

Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers

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S Supporting Information

ABSTRACT: Vitrimers are polymer networks whose cross-links undergo associative exchange processes at elevated temperature, usually in the presence of an embedded catalyst. This design feature enables the reshaping of materials with mechanical properties similar to thermoset resins. Here we report a new class of vitrimers consisting of polyhydroxyurethanes (PHUs) derived from six-membered cyclic carbonates and amines. PHU networks relax stress and may be reprocessed at elevated temperature and pressure in the absence of an external catalyst. The as-synthesized networks exhibit tensile properties comparable to those of leading thermosets and recover ca. 75% of their as-synthesized values following reprocessing. Stress relaxation occurs through an associative process involving nucleophilic addition of free hydroxyl groups to the carbamate linkages and exhibits an Arrhenius activation energy of 111 ± 10 kJ/mol, which is lower than that observed for molecular model compounds (148 ± 7 kJ/mol). These findings suggest that transcarbamoylation is activated by mechanical stress, which we attribute, on the basis of DFT calculations, to the twisting of N lone pairs out of conjugation with the carbonyl π orbitals. PHU vitrimers are a promising new class of repairable networks because of their outstanding mechanical properties, avoidance of toxic isocyanate monomers, and catalyst-free repair processes.

Thermosets are cross-linked polymer networks with outstanding mechanical strength and solvent resistance that are used in durable goods, adhesives, and composites. Their static cross-links cause thermosets to be irreparable and difficult to recycle. Cross-links capable of dynamic exchange¹ impart repair and reshaping capabilities but reduce toughness and shape persistence. A subset of dynamic cross-linked polymers, classified as vitrimers,^{1a,b} combine excellent mechanical properties at service temperatures and malleability at elevated temperatures by employing cross-links that undergo associative, rather than dissociative, exchange reactions. This design results in gradual viscosity changes with respect to temperature, in contrast to the abrupt viscosity change observed just above the glass transition temperatures of thermoplastics, enabling vitrimers to be easily reprocessed.

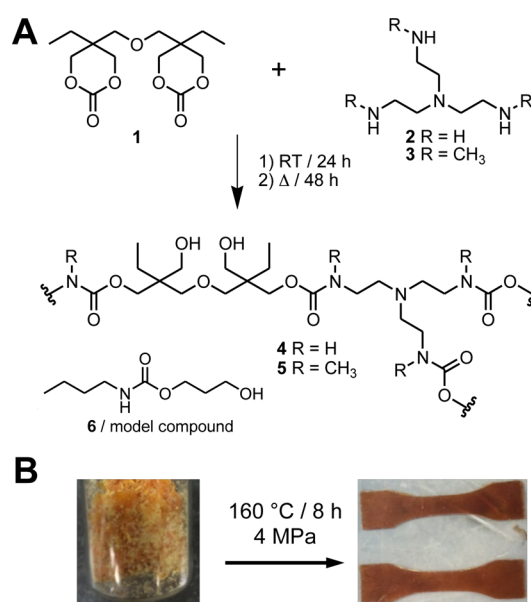


Figure 1. (A) The reaction of bis(cyclic carbonate) 1 and triamines 2 and 3 provides PHUs 4 and 5, respectively. 6 is a hydroxyurethane model compound used for transcarbamoylation studies. (B) Photograph of a ground sample of 4 (left), which was reprocessed into tensile bars (right) by heating to 160 °C at 4 MPa pressure for 8 h.

Broadening the chemical scope of vitrimers beyond polyester resins (based on transesterification)² and polybutadiene rubbers (based on alkene metathesis)³ provides a means to improve and expand both their performance and sustainability. Cross-linked polyurethanes (PUs) are used extensively for cushioning and thermal insulation, yet the efficient reprocessing of PU thermosets is poorly established. Associative transcarbamoylation processes are sluggish for carbamates, and the dissociative reversion of carbamates to isocyanates and alcohols that typically occurs at high temperatures (>200 °C) can be associated with deleterious side reactions. Thus, existing healable cross-linked PUs either incorporate additional dynamic functional groups and/or are limited to elastomeric materials.⁴ Inspired by historic reports of enhanced stress relaxation in cross-linked polyurethanes containing free hydroxyl groups,⁵ we evaluated the

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vitrimeric properties of polyhydroxyurethane (PHU) networks, whose synthesis from polyfunctional cyclic carbonates and amines provides one hydroxyl group per carbamate linkage, avoids the use of toxic isocyanates, and is amenable to monomers derived from renewable sources.⁶

Here we report PHU networks derived from six-membered cyclic carbonates and polyfunctional amines as a new class of vitrimers that does not require the incorporation of an external catalyst. Stress relaxation in these polymers is consistent with an associative transcarbamoylation process yet exhibits a lower Arrhenius activation energy in the polymer than that observed in molecular model compounds. We attribute this phenomenon to mechanical activation of the transcarbamoylation and present supporting density functional theory (DFT) calculations. The combined thermal and mechanical activation of vitrimers represents a new and desirable reprocessing mechanism that will increase the utility of repairable polymer networks and the scope of chemical transformations available to these materials.

