

# Reprocessing Cross-linked Polyurethanes by Catalyzing Carbamate Exchange

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## Abstract

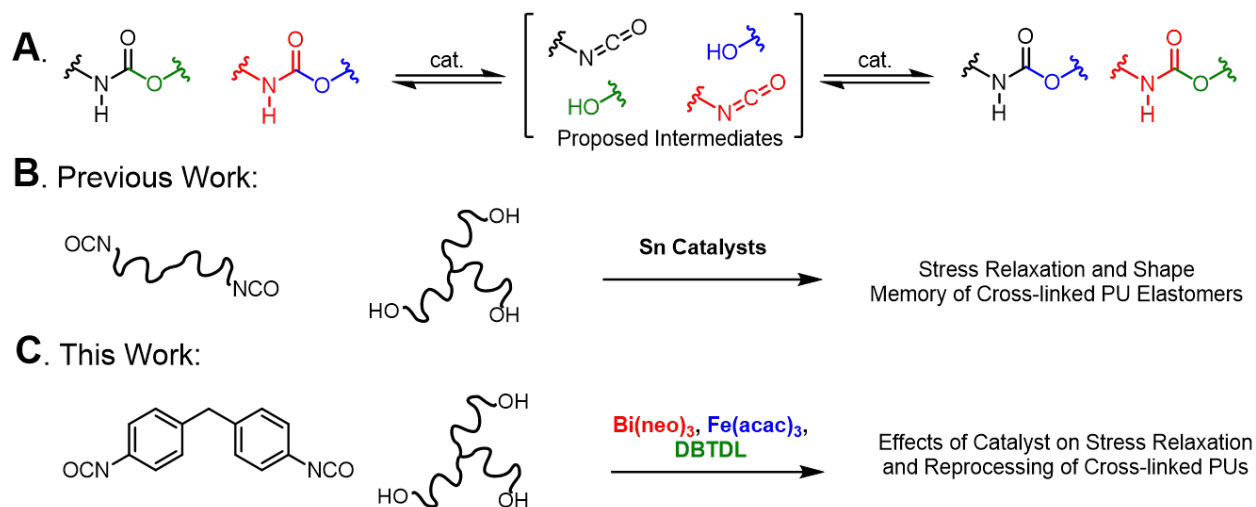
The reprocessing or recycling of cross-linked polymers by incorporating dynamic covalent cross-links has the potential to increase their usable lifetimes and reduce their environmental impact. Polyurethanes (PUs) are the largest class of cross-linked polymers; however, their direct recycling into similar value materials is not well-developed. We demonstrate that several Lewis acid catalysts mediate urethane exchange selectively and under mild conditions. Incorporating these catalysts into cross-linked polyether and polyester PUs with structures similar to commercial PU thermosets gives cross-linked materials that can completely relax stress in 100 seconds at temperatures as low as 140 °C. The dynamic polymers were reprocessed via compression molding to provide materials with similar cross-linking densities to as-synthesized materials. Because these systems are based on commercially available PU monomers and inexpensive Lewis acid catalysts, we anticipate that these findings will enable the recycling of traditional thermosetting PUs.

## Introduction

Although cross-linked polymers are traditionally not recyclable, judiciously incorporating dynamic crosslinks can impart mechanical properties competitive with traditional thermosets and recyclability associated with thermoplastics.<sup>1-5</sup> Dynamic covalent bonds, including imines,<sup>6</sup> boronate esters,<sup>7</sup> disulfides,<sup>8,9</sup> and reversible Diels-Alder adducts<sup>10</sup> have enabled polymer networks to be reprocessed. These approaches promise to improve the sustainability of thermosets and enable emerging applications of dynamic networks. However, these dynamic linkages are uncommon in commodity polymers, and incorporating them will require continued development and increase costs. Controlling the dynamic nature of linkages already prevalent in commodity polymers has the greatest potential to allow for direct reprocessing of materials already used in the marketplace. Leibler and coworkers demonstrated that incorporating a transesterification catalyst into polyester-linked epoxy resins enables their recycling.<sup>11,12</sup> The power and simplicity of this approach has inspired many further studies, including the development of shape memory materials,<sup>13,14</sup> polymer composites,<sup>15,16</sup> and fundamental studies on the dynamic behavior of these materials.<sup>17,18</sup> Developing a similar approach to enable these features in other commodity polymers is desirable.

