Research Progress Report: Vinylogous Urethane Vitrimers from Vinyl Polymers

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Catalyst-Free Vitrimers from Vinyl Polymers

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ABSTRACT: Crosslinked networks feature exceptional chemical and mechanical resilience, but consequently lack recyclability. Vitrimers have emerged as a class of materials that feature the robustness of thermosets and the recyclability of thermoplastics without compromising network integrity. Most examples of vitrimers have involved new polymers with exchangeable bonds within their backbones. In pursuit of a more universal, commercially viable route, we propose a straightforward method utilizing commercially available and inexpensive reagents to prepare vitrimers from vinyl monomer-derived prepolymers that contain crosslinkable β-ketoester functional groups. Controlled radical copolymerization of methyl methacrylate and (2-acetoacetoxy)ethyl methacrylate afforded linear prepolymers that were converted into vitrimers in a single step by treatment with a trifunctional amine. These materials displayed the characteristic features and reprocessability of vitrimers over as many as six (re)processing cycles. Critically, the networks prepared through this process largely retain the chemical, and thermal properties of their linear counterparts, suggesting this method holds significant utility as a user-friendly and commercially relevant approach to the rational design of vitrimers with diverse properties.

INTRODUCTION

Commodity plastics are traditionally classified according to two different categories—thermoplastics and thermosets. Thermoplastics lack covalent interactions between chains and can therefore be readily repurposed or recycled. However, the properties of these materials are often compromised in harsh environments (e.g., high temperatures or exposure to solvents). In contrast, thermosets are covalently crosslinked, endowing them with significant thermal, mechanical, and chemical resistance, but the presence of a permanent network prohibits the use of traditional recycling methods. Recent advances have been made to bridge these two classes of materials by creating networks with crosslinks that are dynamic under specific stimuli, enabling the preparation of materials that are recyclable while still retaining adequate physical properties. Many exchangeable crosslinks have been explored, including both supramolecular interactions1,6 and dynamic-covalent bonds.7–20 However, many of these networks suffer from creep, stress relaxation, and/or loss of network integrity,3,21 and effective means of addressing these limitations are needed.22–23

Recently, a new class of networks with dynamic crosslinks was developed to circumvent the drawbacks typically associated with many of the previous strategies toward recyclable thermosets. First reported by Leibler and coworkers, “vitrimer” are a class of covalent adaptable networks24 that behave as traditional thermosets at ambient temperature, while at elevated temperatures, the crosslinks undergo dynamic exchange by an associative mechanism, allowing the material to flow and be reprocessed.25–26 This mechanism of crosslink exchange is essential to the unique properties of vitrimers. In a traditional dynamic network, a reversible crosslink must first break before finding a suitable partner to re-form the crosslink (“dissociative” exchange). In vitrimers, exchange occurs when pendant reactive groups dispersed within the network react directly with an existing crosslink to form a new crosslink and another reactive functional group capable of further exchange. This degenerate process conserves the number of crosslinks at all times via “associative” exchange, as shown in Figure 1. Associative exchange results in a constant crosslink density, ensuring the fidelity of the network and not compromising the material properties during (re)processing.

Many vitrimers require an exogenous catalyst to activate crosslink exchange on relevant timescales.26–34 While this can produce very rapid and modifiable rates of exchange, the catalyst may be unstable or prone to leaching from the network, potentially undermining the recyclability of the material.35 Therefore, a number of catalyst-free vitrimers have been developed that rely on the exchange of silyl ethers,36 vinlylogous urethanes,37–40 vinlylogous amines,41 trialkylsulfonium salts,42 dioxaborolanes,42 boroxines,43 Meldrum’s acid derivatives,44 and hydroxyurethanes.45