Cross-linked PHU **4** was prepared through the reaction of bis(cyclic carbonate) **1** and tris(2-aminoethyl)amine (**2**) (Figure 1A) in CH₂Cl₂ at room temperature, after which the solvent was removed by heating to 90 °C under reduced pressure for 48 h. Polymer **4** was isolated as an orange solid that conformed to the shape of its mold. The FT-IR spectrum of **4** (Figure S1) exhibits a single peak in the carbonyl region at 1690 cm⁻¹, corresponding to a hydrogen-bonded carbamate C=O stretch. The spectrum also contains a new broad stretch at 3300 cm⁻¹, corresponding to the O–H stretch of hydroxyl groups, and no C=O stretch signals associated with residual cyclic carbonates. Swelling tests of the polymer in tetrahydrofuran (25 °C, 24 h) indicate gel fractions in excess of 0.98, consistent with a densely cross-linked network. As-synthesized samples of **4** had average Young's moduli (E) of 2.2 ± 0.4 GPa, strain-at-break (ϵ_b) of $6.9 \pm 3.8\%$, and tensile strength (σ_b) of 72 ± 11 MPa, all competitive materials properties for typical thermosets.^{1a,e,f,2e} Also, **4** shows little weight loss up to 250 °C, as determined by thermogravimetric analysis (TGA) (Figure S4) and exhibits a glass transition temperature (T_g) of 54 °C, as determined by differential scanning calorimetry (DSC) (Figure S3). Dynamic mechanical thermal analysis (DMTA) revealed a precipitous drop in modulus near 61 °C, similar to the T_g determined by DSC. Above this temperature, the material has a constant plateau modulus of 7.5 MPa, corresponding to an estimated molar mass between cross-links of 1.2 kg/mol (Figure S6). These combined observations indicate that **1** and **2** readily condense to provide a densely cross-linked, rigid PHU network.

The dynamic properties of **4** were characterized using tensile stress relaxation analysis (SRA) at elevated temperatures in the linear viscoelastic regime (Figure 2A). Samples were thermally equilibrated and subjected to a controlled strain of 5%, and the mean relaxation lifetime (τ^* , where $G/G_0 = e^{-1}$) was determined. SRA was performed at 170, 180, and 190 °C, and the results were reproducible. The topology-freezing transition temperature (T_v), at which the viscosity (η) crosses the traditionally defined solid-to-liquid transition of 10^{12} Pa·s,⁷ was 111 °C (see the Supporting Information); below T_v , **4** behaves as a traditional thermoset. FT-IR spectra recorded after SRA was performed at each temperature were unchanged relative to those of the as-synthesized networks, suggesting no significant change in the network functionality (Figure S8) and indicating the stability of **4** toward the reprocessing conditions and stress relaxation through degenerate carbamate exchange reactions.

