Alkyl Substituted Polycaprolactone Poly(Urethane-Urea)s as Mechanically-Competitive and Chemically-Recyclable Materials

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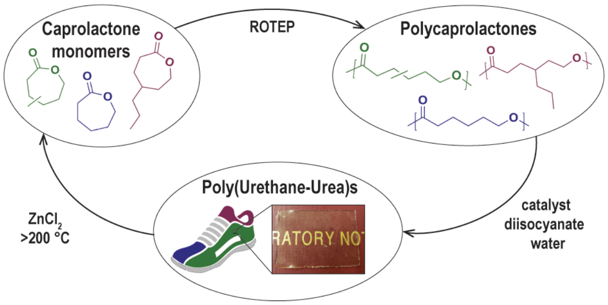
TOC graphic



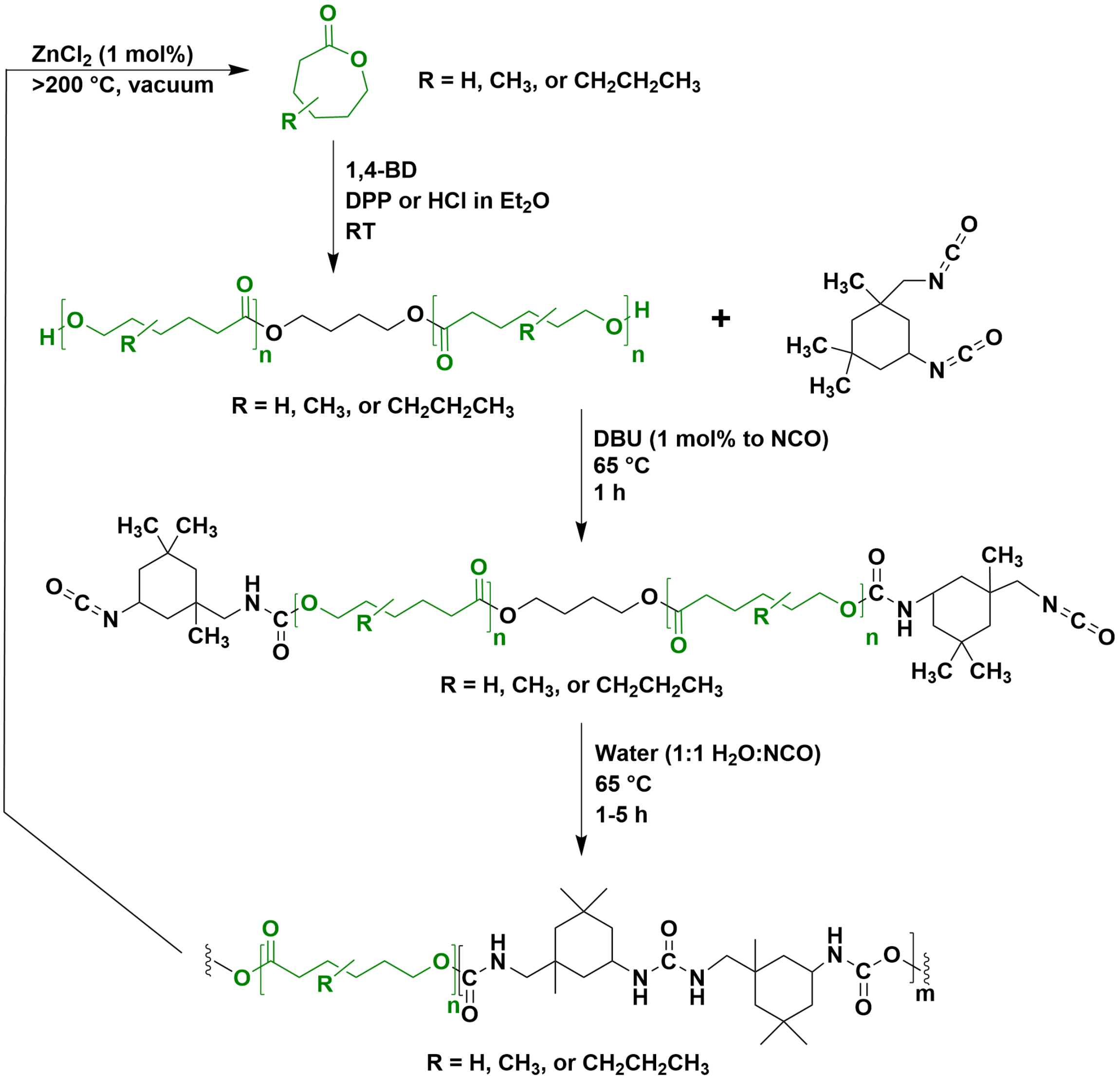
Abstract

We report the mechanical performance and chemical recycling advantages of implementing alkyl-substituted poly(ε-caprolactones) (PCLs) as soft segments in thermoplastic poly(urethane-urea) (TPUU) materials. Poly(4-methylcaprolactone) (P4MCL) and poly(4-propylcaprolactone) (P4PrCL) were prepared, reacted with isophorone diisocyanate, and chain-extended with water to form TPUUs. The resulting materials' tensile properties were similar or superior to a commercially available polyester thermoplastic poly(urethane) and had superior elastic recovery properties compared to a PCL analogue due to the non-crystalline nature of P4MCL and P4PrCL. Additionally, monomers were recovered from the TPUU materials in high yields via ring-closing depolymerization using a reactive distillation approach at elevated temperature and reduced pressure (240–260 °C, 25–140 mTorr) with zinc chloride ($ZnCl_2$) as the catalyst. The thermodynamics of polymerization were estimated using Van't Hoff analyses for 4MCL and 4PrCL; these results indicated that the propyl group in 4PrCL results in a lower practical ceiling temperature (T_c) for P4PrCL.

Polyurethanes (PUs) and poly(urethane-ureas) (PUUs) accounted for greater than 25 million metric tons of plastic produced globally in 2022, with an expected 10% growth rate over the next five years.[1] PU/PUUs are segmented copolymers with hard segments (HS) composed of urethane/urea linkages and soft segments (SS) typically consisting of amorphous polyesters or polyethers that, depending on specific chemical identify, give versatile materials with wide ranges of properties. PU/PUUs are used in a numerous applications including construction materials, furniture, automotive, electronics, packaging, footwear, and biomedical devices.[2-5] However, these materials have several sustainability drawbacks. PU/PUUs are typically synthesized from petrochemical-derived starting materials and ~75% of postconsumer PU/PUU waste ends up in landfills every year; for flexible foams and elastomers, collected waste actually exceeds production volume indicating opportunities for improved recycling methods.