Du Prez and coworkers recently reported a promising class of vinlylogous urethane vitrimers for which the dynamic crosslinks were easily synthesized in a single step from the condensation of a primary amine with a β-ketoester.38,40 This approach allowed the vitrimer properties to be tuned by introducing acidic or basic additives.39 In these examples—as in most others—the vitrimers were prepared by step-growth polycondensation of A–A and B–B monomers with B3 crosslinkers. Recently, Nicolay, Leibler and co-workers showed that commodity vinyl polymers such as poly(methyl methacrylate) (PMMA) and polyethylene could be converted into vitrimers through the incorporation of dynamic dioxaborolanes.32 Extending the vitrimer concept to existing commercially relevant polymers has obvious benefits. This approach allows the chemical composition (e.g., crosslink density) and physical properties of the materials to be tuned in a modular manner, though the reliance on organoboron compounds may prove challenging for large-scale production.
In this report, we propose a straightforward approach using only commercially available methacrylic monomers and a trifunctional amine to synthesize catalyst-free vitrimer networks utilizing the associative exchange of vinylogous urethanes. Copolymers of methyl methacrylate (MMA) and (2-acetoacetoxy)ethyl methacrylate (AAEMA), an amine-crosslinkable unit, were prepared and then converted into networks via a condensation reaction with tris(2-aminoethyl)amine (TREN) in one step. Critically, this strategy decouples the network curing and polymerization steps, potentially allowing for significant variation in the linear segment molecular weight and functionality. The cured networks displayed the characteristic properties of vitrimers and exhibited high network fidelity over as many as six destruction-(re)processing cycles.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

We targeted PMMA vitrimers in anticipation that the properties of the linear polymer, a critically important commodity plastic, would be reflected in those of the final material. We began our investigation by preparing statistical copolymers of MMA and AAEMA, an amine-crosslinkable unit, to be used as reactive polymeric precursors (prepolymers) capable of network formation in the presence of multifunctional amines. Compositions containing 10 mol% AAEMA were targeted to maximize the content of MMA to achieve desirable thermal and mechanical properties while also retaining sufficient crosslink density to promote facile exchange. Conventional radical polymerization was initially used to prepare the prepolymer due to its ease of use, requiring no specialty reagents or stringent reaction conditions. However, we encountered challenges processing the networks derived from these prepolymer on viable timescales, presumably due to significant chain entanglement of the high molecular weight polymers produced by this route. Therefore, reversible addition-fragmentation chain transfer (RAFT) polymerization was adopted to target prepolymer molecular weights closer to the critical entanglement molecular weight ($M_e$) of PMMA.$^{46}$

Characterization of prepolymer by both gel permeation chromatography (GPC) and NMR spectroscopy confirmed that molecular weights remained below $M_n$ of 11 kg/mol and that the incorporation of AAEMA was readily controlled by the initial comonomer feed (Figure S1-6). We also investigated the polymerization kinetics to confirm the copolymerizations were controlled, as expected for a reversible-deactivation radical polymerization process (Figure 2, Figure S1). As shown in Figure 2B, the growth of prepolymer molecular weight remained uniform with monomer conversion and dispersities consistently low, indicating that side reactions that could produce ill-defined prepolymer were largely absent. Furthermore, analysis of monomer conversion over time revealed pseudo-1$^{st}$ order incorporation of both MMA and AAEMA throughout the reaction (Figure 2C) and that both co-monomers were incorporated at similar rates (Figure S2), suggesting that reactive sites for crosslinking are uniformly distributed throughout the prepolymer.

While well-defined prepolymer were obtained in a single polymerization step, polymers synthesized by the RAFT process are predominantly terminated by the thiocarbonythio chain transfer agent moiety, which is prone to rapid aminolysis upon treatment with primary amines. In addition to consuming free amines that are necessary for associative bond exchange, this side reaction generates chain-end mercaptans that can further undergo oxidative chain coupling reactions. We therefore employed an end-group removal strategy to replace the reactive trithiocarbonate chain ends with inert cyanopropyl groups (Figure 2) by treatment of prepolymer with excess free radical initiator at 70 °C.$^{57}$ Characterization by $^1H$ NMR spectroscopy, GPC, and ultraviolet-visible (UV-vis) spectroscopy confirmed the
success of the employed end-group removal strategy (Figure 2, Figure S3-7), as shown by the disappearance of resonances corresponding to the trithiocarbonate dodecyl group as well as disappearance of the absorption corresponding to the thiocarbonyl $\pi \rightarrow \pi^*$ electronic transition in the prepolymer UV-vis spectrum (Figure S7). Additionally, complete removal of the trithiocarbonate end group was further confirmed by GPC analysis utilizing UV-vis detection corresponding to the thiocarbonyl $n \rightarrow \pi^*$ electronic transition (420 nm, Figure 2D). Lastly, a distinct change in visual appearance of copolymer from yellow to white was observed following the removal of the thiocarbonylthio end group (inset of Figure 2D).