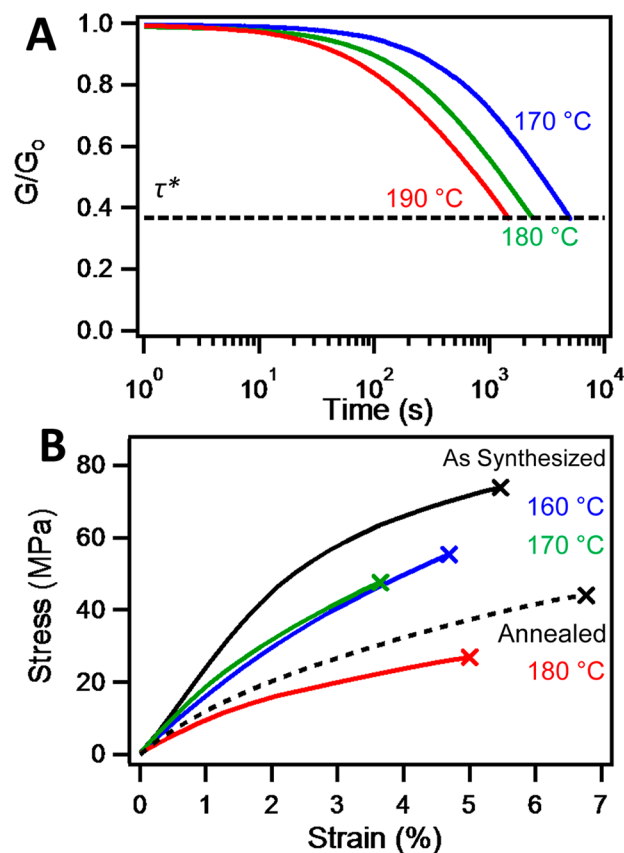


Figure 2. (A) Normalized stress relaxation analysis performed on **4** at elevated temperatures. The dashed-black line represents $G/G_0 = e^{-1}$; the time at which this value is reached is defined as the characteristic relaxation time, τ^* . (B) Representative tensile tests of as-synthesized **4** (black), samples reprocessed (see Figure 1B) for $3\tau^*$ at 160 °C (blue), 170 °C (green), and 180 °C (red) and 4 MPa pressure, and an as-synthesized sample annealed for $3\tau^*$ at 160 °C (dashed black).

Uniaxial tensile testing was performed on both pristine and recycled dogbone samples to characterize the mechanical properties and reprocessability of polymer **4**. The process of repairing and reshaping broken samples by compression molding was optimized with respect to the reprocessing temperature and time. Reprocessing performed at 160 °C for $3\tau^*$ (ca. 8 h; Figure 1B) provided the maximum recovery of tensile properties relative to a tensile bar prepared directly from the polymerization (Figure 2B), with $E = 1.6 \pm 0.2$ GPa (76% recovery), $\epsilon_b = 4.8 \pm 0.8\%$ (69% recovery), and $\sigma_b = 53 \pm 8$ MPa (74% recovery). We attribute the incomplete recovery of the tensile properties to minor decomposition in the network that occurs slowly at elevated temperature over long times, as evidenced by the discoloration of the materials and TGA isotherms showing modest mass loss (ca. 7% over 5 h at 190 °C; Figure S5). Furthermore, tensile bars prepared directly from the polymerization that were heated to 160 °C for $3\tau^*$ prior to the analysis exhibited similarly reduced tensile properties (Figure 2B and Table S2), suggesting that the bond-formation process is efficient but that the polymers also undergo slight decomposition. Consistent with the FT-IR analysis after the SRA experiments (Figure S8), the FT-IR spectra of the reprocessed samples are identical to those of the as-synthesized samples, corroborating isodesmic carbamate exchange reactions. A similar T_g and an 80% recovery of the plateau modulus were observed by DMTA after reprocessing (Figure S6), further indicating that the dynamic