Polyurethanes (PUs) are the sixth largest class of synthetic polymers and are commonly used in cross-linked architectures as foams, adhesives, coatings, and structural components.<sup>19</sup> Because of their broad use, prior work has focused on the repurposing or recycling of cross-linked PU waste. The most common approaches rely on chemical recycling via glycolysis to produce new urethane-based monomers that can be repolymerized.<sup>20</sup> Incorporating other dynamic bonds into PUs offers a means to directly recycle the cross-linked polymers,<sup>21-24</sup> but these new chemistries inevitably alter other properties of the PUs and face a challenging path to achieve commercial

adoption over existing materials. Therefore, controlling the dynamic nature of urethane linkages themselves represents a more straightforward approach to enable recycling of these materials on large scale. Tobolsky and coworkers demonstrated that urethane dissociation to isocyanates and alcohols at elevated temperatures causes cross-linked PUs to relax stress,<sup>25,26</sup> a phenomenon which has recently been recognized as a feature of other useful dynamic cross-linked polymers. More recently, Xie and coworkers showed that incorporation of catalytic dibutyltin dilaurate (DBTDL)<sup>27</sup> or tertiary amines<sup>28</sup> into cross-linked PUs causes more rapid stress relaxation via urethane exchange reactions (Figure 1A) and leveraged this phenomenon to develop shape memory materials with adjustable permanent shapes (Figure 1B). Further work has demonstrated that tin-mediated urethane exchange is a common way to achieve stress relaxation and some degree of reprocessability in cross-linked polyurethanes.<sup>29-33</sup> However, the nature of this stress relaxation and reprocessing behavior remains nearly unexplored. Here we explore whether safer, readily available catalysts can mediate PU stress relaxation and enable the efficient reprocessing of various cross-linked PUs (Figure 1C).

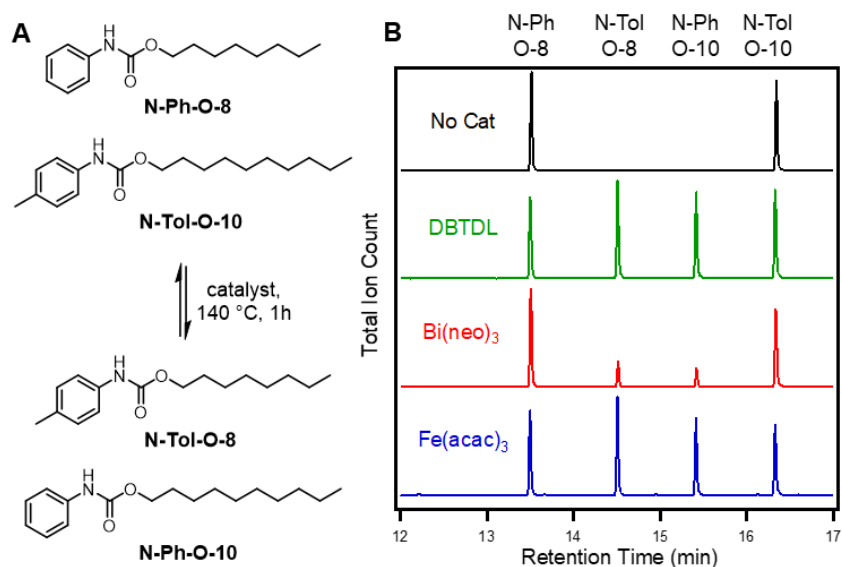


**Figure 1.** **A.** Schematic of urethane exchange process. **B.** Prior investigations of dynamic urethane exchange processes using Sn catalysts in cross-linked PU elastomers. **C.** This work, studying the impacts of catalyst choice on the urethane exchange process in different polyurethane networks.