Vitrimer Synthesis, Reprocessing, and Characterization

After end-group removal, prepolymers were converted to vitrimers in a straightforward solution cast procedure. First, a solution of P(MMA-co-AAEMA) in tetrahydrofuran (THF) was treated with TREN at room temperature. The resultant organogel was evaporated to yield homogeneous, optically transparent vitrimer films (Figure 3B). Formation of vinylogous urethanes was confirmed by FTIR spectroscopy—after initial processing, new absorbances appeared in the FTIR spectrum corresponding to N-H bending and C=C stretching modes at 1655 cm$^{-1}$ and 1600 cm$^{-1}$, respectively (Figure 4A).$^{48}$ Thermal and mechanical properties of vitrimer films were then characterized by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and rheological studies. According to TGA, networks were shown to exhibit similar thermal stability to a poly(methyl methacrylate) standard (12.6 kg/mol), with 50% degradation observed at a slightly higher temperature than the standard (Figure S9).

Figure 2. RAFT copolymerization of MMA and AAEMA and subsequent thiocarbonylthio end-group removal. (A) general reaction scheme, (B–C) polymerization kinetics, (D) GPC UV-vis trace of polymer before (blue) and after (orange) end-group removal with a visible color change of the polymer before (yellow) and after (white) end-group removal.

Figure 3. PMMA vitrimer network formation and processing. (A) network formation via condensation with trifunctional amine (TREN) and amine exchange as a route for reprocessability (B) cured solution-cast network (C) before and (D) after compression molding at 160 °C (rheology sample) (E) Processed rheology sample and processed (left bar) and reprocessed (right bar) DMA samples.
Figure 4. Reprocessing and characterization of PMMA vitrimer networks. (A) FTIR spectroscopy showing the appearance of vinylogous urethane in the processed sample vs. prepolymer. (B) FTIR of processed (P) and reprocessed (R) samples showing retention of vinylogous urethane-functional crosslinks. (C) Storage modulus from DMA over six compression cycles, (D) Tan delta from DMA over six compression cycles, and (E) DSC thermograms over six compression cycles (cooling cycles).

Additionally, cured networks show no isothermal degradation over 6 h at 160 °C under nitrogen flow (Figure S10). DSC and DMA furthermore revealed glass transition temperatures ($T_g$) of 108 ± 8 °C and 110 ± 12 °C, respectively, which are in good agreement with observed $T_g$ values for atactic PMMA. 49

Finally, processed vitrimers exhibited a tensile storage modulus of up to 1,800 MPa at room temperature, which again is in good agreement with observed PMMA commercial materials (Figure S29-S30). 42

As a consequence of the dynamic nature of the crosslinks, vitrimers feature the ability to be remolded or reprocessed into new materials after curing. To simulate a potential reprocessing approach, initial vitrimer films were either fragmented into small shards or ground into a powder before being compression molded at elevated temperatures to yield processed disks or bars for further testing (Figure S13-S15). Networks were reprocessed over five compression cycles (Figure 4) and characterized in a similar manner to the processed materials. As shown in Figure 4B, the characteristic peaks in the FTIR spectrum corresponding to vinylogous urethanes are retained over all reprocessing cycles, indicating that the crosslinks remain stable under the thermal and mechanical stresses of destruction and reprocessing. Retention of network integrity was further proven through the lack of appreciable change in storage modulus (Figure 4C) and $T_g$ (Figures 4D and 4E) after reprocessing.

Stress-relaxation experiments were carried out to obtain the activation energy ($E_a$) of crosslink exchange by the Arrhenius relationship (Figure 5, equation S2). In this case, $E_a$ is the energy required for macroscopic flow of the material, which was calculated to be 102 ± 8 kJ/mol, higher than some values previously reported for small molecule vinylogous urethanes and vinylogous urethane-containing materials without catalyst (60 - 81 kJ/mol), 38-39 but not unprecedented. 50 The higher $E_a$ in our case can potentially be attributed to limited diffusion of the reactive species due to polymer topology. 30

The rate of flow for vitrimer materials is dictated by the exchange rate of the crosslinker. This is significant because rate of crosslinker exchange can afford a secondary transition temperature, the topology freezing transition temperature ($T_v$). $T_v$ is the point in which the dynamic crosslink exchange rate increases enough to enable macroscopic flow (elastic solid to viscoelastic fluid) and, by convention, is the temperature in which the network reaches a viscosity of $10^6$ MPa*s. 25
Figure 5. Stress relaxation and Arrhenius relationship (A) stress relaxation at various temperatures and (B) Arrhenius relationship of the vitrimer network. The individual colors in A and B correspond to identical samples.