[6] While advancements have been made for mechanical recycling of PU/PUUs, primarily revolving around the use of compatibilizers, material properties can diminish with repeated processing cycles.[7-10] Consequently, alternative recycling methods, such as introducing catalysts that facilitate bond exchange to reprocess foams[11, 12] or using glycolysis to recover polyols,[3, 6] have been studied to enable greater circularity in the PU/PUU market. The use of bio-derived isocyanates and polyols has also been studied extensively to reduce dependence on petrochemicals.[13-20] Nonetheless, there remains a need to develop bio-derived PU/PUU materials with commercially competitive properties that can be effectively recycled.

Polyester polyols, particularly poly(ε-caprolactone) (PCL) polyols, are the fastest growing market segment for thermoplastic PU/PUUs (TPU/TPUUs).[21] The use of bio-derived alkyl-substituted PCL polyols presents an opportunity to improve the sustainability footprint of this class of TPU/TPUUs. We have previously reported the use of 4-methylcaprolactone (4MCL), which can be derived from cresols in, for example, lignin oils, to prepare mechanically robust block polymer thermoplastic elastomers.[22-25] Considering that bio-based feedstocks may include a variety of structural isomers, statistical copolymers of 3MCL, 4MCL, and 5MCL were also previously prepared; this poly(methylcaprolactone) terpolymer (PMCL) was shown to have similar properties to poly(4-methylcaprolactone) (P4MCL) and may also be useful in elastomer formulations from heterogeneous feedstocks.[22] The reductive catalytic fractionation (RCF) of lignin biomass most commonly yields guaiacol and syringol with a propyl group at the para position of the aromatic ring[26] that can be converted to 4-propylcaprolactone (4PrCL). The polymerization of 4PrCL by ring-opening transesterification polymerization (ROTEP) has not been previously reported. Herein, we report the synthesis and characterization of P4MCL, PMCL, and P4PrCL-based TPUUs with outstanding tensile properties and elastic hysteresis performance and compare them to PCL-based materials. Additionally, we demonstrate chemical recycling to monomer and repolymerization to prepare new TPUUs thus offering a potential pathway towards greater circularity of TPUUs without sacrificing their utility.

