

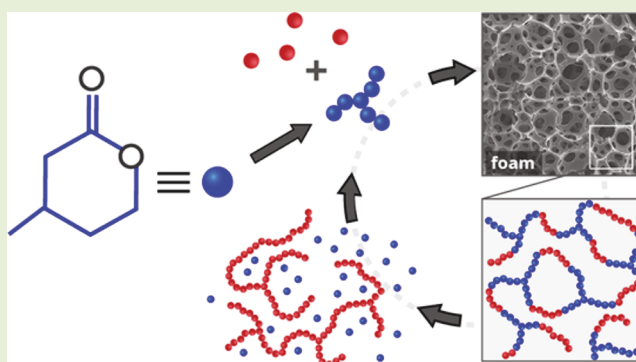
Chemically Recyclable Biobased Polyurethanes

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S Supporting Information

ABSTRACT: Polyurethanes (PUs), in the form of coatings, adhesives, sealants, elastomers, and foams, play a vital role in the consumer goods, automotive, and construction industries. However, the inevitable disposal of nondegradable postconsumer polyurethane products constitutes a massive waste management problem that has yet to be solved. We address this challenge through the synthesis of biobased and chemically recyclable polyurethanes. Our approach employs renewable and degradable hydroxy telechelic poly(β -methyl- δ -valerolactone) as a replacement for petroleum-derived polyols in the synthesis of both thermoplastic polyurethanes and flexible foams. These materials rival petroleum-derived PUs in performance and can also be easily recycled to recover β -methyl- δ -valerolactone monomer in high purity and high yield. This recycling strategy bypasses many of the technical challenges that currently preclude the practical chemical recycling of PUs.



Millions of tons of polyurethanes (PUs) are produced annually for use in widespread applications.¹ The incredible commercial success of these materials can be traced to their low cost and high versatility. The same basic reaction, the condensation of polyols and multifunctional isocyanates, can be optimized for applications ranging from footwear to soft and flexible foams for cushioning, to hard and rigid materials for construction. Because most commercial PUs are petroleum-derived and resistant to degradation, there are significant environmental challenges associated with their large-scale production and disposal.² In recent years, changing consumer preferences and government policies have increased the demand for biobased polymers, including PUs.^{3,4} Low cost and abundant natural oil polyols (NOPs) have attracted considerable attention as sustainable feedstocks to meet this demand.^{5,6} However, limitations inherent to most NOPs (i.e., lower end group reactivity and marginal control over functionality and total molar mass) have limited their utility as building blocks for PUs.^{7,8} Additionally, since most renewable PUs derived from NOPs are resistant to degradation, they present similar disposal challenges as do their petroleum-derived counterparts.

The cross-linked chemical structure of thermoset polymers (e.g., PU foams) prevents solution or melt reprocessing. Although some foam is recycled to make carpet rebond, the majority of PU thermosets are incinerated or landfilled.⁹ Chemical recycling of PUs has previously been described; yet, it is not widely practiced.^{9,10} The two most successful methods of chemical recycling, glycolysis and hydrolysis, employ urethane exchange reactions to recover polyols suitable for the

manufacture of new PUs.^{11,12} The efficacy of these methods is somewhat limited as both naturally produce a mixture of recycled polyols if the waste foams are chemically heterogeneous (prepared from different starting polyols).^{9,10} Not surprisingly, one of the major disadvantages of these chemical recycling methods is the limited purity of the recovered polyol.⁹

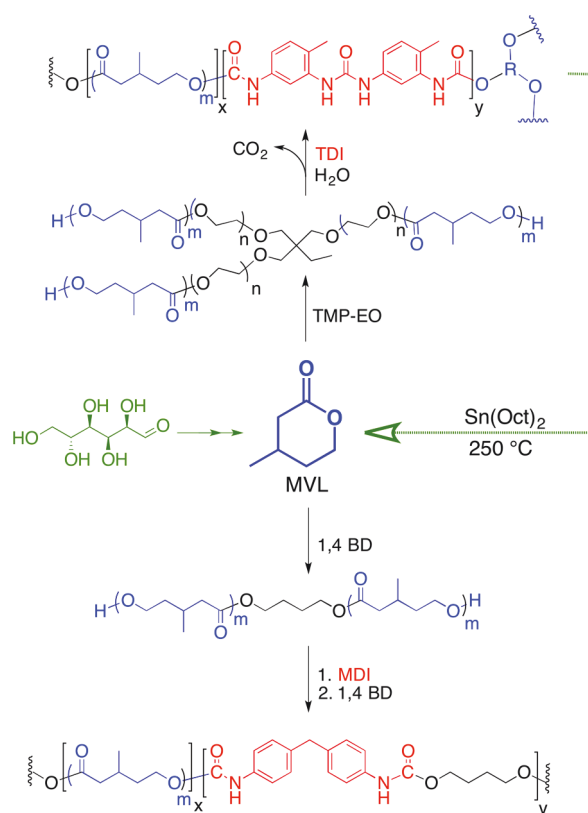
We and our collaborators recently reported an efficient semisynthetic method to produce β -methyl- δ -valerolactone (MVL), a lactone that can be polymerized in the bulk at room temperature to obtain a rubbery polyester poly(β -methyl- δ -valerolactone) (PMVL).¹³ Because PMVL is easily synthesized from sugar and potentially low-cost (MVL has an estimated cost of approximately \$2/kg), it is an appealing feedstock for the manufacture of sustainable materials. In this work, summarized in Scheme 1, we employ PMVL polyols for the synthesis of both thermoplastic polyurethanes (TPUs) and flexible foams. More importantly, we demonstrate cross-linked PMVL PUs can be chemically recycled using a simple process whereby MVL monomer is recovered in excellent yield and high purity.

The PMVL PU foam degrades by reversion of the polyurethane bond. The resulting PMVL-OH quickly depolymerizes to yield MVL monomer and the isocyanate reacts with urethane or urea linkages in the remaining foam to form allophanate or biuret linkages, respectively.

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Scheme 1. Synthesis of TPUs and Chemically Recyclable Foams from MVL^a


^aIn this work, $n \approx 1$ and $m = N_n/f$, where N_n and f are the degree of polymerization and functionality of the PMVL polyol, respectively. Both PUs can be approximated as segmented block polymers, where x and y are proportional to the respective weight fractions of the soft and hard segments.

We synthesized a small library of PMVL polyols, detailed in Tables S1 and S2, via acid-catalyzed ring-opening transesterification polymerization.¹³ Trimethylolpropane ethoxylate (TMP-EO) was used to prepare a trifunctional polyol for use in foam formulations and various diol initiators (e.g., 1,4-butanediol, 1,3-propanediol, or 1,4-benzene dimethanol) were employed to synthesize linear, difunctional polyols for the synthesis of TPUs. As demonstrated in Figures S1 and S2 of the SI, we used matrix-assisted laser desorption/ionization, to confirm molar mass control and to verify hydroxyl end group functionality. Both PMVL TPUs and foams were prepared using standard synthetic methods for the manufacture of commercial PUs.¹⁴ Specifically, TPUs were synthesized from PMVL diols in a one-pot, two-step sequential procedure using 4,4'-methylene diphenyl diisocyanate (MDI) and a diol chain extender (e.g., 1,4-butanediol). Flexible foams were prepared from PMVL triol using toluene diisocyanate (TDI) with water as the sole blowing agent. More detailed synthetic procedures, and characterization of the resulting PUs, are provided in the SI (Tables S3–S7).

While both types of PMVL PUs (TPUs and foams) can be idealized as segmented block polymers, the two differ in both architecture and hard segment structure. The TPUs are ostensibly linear with urethane-rich hard segments; however, the foams are branched networks containing polyurea hard segments. Microphase separation of the hard and soft segments results in the formation of nanoscopic heterogeneities.

Hydrogen bonding, both within the hard segments and at the domain interfaces, reinforces these physical cross-links. Whereas the properties of the PMVL TPUs are largely determined by the overall molar mass and hard segment content, the foam properties are also impacted by microscopic cellular structure. Use of PMVL as the majority component enabled the synthesis of TPUs with high toughness and excellent elasticity, similar to commercial TPUs.¹⁴ As exemplified in Figure 1a,b, a TPU

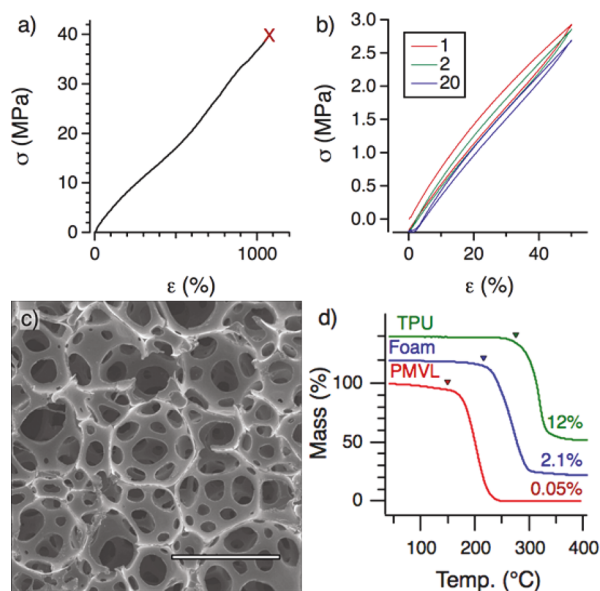


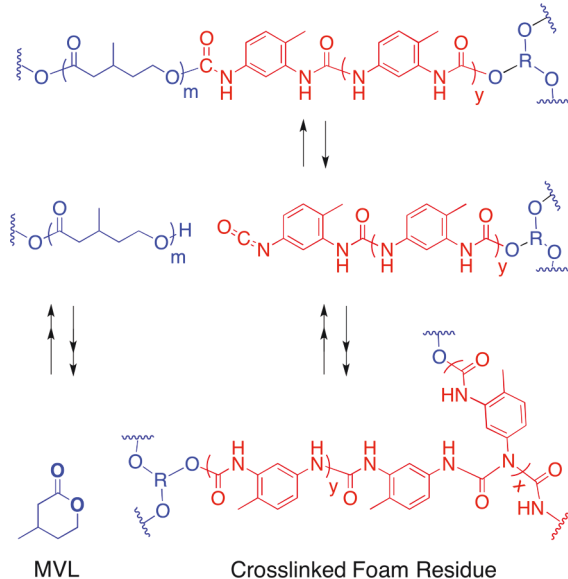
Figure 1. (a) Representative uniaxial extension data for a PMVL TPU. Experiments were conducted with a constant crosshead velocity of 60 mm min⁻¹. (b) Representative cyclic tensile experiment (1, 2, and 20 cycles, 60 mm min⁻¹, without rest between cycles). (c) SEM of a representative PMVL foam, the scale bar is 1 mm. (d) TGA of representative PMVL materials (under nitrogen, at 10 °C min⁻¹). The data for the PUs have been shifted up (20% on y-axis) for clarity. The markers indicate the temperature at 5% mass loss, and the mass remaining at 400 °C is also indicated for each.

composed of 60 wt % PMVL exhibited high tensile strength (~40 MPa) and strain at break (~1100%) as well as nearly complete recovery of applied strain over multiple cycles of extension and relaxation (characterized by only a few percent residual strain at the end of the test). Importantly, as shown in Figure 1c, PMVL foam formulations could be tuned to access fully open-cell foams and were comparable to soft commercial foams in both mechanical performance and density (for detailed results, see Table S6).

Using thermogravimetric analysis (TGA), shown in Figure 1d, we discovered that soft foams and TPUs both exhibit significantly higher degradation temperature values than PMVL homopolymer. Notably, MVL is known to possess a relatively low ceiling temperature (~220 °C at 9.1 M).¹³ Thermal degradation of PMVL polyol therefore most likely occurs by depolymerization.¹⁵ This improved stability is likely due to the absence of reactive hydroxyl end groups.¹⁶ Blocking the end group of the polymer with a urethane linkage, however, cannot fully prevent thermal degradation. In situ hydrolysis of the PMVL backbone (by water adsorbed or produced by degradation) can lead to the formation of new alcohol end groups.^{16,17} Additionally, in a pyrolytic environment urethane linkages can revert to isocyanates and alcohols (typically above 180 °C).^{18,19}

Therefore, we believe that urethane dissociation, followed by depolymerization of the resulting hydroxy-terminated PMVL, is the major degradation pathway for PMVL PUs under pyrolysis conditions. Consistent with this interpretation, when no catalyst is present (removed from TPUs by precipitation in methanol and from foams by extraction with ethyl acetate), both types of PU are stable at temperatures below the expected reversion temperature of the urethane bond (Figures S23–S27). Although the PMVL foams are chemically cross-linked and cannot be mechanically reprocessed at elevated temperature, this mechanism of pyrolytic degradation provides a convenient method for chemical recycling (summarized in Scheme 2).

Scheme 2. Recycling PMVL Foams to Recover MVL^a



^aThe PMVL PU foam degrades by reversion of the polyurethane bond. The resulting PMVL–OH quickly depolymerizes to yield MVL monomer and the isocyanate reacts with urethane or urea linkages in the remaining foam to form allophanate or biuret linkages, respectively.

To verify this, we simply heated bulk, solid foam samples in a short path distillation apparatus to 200–250 °C at ~100 mTorr. We believe that atmospheric pressure may also be viable due to the moderate boiling point of MVL (~215 °C). During this experiment, volatile products were trapped in a receiving flask. Relative to foams containing no residual catalyst, we found the rate of depolymerization was faster when Sn(Oct)₂ was present (either added to the initial foam formulation or immediately prior to recycling). As described in Tables S8 and S9, the MVL yield was dependent on time, temperature, foam composition, and catalyst concentration. In all cases, the monomer was isolated in high purity (≥95% by ¹H NMR spectroscopy); under optimized conditions we were able to recover up to 97% of the MVL.