With many exchange kinetics occurring rapidly at low temperatures, this transition is rarely observed for high-$T_g$ polymers due to the crosslinks being effectively locked in place below the $T_g$. However, a theoretical value can be extrapolated from the Arrhenius relationship as the temperature at which the viscosity reaches $10^6$ MPa*s (equation S2-3). The $T_v$ for our PMMA vitrimers was extrapolated from the Arrhenius plot (Figure 5) to yield a value of 47 °C, which is comparable with previously reported values and, as expected, is much below the PMMA vitrimer $T_g$. Additionally, we also observed a high apparent $E_a$ (91 kJ/mol) for high molecular weight (52 kg/mol) PMMA from stress relaxation experiments, which may explain the difficulty processing high molecular weight PMMA vitrimers (Figure S31).

The results from control reactions were consistent with enaminone exchange being responsible for the vitrimer properties of the networks. To further probe the thermal stability of the PMMA vitrimer, PMMA homopolymer was subjected to benzyl amine at the operating temperature for (re)processing (160 °C). After 12 h of heating followed by dialysis, the benzylamine treated PMMA showed no evidence of side-chain amidation by NMR spectroscopy or GPC (Figure S33-S36), agreeing with current literature. These results led us to believe that permanent crosslinking of the networks, if apparent, occurs on significantly longer timescales than that of material (re)processing (Figure S20, S38) or at much higher temperatures, such as over 180 °C. Additionally, retardation of healing was observed for PMMA vitrimers exposed to air at high temperatures for long durations of time. In consideration of the lack of observable amine exchange, retardation of flow at elevated temperatures was attributed to free amine oxidation from exposure to air for long durations during testing.

To design a more robust system, we devised an alternative form of recycling by the addition of excess mono-functional amine with heat (Figure 6, S37). By displacing TREN-derived crosslinks, this process enabled networks to be successfully uncrosslinked at temperatures above $T_v$. The modified prepolymer was recovered by precipitation, and no chain scission was observed over reprocess cycles (Figure S38). By selecting a low boiling monofunctional amine, such as n-butylamine, TREN can be reintroduced to the modified prepolymer to again produce a network upon a successive curing cycles (Figure S37). The resulting network could not be dissolved with introduction of solvent and heat, indicating that crosslinks were reestablished with the addition of the crosslinker.

Figure 6. Chemical recycling of vitrimers. (i) Addition of excess monofunctional amine, (ii) precipitation of modified prepolymer, and (iii) reintroduction of TREN to yield rejuvenated networks.

CONCLUSIONS

Upcycling commodity polymers into next-generation materials is crucial to novel material development with industrial relevance. We have demonstrated a straightforward, modular approach to synthesize catalyst-free vinylogous urethane vitrimers from vinyl monomer-derived prepolymers. Solution cast crosslinking of prepolymers and compression molding, using commercially available monomer and crosslinker, was used to synthesize vinyl-polymer-derived vitrimer networks. Nevertheless, networks showed retention of vinylogous urethane crosslinks and mechanical and healing properties over several processing and reprocessing cycles. Additionally, a secondary form of recycling was implemented by uncrosslinking the network with mono-functional amine to yield a modified prepolymer, which could be repurposed or recrosslinked. This system demonstrates excellent reprocessability and tunability, and we envision this approach...
leading to development of similar systems and a variety of applications. By decoupling the formation of polymer backbone and crosslinking, a variety of networks formed from commodity monomers can potentially be modified in a simple fashion to yield materials with customizable functionality or properties.

ASSOCIATED CONTENT

Supporting Information.
All experimental details including materials, instrumentation, synthesis, characterization, images, and calculations.
This material is available free of charge via the Internet at http://pubs.acs.org.

INFORMATION

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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 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-Cyano-4- [(dodecylsulfanylthiocarbonyl)sulfanyl]petanoic acid (CDP, RAFT CTA) was synthesized from previous literature.¹

Instrumentation:

**Nuclear Magnetic Resonance (NMR) Spectroscopy.** ¹H NMR spectra were recorded on an Inova 500 spectrometer. ¹H NMR chemical shifts in DMSO-δ6 were referenced to CHD2SOCD3 (2.50 ppm).