ROTEP kinetics of P4MCL and PMCL with various catalysts and material properties such as entanglement molar mass (M_e, P4MCL M_e = 2.9 kg/mol, PMCL M_e = 3.7 kg/mol) have been previously determined.[22, 23] Likewise, 4PrCL was successfully polymerized using a range of catalysts which are known to catalyze ROTEP of 7-membered lactones (**Table S1** and **Figures S1-S6**). The M_e for P4PrCL (M_e = 5.1 kg/mol) was expectedly higher compared to P4MCL's M_e due to the presence of the larger pendant propyl group (**Figures S7–S8**).[27] For TPUU syntheses, a two-step prepolymer method was used (**Scheme 1**). First, P4MCL, PMCL, P4PrCL, and PCL telechelic diols with a target number average molar mass (M_n) of 1 or 2 kg/mol were synthesized by ROTEP catalyzed by either diphenyl phosphate (DPP),[22] or hydrochloric acid in ether (HCl in Et_2O) to afford solvent-free purification (**Table S2**, **Figures S9-S24**). Then, TPUUs were prepared using excess isophorone diisocyanate (IPDI), water as the chain extender, and 1,8-diazobicyclo(5.4.0)-undec-7-ene (DBU) as the catalyst, which could conveniently be removed by devolatilization at the end of the polymerization. In addition to being solvent-free, this procedure was also shown to be successful in the presence of excess water (**Table S3**), demonstrating a potential advantage over more traditional TPUs which require a dry environment.[28, 29] To evaluate the effect of HS content, isocyanate to polyol hydroxyl ([NCO]:[OH]) molar ratios of 2:1 and 4:1 were prepared. ATR-FTIR was used to monitor the TPUU reaction based on the disappearance of the isocyanate peak at 2250 cm^{-1} (**Figure S25**); final TPUU products showed a strong carbonyl stretch signal at ~1730 cm^{-1} as well as a second less intense one at ~1630 cm^{-1}, indicating the presence of bidentate hydrogen bonded carbonyl groups (**Table S5**, **Figures S26-S29**).[30-32] Each TPUU was melt-pressed (180 °C, ~24 MPa, 10 min) and the resultant films were characterized by size-exclusion chromatography (SEC), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical and thermal analysis (DMTA), small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS) and uniaxial tensile testing (**Table S6**, **Figures S30-S67**).



Scheme 1. Synthetic scheme for the synthesis of P4MCL, PMCL, P4PrCL, and PCL TPUUs using IPDI as the isocyanate, water as a chain extender, and DBU as the catalyst.

TPUU films exhibited a range of robust elastomeric tensile properties (elastic moduli: $E \geq 2$ MPa, stresses at break: $\sigma_B \geq 6$ MPa, and strains at break: $\varepsilon_B > 600\%$) as summarized in **Figure 1** and **Table 1**. Compositions using 1 kg/mol polyols and [NCO]:[OH] = 4:1 resulted in a HS content of 44–46 wt% leading to plastic deformation and $\varepsilon_B < 200\%$ (**Figure S67**). In general, the PMCL-based TPUUs did not significantly differ from the P4MCL TPUUs indicating that tensile properties