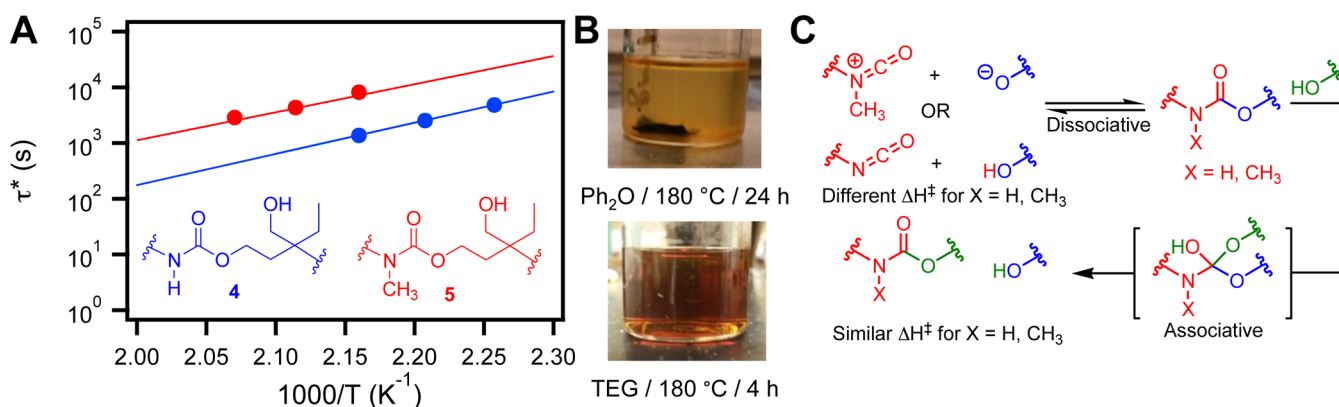


Figure 3. (A) Arrhenius plots for the thermal activation of stress relaxation in **4** (blue) and **5** (red) are consistent with vitrimeric behavior. (B) Swelling in Ph_2O ($180^\circ C$, 24 h) does not dissolve **4** (top), but **4** fully dissolves in tetraethylene glycol after 4 h (bottom). (C) The similar activation energies for stress relaxation in **4** and **5** are suggestive of an associative transcarbamoylation mechanism.

bonds preserve the cross-linking density and mechanical properties of **4**.

The temperature dependence of the SRA experiments (Figure 2A) indicates that PHU network **4** undergoes more rapid transcarbamoylation than model compounds under similar conditions. The temperature dependence of τ^* for **4** was fit to an Arrhenius relationship to determine an apparent activation energy (E_a) of 111 ± 10 kJ/mol (Figure 3A), which is significantly lower than that for uncatalyzed transcarbamoylation observed in model compound **6** (148 ± 7 kJ/mol; Figures S10 and S11) and similar to the lowest reported values of catalyzed transcarbamoylation in traditional urethanes [$Bi(OTf)_3$, $E_a = 112 \pm 9$ kJ/mol].⁸ We hypothesize that this phenomenon arises from the mechanical activation of the transcarbamoylation reaction, as model hydroxyurethane **6** shows relatively little conversion in the presence of excess alcohol at similar temperatures and time scales (Figure S10). Previous vitrimers have shown consistent E_a values between their stress relaxation behavior and their catalyzed exchange reactions,^{1a,f} with the notable exception of another urethane-containing material.^{2c}

The decomposition of carbamates to isocyanates and alcohols, the most likely dissociative stress relaxation mechanism, generally occurs at much higher temperatures than those at which **4** exhibits rapid stress relaxation, particularly for urethanes derived from aliphatic isocyanates ($>250^\circ C$).^{9a} Swell tests of **4** in Ph_2O at $180^\circ C$ for 24 h (Figure 3B) showed no evidence of dissolution, consistent with associative exchange in the presence of an unreactive solvent.^{9b} On the other hand, the network dissolved completely in the reactive solvent tetraethylene glycol (TEG) within 4 h under identical conditions, consistent with transcarbamoylation being the dominant exchange mechanism. Stress relaxation experiments performed on **5**, which is linked by *N*-methylurethanes incapable of forming neutral isocyanates (Figure 3C), exhibited an E_a of 101 ± 7 kJ/mol, similar to that for stress relaxation in **4**. These experiments cast doubt that the reversion of carbamates to isocyanates is significant under the stress relaxation conditions and demonstrate that alcohols significantly contribute to the stress relaxation. The stress relaxation rates of **5** were significantly slower than those of **4**, indicating a difference in pre-exponential factor that may be associated with steric effects related to nucleophilic addition to the methyl-substituted carbamate. The absence of isocyanate or isocyanurate peaks in the FT-IR spectra of both **4** and **5** (Figures S8 and S9) after SRA is consistent with negligible isocyanate formation. To further support an associative mechanism of

reprocessing, the reprocessability of the polymer was characterized after the hydroxyl groups of ground polymer **4** were acetylated (Scheme S6 and Figure S12). The acetylated polymers showed only ca. 10% recovery of the mechanical properties, indicating the necessity of free hydroxyl groups for efficient reprocessing (Figure S13). These observations suggest that PHU stress relaxation and reprocessing occur primarily through associative transcarbamoylation reactions, which is a key feature for accessing the desirable toughness, malleability, and creep resistance associated with vitrimers.

The discrepancy in activation energy between PHU stress relaxation and model compound transcarbamoylation, along with dissociative exchange processes appearing to be inoperative, suggests that transcarbamoylation reactions are mechanically activated. Thermoplastic PUs previously exhibited decreased molar mass and increased dispersity when subjected to mechanical strain at high temperatures.¹⁰ These changes were attributed to the breaking of urethane bonds, whose rate increases with increased polymer size, a common trait of mechanically activated reactions in polymeric systems.¹¹ We propose that transcarbamoylation is accelerated when mechanical strain causes the lone pair of the nitrogen atom to twist out of conjugation with the carbonyl π -electron system, thereby rendering the carbamate more susceptible to nucleophilic attack. The resulting orthocarbamate intermediate is most likely to reform the carbamate by expelling the alkoxy group so as to relieve the most stress.