**Gel Permeation Chromatography (GPC).** GPC was performed in DMAc with 50 mM LiCl at 50 °C 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 × 10⁹ and 0–100 × 10⁹ 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 °C. 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 °C isotherm for 30 min prior to each run to remove any possible moisture or residual solvent. RAMP experiments were heated at 10 °C/min from room temperature to 600 °C under nitrogen flow (25 mL/min). Isothermal experiments were heated under nitrogen flow (25 mL/min) at 20 °C/min from room temperature to 160 °C, 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 flat-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 purged 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 (0.0896 g, 0.222 mmol), AIBN (0.0036 g, 0.022 mmol) were added to a Schleck flask containing 1,4-dioxane (20 mL). The solution was purged 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:

Figure S1. GPC chromatograms from kinetic study.

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

10% AAEMA prior to end-group removal

![Figure S3. 1H NMR spectrum of P(MMA-co-AAEMA) prior to end group removal. 10% AAEMA after end-group removal](image)

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

10% AAEMA after end-group removal

![Figure S4. 1H NMR spectrum of P(MMA-co-AAEMA) post end group removal. Calculation of AAEMA incorporation:](image)

Figure S4. 1H 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)

\[
\% \text{ AAEMA} = \frac{(A_a)}{((A_c + d) - 2) + (A_e)} \times 100\%
\]

\[
\% \text{ AAEMA} = \frac{3}{(29.43 - 2 + 3)} \times 100\% = 9.9\% \text{ AAEMA incorporated into polymer backbone}
\]
Gel Permeation Chromatography (GPC):

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

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

**Figure S6.** GPC chromatogram of P(MMA-co-AAEMA) post end group removal (molecular weights were determined by MALLS assuming 100% mass recovery).

\[ M_n = 9.7 \text{ kg/mol} \]
\[ M_w = 10.4 \text{ kg/mol} \]
\[ D = 1.07 \]
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 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.
TGA: *(taken prior to compression molding)*

![TGA Graph](image)

- **95% at 273 °C**
  - (PMMA 12.6 kg/mol: 277 °C)
- **80% at 335 °C**
  - (PMMA 12.6 kg/mol: 310 °C)
- **50% at 380 °C**
  - (PMMA 12.6 kg/mol: 333 °C)

**Ramp rate: 10 °C/min**

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

**Isothermal TGA:**

![Isothermal TGA Graph](image)

**Figure S10.** Isothermal TGA experiment of P(MMA-co-AAEMA) 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:

\[
\begin{align*}
\text{O} & \quad \text{N}^\text{R'} \quad \text{H} \\
\text{H}_2\text{N}^\text{R'} & \quad \text{H}_2\text{N}^\text{R'} \quad \text{H} \\
\end{align*}
\]

**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).
DSC:

Figure S18. DSC thermograms of (re)processed vitrimers over 6 compression cycles.

Solubility Fractions:

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 balance error was within 1% for all samples.

Figure S19. Gel fractions of (re)processed vitrimer networks.
Rheology:

- DMA Temperature Sweep:

![Diagram](image)

- Figure S20. 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 S21.** Strain sweeps of P(MMA-co-AAEMA) vitrimer network at various temperatures.

**Figure S22.** Strain sweeps of P(MMA-co-AAEMA) vitrimer network at various temperatures, with linear fits depicting the linear viscoelastic region.
Figure S23. Stress relaxation of P(MMA-co-AAEMA) vitrimer network (from Figure 5).

Figure S24. Stress relaxation of P(MMA-co-AAEMA) vitrimer network showing complete relaxation at 140 and 150 °C.
Figure S25: 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 S26. 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 ($T_v$):

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

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

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

$T_v$ can be calculated from the relaxation time ($\tau$) via equation 1 using the Arrhenius relationship.

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

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

$$T_v = 47 \degree C$$

- Maximum stress at 1% strain:

![Figure S27](image)

**Figure S27.** Maximum stress at 1% strain at various temperatures. The maximum strain for 95 °C was above the limitations of the instrument
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 S28. GPC chromatogram of PMMA used for comparison studies.*
Figure S29. Storage modulus from DMA for PMMA (blue) and PMMA vitrimer (black).

Figure S30. Storage modulus prior to $T_g$ ("glassy modulus") for PMMA (blue) and PMMA vitrimer (black).
Figure S31. Arrhenius relationship for stress relaxation of PMMA (blue) and PMMA vitrimer (black).
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 S32. 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 S33. 1H NMR spectrum of PMMA synthesized from modified prepolymer procedure.
$M_n = 7.8 \text{ kg/mol}$

$M_w = 9.8 \text{ kg/mol}$

$D = 1.25$

**Figure S34.** 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 S35. $^1$H NMR spectrum of PMMA showing no aromatic protons after treatment with benzylamine.