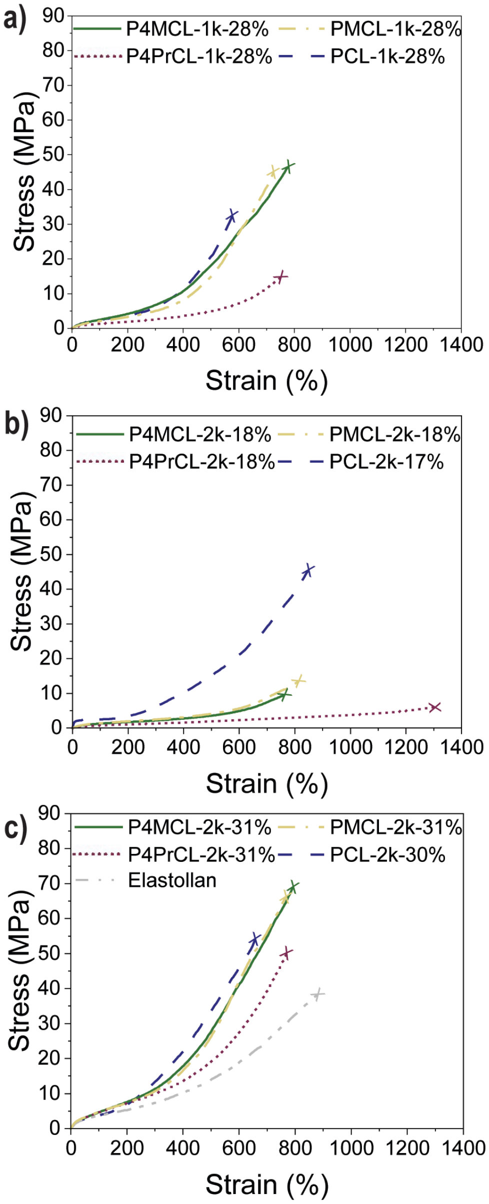


Figure 1. Representative stress-strain data obtained from uniaxial tensile testing of P4MCL, PMCL, P4PrCL, and PCL TPUU specimens. Tensile testing was performed at a strain rate of 50 mm/min. TPUUs were prepared with polyol M_n = 1 kg/mol or (a) 2 kg/mol and (b-c) [NCO]:[OH] was varied from (a-b) 2:1 to (c) 4:1 resulting in different HS wt.% content. Comparisons were also made to a commercially available polyester TPU, Elastollan®.

Table 1. Summary of the uniaxial tensile testing results for P4MCL, PMCL, P4PrCL and PCL TPUUs and Elastollan® TPU melt-pressed films. (N ≥5, strain rate =50 mm/min)

Polyol-M_n-HS%	***E*** **(MPa)**	**σ_B (MPa)**	**ε_B (%)**
P4MCL-1k-28%	6 ±0.4	48 ±9	760 ±65
PMCL-1k-28%	5 ±0.4	45 ±4	730 ±30
P4PrCL-1k-28%	4 ±0.3	14 ±2	733 ±34
PCL-1k-28%	6 ±1	39 ±5	624 ±67
P4MCL-2k-18%	3 ±0.2	9 ±2	741 ±50
PMCL-2k-18%	3 ±0.3	12 ±2	808 ±46
P4PrCL-2k-18%	2 ±0.2	6 ±0.5	1252 ±70
PCL-2k-17%	28 ±5	47 ±4	859 ±49
P4MCL-2k-31%	15 ±1	70 ±5	809 ±37
PMCL-2k-31%	15 ±1	72 ±7	821 ±84
P4PrCL-2k-31%	14 ±1	51 ±5	752 ±18
PCL-2k-30%	14 ±1	60 ±5	667 ±40
Elastollan	10 ±1	38 ±3	924 ±77

were not impacted by using a mixed MCL monomer feedstock to prepare the telechelic diol. The P4PrCL TPUUs demonstrated lower *E* and σ_B values as well as lower glass transition temperatures (T_g, determined by DMTA based on the maximum storage modulus) and flow temperature (T_{flow}, determined by DMTA from the onset of the precipitous drop in storage modulus after the rubbery plateau) compared to the P4MCL/PMCL TPUUs. When HS content was increased at constant polyol M_n (polyol-2k-18% HS versus polyol-2k-31%HS **Figure 1 b-c**), E and σ_B values increased while ε_B decreased (PCL and P4PrCL) or remained constant (P4MCL and PMCL). When HS content was comparable and the polyol M_n was increased (polyol-1k-28% HS versus polyol-2k-31% HS, **Figure 1a and c**), E and σ_B values increased while ε_B did not change, indicating some advantages to the use of a higher M_n polyol SS. Most notably, the polyol-2k-31%HS compositions showed higher stresses at break with slightly lower strains at break in comparison to a commercially available polyester-based TPU, Elastollan® C60A10WH (**Figure 1c**), which may be due in part to improved HS hydrogen bonding from the presence of urea linkages (**Figures S74-S77**).[33] The Elastollan® TPU is known to contain plasticizing agents to improve tensile properties,[34] thus considering that the TPUUs prepared herein are additive-free, their neat tensile properties are competitive with commerical materials.

The PCL-2k-17% TPUU composition also showed tensile properties similar to the Elastollan®; however, exhibited plastic deformation at low strain in hysteresis testing, essentially demonstrating a lack of elasticity with >30% tensile set after 1 cycle (**Figure S71**). This lack of elasticity compared to the other TPUUs studied can be attributed to the semi-crystallinity of the PCL-2k-17% TPUU as evidenced by a dramatic decrease in the loss and storage modulus at 37 °C by DMTA analysis (**Figure S58**). The PCL-2k-30% TPUU did not show any evidence of semi-crystallinity based on DMTA (**Figure S59**), despite the use of the same semi-crystalline polyol for the SS, likely due to restricted SS mobility as a result of the increased HS content.[35] The presence or lack of PCL crystallinity in these two compositions was also corroborated by their SAXS and WAXS traces (**Figure S63** and **S66**).

The PCL-2k-30% composition demonstrated improved hysteresis performance with 45% energy loss after the 1st cycle that was reduced to ~30% in subsequent cycles and tensile set values <14% (**Figure 2a**). The P4MCL, PMCL and P4PrCL 2k-31% TPUUs showed similar hysteresis characteristics with the greatest elastic recovery performance exhibited by the P4MCL-2k-31% composition (1st cycle energy loss <40%, <27% for subsequent cycles, tensile set <11%, **Figure 2a**). The Elastollan® TPU performed similarly after the 1st cycle (~40% energy loss) with slightly improved hysteresis performance in subsequent cycles (≤17% energy loss, **Figure 2b**).

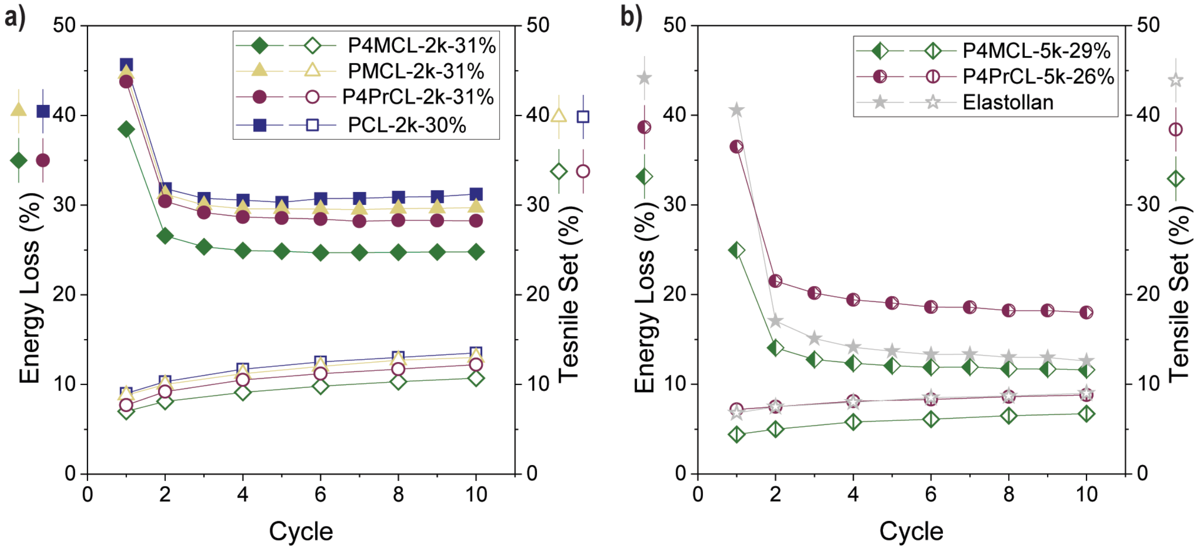


Figure 2. Hysteresis energy loss (%) and tensile set (%) for TPUUs prepared with polyol M_n = 2 kg/mol and HS= 30-31wt.% (a), and TPUUs prepared with polyol M_n = 5 kg/mol and HS = 26-29 wt.% compared to Elastollan® (b). Hysteresis testing was conducted at 50% strain over 10 cycles at a strain rate = 50 mm/min.

Previous reports indicate that hysteresis may be improved by using a SS polyol with a M_n at or above the M_e.[36] We explored this phenomenon by synthesizing 5 kg/mol P4MCL, P4PrCL, and PCL telechelic diols and then preparing TPUUs with HS content = 26–29 wt%. The P4MCL-5k-29% and P4PrCL-5k-26% TPUUs demonstrated overall improved elastic recovery performance with lower hysteresis energy loss after the 1st cycle compared to Elastollan® (**Figure**

2b). For subsequent cycles, the P4MCL-5k-29% TPUU showed hysteresis energy loss (≤14%) and tensile set values (≤7%) on par with Elastollan® (energy loss ≤17% and tensile set ≤9%). The P4PrCL-5k-26% TPUU was shown to have slightly higher values for energy loss (≤21%) in cycles 2-10 but tensile set (≤9%) was comparable to Elastollan.® Increasing the polyol M_n for P4PrCL led to a hysteresis performance improvement, albeit less than the P4MCL analogue potentially due to P4PrCL's higher M_e (P4PrCL M_e = 5.1 kg/mol, P4MCL M_e = 2.9 kg/mol). A PCL-5k-29% TPUU was also prepared but this composition showed the same plastic deformation at low strain that the PCL-2k-17% TPUU exhibited, and similarly showed evidence of PCL semi-crystallinity based on DMTA, SAXS and WAXS (**Figure S60, S63** and **S66**). These results highlight an advantage in implementing a fully amorphous SS like P4MCL or P4PrCL over semi-crystalline PCL SS for improved performance in this class of elastomers.

The TPUU synthetic design herein was guided by the hypothesis that an aliphatic HS (IPDI) would be more susceptible to biodegradation under industrial composting conditions than the more typical aromatic isocyanate derived HS.[37,38] The P4MCL-5k-29% TPUU was tested as a representative sample; however, after 90 days, the P4MCL-5k-29% TPUU did not show any signs of mineralization to CO_2 (**Figure S80-S81**). While the ester bonds in the P4MCL polyol SS were expected to be susceptible to enzymatic hydrolysis,[39] this may have been impeded by the PUU HS content.[40]

As an alternative approach towards end-of-life recycling strategies, pyrolytic ring closing depolymerization (RCD) was considered because this technique was previously shown to be successful with PUs prepared using 6-membered lactones, specifically 3-methyl-δ-valerolactone (3MVL).[17] P4MCL, P4PrCL and PCL TPUU film scraps were collected following tensile testing and were subjected to reactive distillation under vacuum (~250–140 mTorr, ~240–260 °C) using zinc chloride ($ZnCl_2$, ~1 mol% with respect to polyester monomer content) as the catalyst, **Figure S86**, **Table S8**). $ZnCl_2$ was selected after screening various catalysts using TGA and conducting initial reactive distillation trials on P4PrCL-diols whereby the reduced volatility of $ZnCl_2$ compared to $Sn(Oct)_2$ allowed for use of short path distillation resulting in a more efficient process (≤30 min versus ~20 h reaction times respectively, **Figures S82-85** and **Table S7**). All P4MCL,

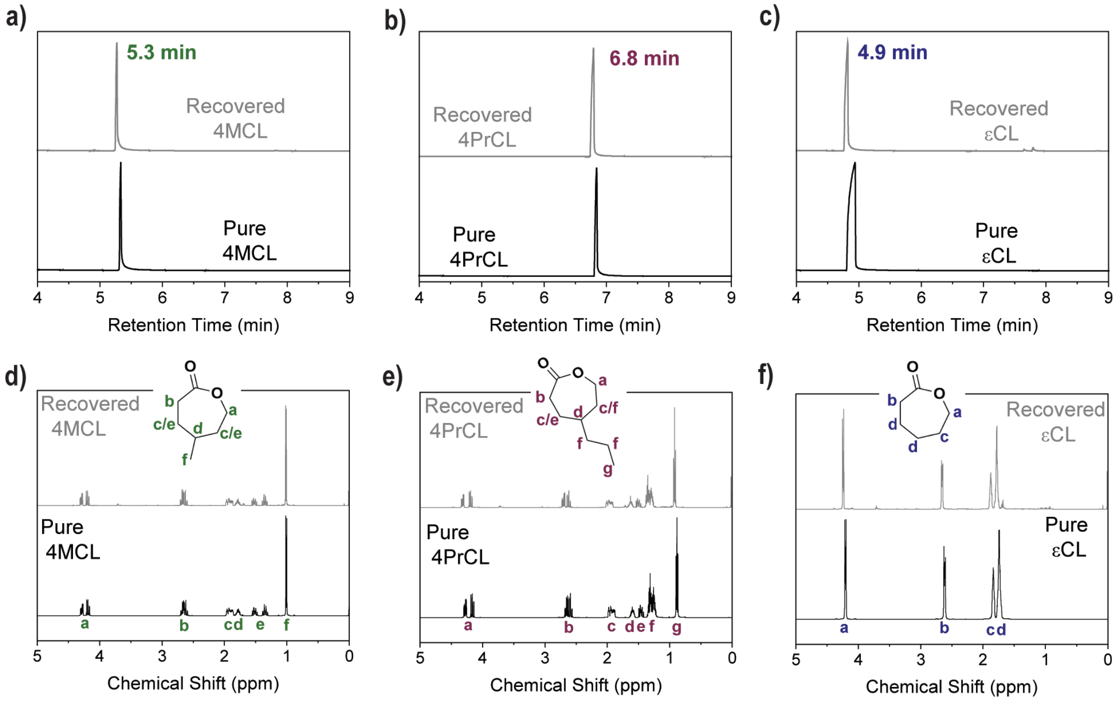
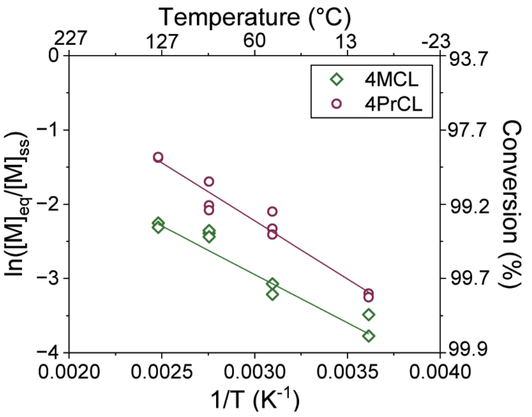


Figure 3. GC traces (a-c) and ^{1}H NMR spectra (d-f) of the recovered and pure monomers. Recovered monomer was obtained via RCD experiments performed using reactive vacuum distillation (240–260 °C, 250-140 mTorr,) with zinc chloride as the catalyst.

P4PrCL, and PCL TPUU film compositions tested (polyol-1k-28%, polyol-2k-18%, and polyol-2k-31%) were successfully chemically recycled back to their respective monomers in good yields (4MCL =71.5 ± 5.3%, 4PrCL = 67.4 ± 8.5%, and εCL = 58.9 ± 6.8%, **Table S8**). Recovered monomer structures were confirmed using GC-MS and ^{1}H NMR compared to pure starting monomers (**Figure 3**, **Figures S87-S89**). The monomers were recovered in high enough purity that they did not require additional purification steps prior to the preparation of new polyols and

TPUUs with target HS ~31% by wt.; these recycled TPUUs showed tensile properties similar to the virgin TPUUs (E = 10-13 MPa, σ_B = 37-54 MPa, ε_B = 693-758%, **Table S9**, **Figures S90-S92**). These results indicate both successful recycling to monomer and successful repolymerization to new TPUUs thereby demonstrating the potential circularity of these materials.