To assess this hypothesis, DFT calculations were undertaken (see the Supporting Information) to predict E_a values for the water-catalyzed reaction of MeOH with *N,O*-dimethylcarbamate to generate the product orthocarbamate. To address the potential influence of torsional strain, the energies of possible reactant and transition-state (TS) structures were computed for fixed OCNC dihedral angles of $\angle O=C(OCH_3)N(H)C\angle H_3$. Interestingly, the E_a values associated with many torsionally strained educt and TS structures were predicted to be much lower than for the analogous fully relaxed reaction (Figure 4). In particular, compared with the adiabatic E_a of 70.7 kJ/mol that is predicted for fully relaxed structures in this model reaction, at an OCNC torsion angle of 90° , the E_a is predicted to drop to 35.5 kJ/mol (Figure 4; see Figure S20 for the full torsional coordinate). This reduction is quite similar to the difference in E_a observed for stress relaxation of **4** and transcarbamoylation processes of the model system. Importantly, the computed TS-structure energies for water-catalyzed reversion of *N,O*-

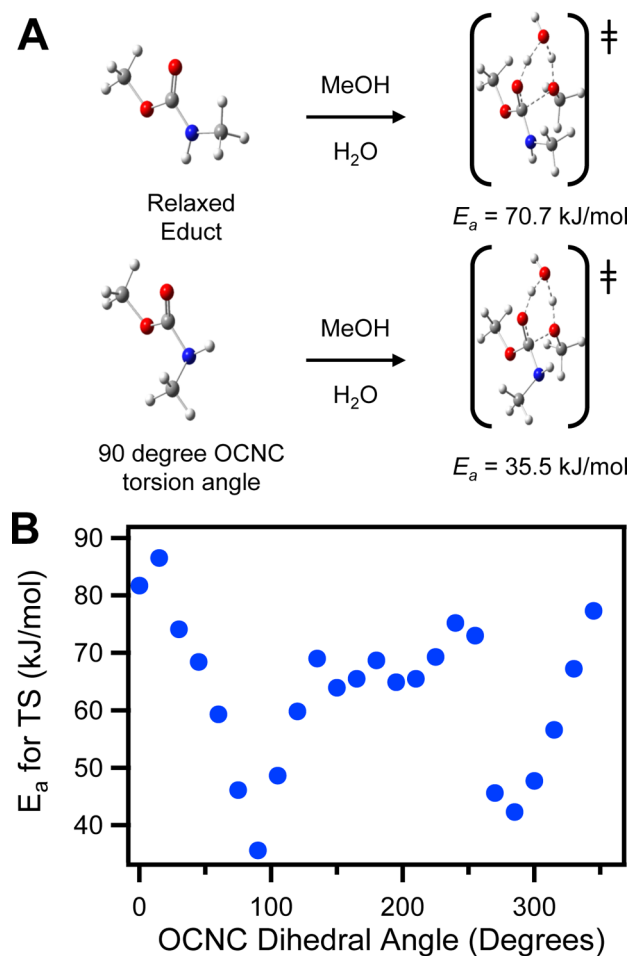


Figure 4. (A) DFT-calculated structures of *N,O*-dimethylcarbamate with their corresponding TS structures for water-catalyzed transcarbamoylation with methanol. H, C, N, and O atoms are shown in white, gray, blue, and red, respectively. (B) Vertical E_a to reach a constrained TS from a constrained educt as a function of the $\text{O}=\text{C}(\text{OCH}_3)\text{N}(\text{H})\text{C}(\text{H})\text{CH}_3$ dihedral angle.

dimethylcarbamate were found to increase greatly because of torsional strain compared with the educt, consistent with the conclusion that isocyanate formation is not responsible for strain relief in this system.

In conclusion, we have demonstrated that cross-linked PHUs derived from six-membered cyclic carbonates and amines display vitrimeric behavior in the absence of an embedded catalyst typically incorporated into such networks. Furthermore, we have posited that transcarbamoylation is the principal relaxation mechanism in PHU networks. These materials display mechanical properties competitive with those of traditional PU thermosets yet enable reshaping and repair that will enhance their long-term utility. Moreover, these networks are prepared from readily accessible and general monomer classes, which will facilitate the full exploration and tuning of their properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08084.

Procedures and additional data (PDF)

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The authors declare no competing financial interest.

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