## Results and Discussion

Stress relaxation of cross-linked PUs has been shown to occur on slow, multiple-hour timescales in the absence of catalyst<sup>26</sup> or very rapidly (seconds to minutes) in the presence of DBTDL.<sup>27,29</sup> Incorporating DBTDL is attractive since it is a common catalyst used in the synthesis of PUs, but alkyl tin species are associated with harmful health and environmental effects<sup>34</sup> and therefore are not ideal catalysts to incorporate at elevated loadings in PU resins. Therefore, we investigated whether tin was unique in its ability to catalyze the urethane exchange reaction. Catalyst performance was first evaluated using a crossover experiment of urethane-containing model compounds. N-phenyl-O-octyl urethane and N-tolyl-O-decyl urethane were combined with 2.5 mol% of catalyst per urethane and heated at 140 °C for 1 hour. The mixture was then analyzed via GC-MS to determine whether the exchange products, N-phenyl-O-decyl urethane and N-tolyl-O-octyl urethane, were formed (Figure 2). In the absence of catalyst, only the two starting materials are observed, consistent with slow stress relaxation observed in cross-linked PUs containing no additional catalyst.<sup>26</sup> The use of DBTDL as a catalyst yielded an approximately statistical distribution of the four urethanes, which was consistent with literature reports.<sup>27</sup> Other Lewis acid catalysts and organocatalysts were screened, and many catalysts showed comparable activity to DBTDL. Zirconium(IV) acetylacetonate, iron(III) acetylacetonate, titanium(IV) isopropoxide, and hafnium(IV) acetylacetonate showed apparent equilibration within 1 hour (Figure 2, Figure S1). Stannous octoate and zirconium(IV) ethylhexanoate showed lower or no conversion (Figure S1), suggesting that both the metal oxidation state and initial ligand set influence the catalytic efficiency. The N-methyl derivatives of the model compounds, which cannot undergo facile reversion to isocyanates and alcohols, exhibit no detectable change under these conditions (Figure S2). This observation is consistent with urethane dissociation and reformation as the exchange

mechanism. A full study of the catalysis mechanism is ongoing, but we also note a preliminary positive correlation between a given catalyst's urethane exchange activity and its reported activity for catalyzing the reaction of isocyanates with alcohols,<sup>35</sup> which further supports the reversion-based exchange mechanism.



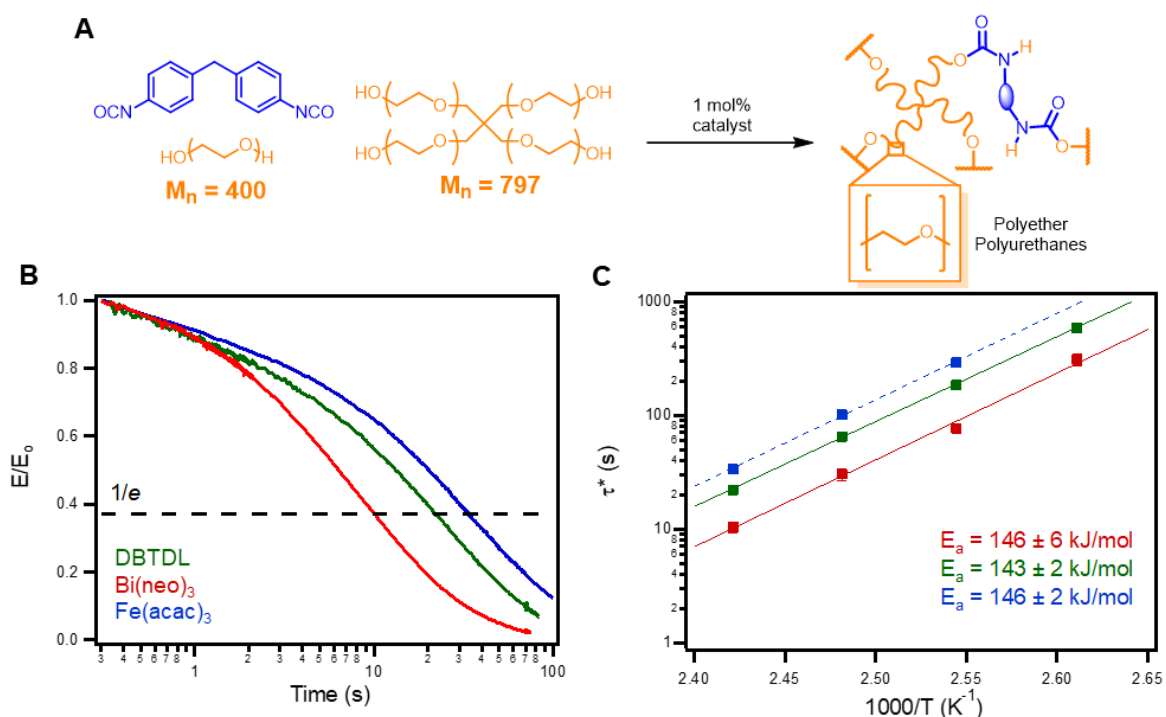
**Figure 2.** **A.** Urethane exchange of N-phenyl-O-octyl urethane and N-tolyl-O-decyl urethane to generate N-tolyl-O-octyl urethane and N-phenyl-O-decyl urethane. **B.** Gas chromatograms of the reaction mixture taken after heating for 1 hour at 140 °C.

The performance of these catalysts when incorporated into PU networks was evaluated, using DBTDL as a benchmark.<sup>27,29</sup> Bismuth neodecanoate [Bi(neo)<sub>3</sub>] was selected despite its lower activity in catalyst screening since it is commonly used as a catalyst in PU synthesis and is thought to be less toxic than DBTDL.<sup>36</sup> Iron(III) acetylacetonate [Fe(acac)<sub>3</sub>] was chosen as a representative example of using abundant, low-toxicity metals to catalyze this reaction.<sup>37</sup> Each catalyst was incorporated into both polyether- and polyester-based PUs, as these functional groups are most common in commercial cross-linked PU materials. These catalysts were first incorporated into cross-linked polyether PU elastomers, which were synthesized by reacting 4,4'-

methylenebis(phenyl isocyanate) (MDI) with a linear polyethylene glycol (PEG,  $M_n \approx 400$  g/mol) and a 4-arm hydroxyl-terminated PEG ( $M_n \approx 797$  g/mol) in the presence of 1 mol% catalyst (Figure 3A). FT-IR spectroscopy of the cured polymers indicated complete disappearance of the -NCO stretching band ( $2285\text{ cm}^{-1}$ ), and the appearance of both the urethane C=O stretching frequency ( $1690\text{-}1715\text{ cm}^{-1}$ , depending on the hydrogen bonding environment of the urethane) and N-H deformation ( $1530\text{ cm}^{-1}$ ) (Figure S3). These polymers display low glass transition temperatures of ca.  $10\text{ }^\circ\text{C}$  as measured by differential scanning calorimetry (DSC, Figure S4) and thermal stability similar to most cross-linked PUs, with decomposition onset temperatures greater than  $280\text{ }^\circ\text{C}$  (Figure S5). Dynamic mechanical thermal analysis (DMTA) shows a plateau storage modulus greater than the loss modulus above the glass transition temperature, indicative of the cross-linked architecture (Figure S6).