Figure S36. GPC chromatogram of PMMA showing no change in elution time after treating with benzylamine.
Recycling Studies:

Vitrimer (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 S37. (Top) Scheme for secondary recycling of vitrimer 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 S38. 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.

Prepolymer:
\[ M_n = 9,546 \text{ g/mol} \]
\[ M_w = 11,680 \text{ g/mol} \]
\[ D = 1.22 \]

Recycled polymer:
\[ M_n = 13,930 \text{ g/mol} \]
\[ M_w = 20,440 \text{ g/mol} \]
\[ D = 1.49 \]
Compression Molds:
Rheology Mold:

DMA and Tensile Test Mold:
References:

(1) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. Polymer 2005, 46, 8458−8468


Current Research and Future Work:

Linear, block copolymers have also played an important role in governing material properties from increased toughness to adjustable thermal properties via self-assembled or blended macrostructures.¹ Vitrimmer pendent groups being localized into a concentrated section of the chain may allow for increased processing rate for block systems. We believe the rate of macroscopic flow will be increased by diminishing topology limited diffusion.² Additionally, block polymers containing a “hard” and a “soft” block have been shown to improve impact resistance due to block self-assembly,³ and the formation of di-block copolymers with larger vitrimer blocks should lead to self-assembly due to the large affinity of the covalently-bonded vitrimer section. Vitrimmer properties, e.g., toughness and impact strength, will be tuned by selecting polymers with varying $T_g$ as the non-vitrimer block.

I have investigated the preparation and formation of P(MMA-$b$-AAEMA) at both a low (96:4) and high (49:50) incorporation of the vitrimer block (Scheme 1). The polymers were then crosslinked in a solution casting procedure to yield the crosslinked network. The low incorporation resulted in transparent, but brittle films that could not be removed from the mold intact. However, the high incorporation led to robust films that showed quite remarkable viscous flow behavior under catalysis when compared to the previous system.

Scheme 1: Synthesis of P(MMA-$b$-AAEMA) and end-group removal.
PMMA ($M_n = 4.86$ kg/mol) was chain extended with AAEMA to afford linear block copolymers (15.7 kg/mol) of MMA (DP = 49) and AAEMA (DP = 50) (Figure 1). The polymer was then end-group removed with the use of excess initiator as shown in the previous system (Scheme 1).

Polymers were then crosslinked with hexamethylene diamine in the presence of $p$-toluene sulfonic acid in a solution cast procedure to form block vitrimer materials (Figure 2a). The solution cast material was cured at 80 °C for 24 h prior to compression molding at 160 °C to yield the processed material (Figure 2b). The vitrimer was then analyzed by rheology though stress relaxation and frequency sweeps (Figure 2c-e). The stress relaxation produced an Arrhenius fit (Figure 2d) that was in good agreement with the previous report. Additionally, the frequency

![Figure 1: GPC chromatograms before (orange) and after (blue) chain extension of PMMA.](image)

![Figure 2: (a) Scheme of block vitrimer crosslinking (20% crosslinked in vitrimer block and 10% crosslinked overall) (b) Image of P(MMA-b-AAEMA) vitrimer, (c) Stress relaxation at various temperatures, (d) Arrhenius fit and the activation energy ($E_a$) for the system, and (d) frequency sweeps showing crossover points at various temperatures.](image)
sweeps show a crossover from a viscoelastic fluid to an elastic solid, which is typical for recyclable thermosets. To show that the exchange chemistry is still responsible for polymer flow, solubility studies were performed (Figure 3). The vitrimer again was unable to dissolve in THF until the addition of excess monofunctional amine to liberate the crosslinker.

![Figure 3: Solubility Studies in THF with and without monofunctional amine (benzylamine).](image)

This system will be used to achieve increased flow through the localization of exchangeable units both intramolecularly (on the chain) and intermolecularly (via self-assembly). Once self-assembly is achieved, low $T_g$ polymers (polyhexylmethacrylate, $T_g = -6$ °C) will be used to create impact resistant vitrimers. AAEMA vitrimers are a terrific template to probe the fundamentals of vitrimers from molecular weight dependence (e.g., above and below $M_c$), thermal properties (e.g., varied $T_g$), and architectural effects (branched, star, & block polymers) due to the simple modularity of reversible deactivation radical polymerization (RDRP). This system, among other unexplored vitrimer and dissociative exchange systems, will be investigated throughout my doctoral research.
References: