

\[
G' = \frac{E'}{2(1+\nu)} = \frac{\rho RT}{M_x} \quad \text{(Equation S1)}
\]

\[
M_x = \frac{2.8(\rho RT)}{E'}
\]

Using the density of PMMA ($\rho = 1150 \text{ kg/m}^3$ at $T_g$), PMMA Poisson’s ratio ($\nu = 0.4$), the ideal gas constant ($R = 8.314 \text{ J/mol*K}$), and the storage modulus at 150 °C (423.15 K), $M_x$ was calculated over the representative reprocess cycles (Figure S20) using Equation S1.
- Strain Sweep:

**Figure S22.** Strain sweeps of P(MMA-co-AAEMA) vitrimer network at various temperatures.

**Figure S23.** Strain sweeps of P(MMA-co-AAEMA) vitrimer network at various temperatures, with linear fits depicting the linear viscoelastic region.
- Stress Relaxation:

Figure S24. Stress relaxation of P(MMA-co-AAEMA) vitrimer network (from Figure 5).

Figure S25. Stress relaxation of P(MMA-co-AAEMA) vitrimer network showing complete relaxation at 140 and 150 °C.
Figure S26: Creep-recovery experiment of P(MMA-co-AAEMA) vitrimer network showing creep and lack of recovery at 150 °C (stress = 5000 Pa).

- Arrhenius relation (calculation of activation energy and $T_v$):

Activation energy and $T_v$ were calculated using relative stress relaxation at 1/e previously shown in literature.$^5$-$^6$

$$\ln(\tau) = \frac{E_a}{RT} + \ln(\tau_0) \quad (equation \ S2)$$

$\tau$ = time at $\frac{1}{e} = time at 0.37 normalized stress

Figure S27. Arrhenius relationship for stress relaxation of P(MMA-co-AAEMA) vitrimer network (from Figure 5)
Calculation of activation energy from stress relaxation ($E_a$):

Using equation S2:

$$E_a = 12.321 \times R \text{kJ}$$

$$E_a = 102 \pm 8 \text{kJ}$$

Calculation of topology of freezing transition temperature ($T_v$):

$$\eta = G' \tau = \frac{E'}{2(1+\nu)} \tau \quad (equation \ S3)$$

Using PMMA Poisson’s ratio ($\nu = 0.4$), tensile storage modulus from DMA temperature sweep (4 MPa at 150 - 160 °C), and equation S3, the relaxation time ($\tau$) can be calculated for when the viscosity reaches $10^6$ MPa s.

$$\eta = 10^6 \text{MPa s} = \frac{E'}{2(1+\nu)} \tau$$

$$\tau = 7.5 \times 10^5 \text{s}$$

$T_v$ can be calculated from the relaxation time ($\tau$) via equation 2 using the Arrhenius relationship.

$$\ln(7.5 \times 10^5) = 12.321 \frac{1000}{T_v} - 25.022$$

$$T_v = (12.321) \frac{1000}{38.6} \text{K} = 320 \text{K}$$

$$T_v = 47 \text{°C}$$

- Maximum stress at 1% strain:

![Graph](image.png)

**Figure S28.** Maximum stress at 1% strain at various temperatures. The maximum strain for 95 °C was above the limitations of the instrument.
“Extra Amine” Example:

Scheme S1. Mole fraction and ratio with cartoon depictions describing the crosslinking of PMMA vitrimers.

Figure S29. Processed (left, rheology) and reprocessed (right, DMA) of the P(MMA-co-AAEMA) vitrimer network for “extra amine” example.
**Figure S30.** Stress relaxation of P(MMA-co-AAEMA) vitrimer network for “extra amine” example.

**Figure S31.** Arrhenius relationship for stress relaxation of P(MMA-co-AAEMA) vitrimer network for “extra amine” example.

\[
y = 12.49x - 27.03 \\
R^2 = 0.995
\]

\[
\ln(\tau) = \frac{E_a}{RT} + \ln(\tau_0) \\
E_a = 104 \text{ kJ/mol}
\]
Figure S32. Frequency sweep at 150 °C for the “extra amine” example showing crossover of storage (G') and loss (G'') modulus for the “extra amine” vitrimer.

Figure S33. Tan delta from DMA over two compression cycles for the “extra amine” vitrimer.
PMMA Comparison Studies:

Uncrosslinked PMMA was compression molded at 160 °C to obtain samples for rheology and DMA analysis. Low molecular weight PMMA ($M_n = 7.8$ kg/mol) was too brittle to remove from the compression mold. Therefore, we utilized commercially available PMMA of higher molecular weight ($M_n = 52$ kg/mol, $D = 1.38$) which was purified by precipitation from hexanes. PMMA was then compression molded at 160 °C under reduced pressure to obtain bars and disks for DMA and rheology testing.

Figure S34. GPC chromatogram of PMMA used for comparison studies.
**Figure S35.** Storage modulus from DMA for PMMA (blue) and PMMA vitrimer (black).

**Figure S36.** Storage modulus prior to $T_g$ ("glassy modulus") for PMMA (blue) and PMMA vitrimer (black).
Figure S37. Stress relaxation of PMMA linear polymer at various temperatures.

Control Studies:
Processed and reprocessed samples were submerged in excess solvent at elevated temperature with no effect (SI Figure 21A). Additionally, processed samples were subjected to excess...
monofunctionalized amine leading to expulsion of crosslinks and dissolution of the polymer (SI Figure 21B). Lastly, the control was left for over 1 year in solvent at room temperature without dissolving or deforming.

Figure S39. Photos before and after heating (60 °C) of (A) PMMA vitrimer in acetonitrile (B) PMMA vitrimer in acetonitrile with excess monofunctional amine.

Additionally, to replicate our (re)processing conditions, PMMA was synthesized under the same conditions as the prepolymer (DP = 90), and the end group was removed with excess AIBN.

Figure S40. $^1$H NMR spectrum of PMMA synthesized from modified prepolymer procedure.
Figure S41. GPC chromatogram of PMMA synthesized from modified prepolymer procedure (molecular weights from conventional calibration).

The synthesized PMMA was treated with benzylamine (0.1 equiv. to each monomer unit) and heated in DMSO for 12 h under inert atmosphere. The resulting solution was diluted with acetone (100 vol% to DMSO) and dialyzed against acetone for 2 d.
Figure S42. $^1$H NMR spectrum of PMMA showing no aromatic protons after treatment with benzylamine.

Figure S43. GPC chromatogram of PMMA showing no change in elution time after treating with benzylamine.
Recycling Studies:

Vitrimers (150-500 mg) were added to a vial containing butylamine (10 mL) and acetonitrile (optional). The solution was refluxed (80 °C) until the vitrimer had dissolved (3-18 h). The polymer was precipitated from hexanes, resulting in an off-white powder. The modified prepolymer was dissolved in THF prior to the reintroduction of TREN (0.5 mol to AAEMA) under argon. The mixture was heated at 45 °C for 18 h under argon to yield a transparent film.

Figure S44. (Top) Scheme for secondary recycling of vitrimers system. (Bottom) (A) Oxidized, reprocessed dogbone vitrimer in acetonitrile after 1 h heating, (B) vitrimer “A” after treatment of excess butylamine & 18 h heating, (C) vitrimer “B” after filtration and precipitation [modified prepolymer], (D) vitrimer “C” after solution casting in the presence of additional crosslinker (TREN) and curing [rejuvenated network].
Figure S45. GPC chromatogram of modified, recycled prepolymer (blue) and prepolymer (orange), molecular weights were determined from conventional calibration. Peak labeled ‘TREN’ was shown to be crosslinker by running dilute TREN through our GPC in a separate run.
Compression Molds:

Rheology Mold:

DMA and Tensile Test Mold:
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