The rates of urethane exchange reactions at elevated temperatures within these networks were inferred from stress relaxation experiments. Samples were equilibrated at a given temperature, a rapid 5% strain was applied, and stress relaxation was monitored; this process was repeated multiple times for a given sample to characterize the reproducibility of the stress relaxation kinetics. All samples relaxed stress very rapidly and reproducibly with characteristic relaxation times ( $\tau^*$ , the time required to relax to  $1/e$  of the initial stress) less than 40 s at  $140\text{ }^\circ\text{C}$  (Figure 3B, Figure S11-S13). While FT-IR analysis of samples containing Bi and Sn show no change afterwards, consistent with degenerate urethane exchange reactions as the cause of stress relaxation, the samples containing Fe showed marked changes in functional groups present (Figure S9), suggesting that side reactions occur under the experimental conditions. Fe(III) catalysts have been reported to cause exchange or dehydration reactions of ethers,<sup>38</sup> so we speculate that these side reactions contribute most strongly to the decomposition. Samples containing  $\text{Bi}(\text{neo})_3$  relaxed

most rapidly at all temperatures measured, but the measured relaxation rates of polymers containing each catalyst were similar. This observation differs from the rates observed in model compounds, in which  $\text{Bi}(\text{neo})_3$  was the least efficient of the three catalysts. This discrepancy, although beneficial in the context of PU reprocessing, may reflect a different ligand environment around the metal center in the polymer experiments. Further experiments are needed to explore this hypothesis. We were surprised to find that all three samples relax stress with similar Arrhenius activation energies (Figure 3C). This behavior differs from that of polyester-based dynamic covalent networks that relax due to associative transesterification reactions.<sup>39</sup> This difference may be associated with a dissociative exchange mechanism, in which the catalysts are rapidly mediating the equilibrium between bound urethane cross-links and free isocyanates and alcohols. If this equilibration is sufficiently rapid, the resulting stress relaxation rate would be governed by the equilibrium constant of the urethane dissociation process at a given temperature, which would not be affected by the catalyst identity.



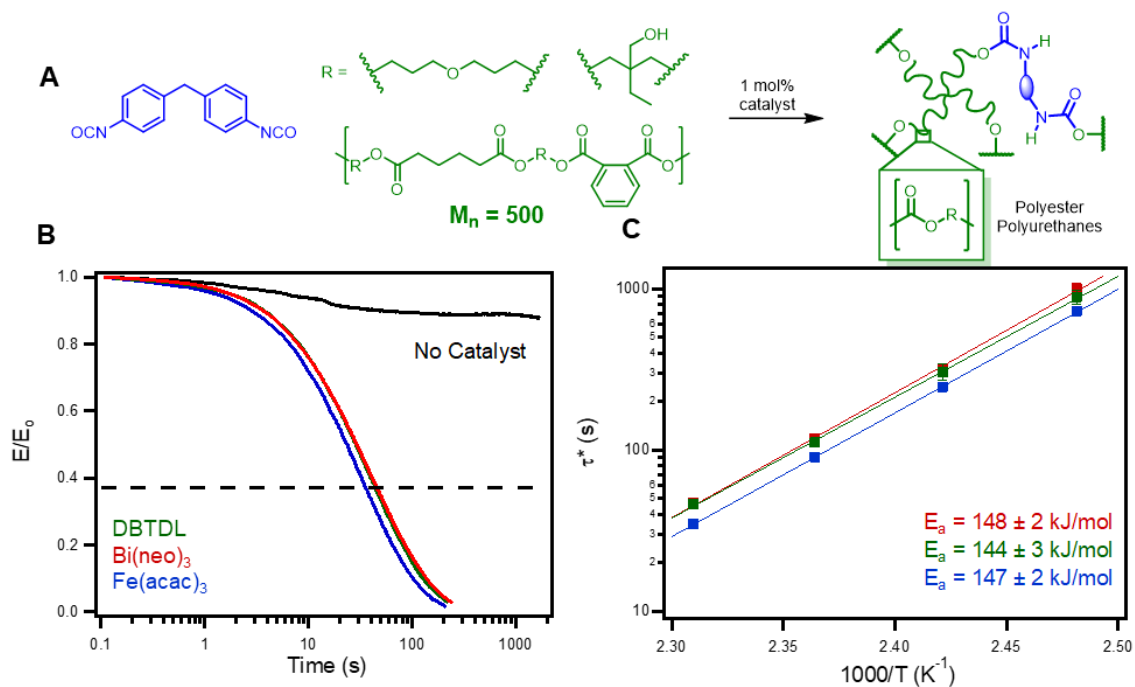
**Figure 3.** **A.** Synthesis of polyether PUs. **B.** Stress relaxation analysis of polyether PUs containing 1 mol% Bi(neo)<sub>3</sub> (red), DBTDL (green), and Fe(acac)<sub>3</sub> (blue) performed at 140 °C. **C.** Arrhenius plots of characteristic relaxation time of polyether PUs, the line for samples containing Fe(acac)<sub>3</sub> is dashed since decomposition occurs during the relaxation process.