We also measured the recovery of MVL from PMVL foam over time (Figure 2a). Most of the MVL monomer (85% of theoretical yield) was recovered within the first 2 h of distillation. Longer reaction times resulted in slightly higher yields (total of 97% of theoretical yield after 10 h). In a parallel experiment, samples of degraded foam and aliquots of recovered monomer were removed after 2, 5, and 10 h. As

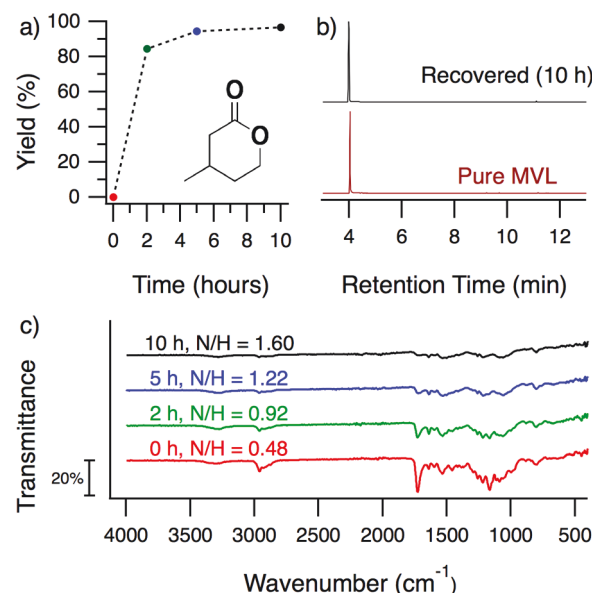


Figure 2. (a) Monomer recovery over time for recycling experiment at 225 °C, 100 mTorr. (b) Gas chromatographs of pure and recycled (cumulative after 10 h) MVL; this sample had a purity of 99.6% by GC. (c) FTIR spectra of foam residue removed at indicated times. The N/H mass ratio of the insoluble foam residue, determined by elemental analysis, is also indicated for each time point.

indicated in Table S9, there was negligible change in MVL purity over time. In fact, as shown in Figure 2b, the MVL recovered after 10 h was over 99% pure by GC. The samples of foam residue were insoluble; however, elemental analysis revealed a monotonic increase in nitrogen content consistent with removal of MVL. Fourier transform infrared (FTIR) spectra of samples of foam residue, shown in Figure 2c, displayed a concomitant decrease in the intensity of stretch corresponding to the PMVL ester (C=O, 1729 cm⁻¹) over time, yet the urea signal (C=O, 1640 cm⁻¹) was preserved. Together these results are consistent with removal of MVL and retention of cross-linked biuret and allophanate products.^{20,21}

Because MVL is separated from both remaining foam and cross-linked degradation products by distillation, it is also possible to recycle PMVL foams that have been mixed with other types of PU foam. As described in the SI, a commercial PU foam added to a PMVL recycling experiment did not significantly diminish the yield or purity of MVL recovered after 10 h. We note that this is a significant improvement over other methods used for the chemical recycling of PU foams. To further explore the potential of this recycling approach, we used MVL recovered from the depolymerization of PMVL foam to synthesize new PMVL polyols. As demonstrated in Figures S3 and S4, the resulting polyol was indistinguishable from an analogous sample prepared from virgin monomer using the same synthetic method.

We have demonstrated that MVL is a versatile and renewable building block for the synthesis of TPUs and PU foams. In both cases, the resulting materials were tuned to access properties that compared favorably to commercial analogs. The PUs investigated in this work are stable at typical use temperatures but can be simply and easily chemically recycled by exploiting the reversibility of the urethane bond and the thermodynamic tendency of PMVL to depolymerize. Unlike glycolysis and hydrolysis, this thermochemical recycling method does not require the addition of any solvents, alcohol, or water.

Because MVL monomer is regenerated, it can be easily removed from both intact foam and degradation products by distillation. This method bypasses many of the technical challenges that currently preclude practical chemical recycling of PUs (e.g., low purity of recovered polyol). We note that MVL is not unique in its moderate ceiling temperature.^{13,15,22,23} We therefore believe that this strategy could be extended to other polyols to create a wide range of recyclable materials. We posit that the PUs described in this work are the harbingers of a new class of sustainable, high-performance polymers designed to fit a circular economy.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00193.

Details of synthesis and characterization (PDF).

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Notes

The authors declare no competing financial interest.

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