To determine whether this unexpected behavior was general for other PU classes, we synthesized cross-linked polyester PUs by reacting MDI with a commercially available polyester oligomer polyol ( $M_n \approx 500$  g/mol, -OH functionality  $\approx 2.5$ ) in the presence of 1 mol% of catalyst (Figure 4A). A control sample was synthesized in the absence of catalyst to determine each catalyst's role on the properties of the material. All polymers show complete disappearance of the -NCO functionality by FT-IR spectroscopy (Figure S3) and swell in DCM to give relatively high gel fractions ( $>0.9$ ), suggesting a cross-linked architecture. DSC indicates moderate glass transition temperatures of 45-50 °C (Figure S7), and TGA shows thermal stability to temperatures greater than 250 °C, even in the presence of catalyst (Figure S8). DMTA shows a rubbery plateau modulus consistent with the expected covalently cross-linked architecture, and all catalysts give similar values of the rubbery storage modulus (3.18-5.39 MPa) and  $\tan \delta$  curves, suggesting that the different catalysts do not significantly affect the polymer curing reaction.

Elevated temperature stress relaxation experiments were again used to evaluate the dynamic nature of the polymers. In all polymers containing catalyst, rapid, reproducible stress relaxation is observed, with characteristic relaxation times of 35-47 s at 160 °C (Figure 4B). FT-IR analysis of polymers containing each of the three catalysts before and after stress relaxation suggests no chemical changes (Figure S10). Similar rates and Arrhenius activation energies of stress relaxation are again observed with all catalysts (Figure 4C, Figure S14-S16). These activation energies agree quantitatively with those obtained for polyether PU stress relaxation; this provides further support for our hypothesis that the rapid equilibration of urethanes and isocyanates/alcohols govern the kinetics of stress relaxation. Samples in which the aromatic



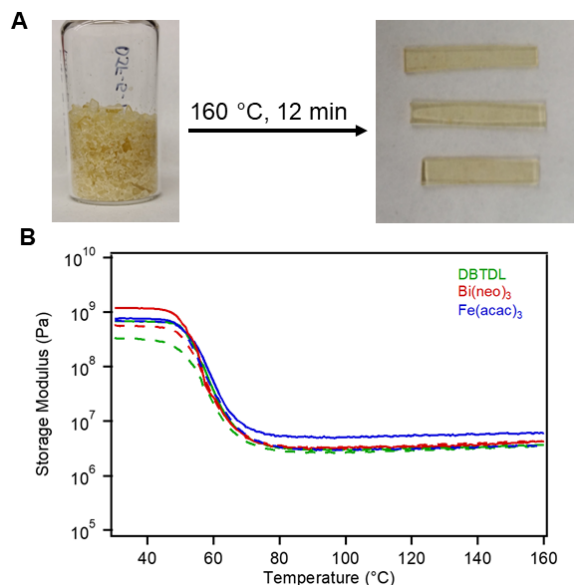
diisocyanate was replaced with an aliphatic isocyanate showed slower relaxation rates and similar activation energies of stress relaxation, which is consistent with this hypothesis and the higher thermal stability of aliphatic-isocyanate-derived polyurethanes (Figure S17-19). A control sample synthesized in the absence of catalyst shows little to no stress relaxation at the same temperature (Figure 4B), indicating that the presence of catalyst is essential for rapid stress relaxation, which is consistent with the model compound studies and provides support for urethane exchange as the mechanism for relaxation in these materials.



**Figure 4.** **A.** Synthesis of polyester PUs. **B.** Stress relaxation analysis of polyether PUs containing  $\text{Bi}(\text{neo})_3$  (red), DBTDL (green),  $\text{Fe}(\text{acac})_3$  (blue), or no catalyst (black) performed at 160 °C. **C.** Arrhenius plots of characteristic relaxation time of polyester PUs.

The fast and reproducible relaxation dynamics of these materials at elevated temperatures suggest that direct reprocessing of these cross-linked materials should be possible. Polyester PU samples were ground to small pieces, and then reprocessed via compression molding at elevated temperature. In all cases, compression molding samples for 12 minutes at 160 °C gave

homogeneous samples with similar properties to the as-synthesized materials (Figure 5A, Figure S22). DMTA of the reprocessed polymers indicated similar glass transition temperatures and plateau moduli of the reprocessed Bi and Sn samples and moderate cross-link density recovery of Fe samples (Sn 83% recovery, Bi 100% recovery, Fe 56% recovery, Figure 5B). Despite near quantitative recovery of cross-link density of Bi and Sn, tensile testing of pristine samples and samples after one or two reprocessing cycles indicated moderate recovery of tensile strengths for all catalysts (39-67%). In contrast, tensile testing conducted at elevated temperatures (90 °C) showed quantitative tensile strength recovery for Sn-based catalysts, suggesting that the loss in tensile strength is possibly related to the glassy state properties of the polymers. Moderate tensile strength recovery was observed at elevated temperatures for reprocessed Fe and Bi-containing samples, and further investigation is ongoing to fully understand the relationship between the recovery of cross-link density and mechanical properties, and to develop more efficient methods of reprocessing these materials. Attempted reprocessing of a catalyst-free sample showed no evidence of reprocessing (Figure S29), further supporting the requirement of catalyst to observe dynamic behavior under these conditions in polyurethanes.



**Figure 5.** **A.** Photographs of ground and reprocessed polyester PUs containing 1 mol% Bi(neo)<sub>3</sub>. **B.** DMTA of as-synthesized PUs (solid) containing DBTDL (green), Bi(neo)<sub>3</sub> (red), and Fe(acac)<sub>3</sub> (blue), and samples after reprocessing for 12 min at 160 °C (dashed).

## Conclusions

We have demonstrated that several Lewis acids catalyze the exchange of urethane bonds under relatively mild conditions. Incorporation of these catalysts into cross-linked PUs gives materials that relax stress extremely rapidly compared to many dynamic covalent networks. This approach is compatible with both polyether and polyester-based PUs, and is therefore likely to be directly applicable to commercially produced cross-linked PUs. Surprisingly, polymers with two different backbones synthesized in the presence of three different catalysts display very rapid rates of stress relaxation and similar activation energies of relaxation, which may arise from the relaxation being governed by the urethane dissociation equilibrium. Finally, incorporating these catalysts enables cross-linked PUs to be reprocessed rapidly. Further optimization of this process as well as applying more industrially-relevant reprocessing techniques may enable reprocessing of the vast amounts of PU waste (approximately 700,000 tons in Europe in 2017)<sup>40</sup> that is produced annually. Furthermore, we expect that this approach will continue to be refined and applied to

other dynamic covalent networks given the wide scope of available Lewis acids and urethane monomers that might be employed.

## **ASSOCIATED CONTENT**

**Supporting Information.** The Supporting Information is available free of charge on the ChemRxiv website by searching for this preprint.

Experimental procedures and characterization data (PDF)

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### **Notes**

Northwestern University has filed patent applications related the findings described in this manuscript.

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## TOC IMAGE