To better understand the RCD of P4MCL and P4PrCL, the thermodynamics of polymerization for 4MCL and 4PrCL were explored. Using heat of combustion data and Hess's law, we estimated the enthalpy of polymerization (ΔH_p°) for liquid (l) 4MCL to amorphous (a) P4MCL ΔH_p° (la) = –13.4 ± 3.6 kJ mol^{-1} (**Table S10**) and for (l) 4PrCL to (a) P4PrCL ΔH_p° (la) = –12.8 ± 7.5 kJ mol^{-1} (**Table S11**). These values were similar to the ΔH_p for unsubstituted PCL (la), which has previously been determined ($\Delta H_p = $ –13.9 kJ mol^{-1}).[43] We then explored the catalyzed ROTEPs of neat 4MCL and 4PrCL at four different temperatures (3.6, 50, 90, and 130 °C); reactions were conducted in triplicate in vacuum sealed ampoules and were allowed to proceed for at least two week such that equilibrium could be achieved. Van't Hoff analysis was performed, to estimate enthalpy (ΔH_p) and entropy of polymerization (ΔS_p), using the equation $ln\left(\frac{[M]_{eq}}{[M]_{SS}}\right) = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R}$ where $[M]_{eq}$ is the monomer equilibrium concentration, based on conversion from ^{1}H NMR, and $[M]_{ss}$ is the monomer standard state concentration based on bulk reaction conditions (see Supporting Information for calculation details). The ceiling temperature (T_c) of the pure monomers was then estimated by $T_c = \frac{\Delta H_p}{\Delta S_p}$ (**Figure 4**). The ΔH_p for P4MCL and P4PrCL was determined to be -10.8 ± 1.1 kJ mol^{-1} and -13.0 ± 1.1 kJ mol^{-1}, respectively, which were both within error of the value determined by combustion analysis.



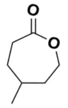
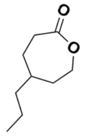
Monomer	ΔH_p (kJ mol^{-1})	ΔS_p (J mol^{-1} K^{-1})	T_c (°C)
	-10.8 ± 1.1	-8.7 ± 3.4	968 ± 380
	-13.0 ± 1.1	-20.5 ± 3.2	361 ± 56

Figure 4. ROTEPs were performed at four temperatures using 4MCL or 4PrCL over the course of ≥2 weeks such that $[M]_{eq}$ could be assessed. Reactions were conducted in the bulk and $[M]_{ss}$ was approximated using monomer density. The Van't Hoff equation was then used to fit the data and to estimate ΔH_p and ΔS_p. Subsequently the Gibbs equation was used to calculate T_c.

Previously studied six-membered valerolactones, demonstrated slightly more enthalpically favored ROTEPs (ΔH_p = -13 to -19 kJ mol^{-1} for methyl valerolactones depending and ΔH_p = -18.5 kJ mol^{-1} for 5-propylvalerolactone)[14] compared to the 7-membered lactones studied herein.

While the absolute entropies of polymerization are less reliable given the assumptions and approximations made above, the ROTEP of 4PrCL was more entropically disfavored (ΔS_p= –20.5 ± 3.2 J mol^{-1} K^{-1}) compared to that of 4MCL (ΔS_p = –8.0 ± 3.4 J mol^{-1} K^{-1}), which is consistent with trends in valerolactones where substituents on the ring decreased the gain in rotational entropy upon ring opening to the polymer. Combined, this leads to an estimated T_c for neat 4PrCL (T_c = 361 ± 56 °C) that is much lower than for neat 4MCL (T_c = 968 ± 380 °C) or for neat εCL (T_c ≈ 1060 °C). Overall, these T_c values are higher than those of six-membered lactones such as 3MVL, which have been shown to have a relatively low T_c (226 °C).[14] Moreover, the higher T_c values of the seven-membered lactones studied herein may impart improved material stability without hindering chemical recyclability, and the implementation of bulkier alkyl substituent groups may offer tunability of T_c values.

In summary, these alkyl substituted PCL TPUUs address the growing environmental need for the development of thermoplastic elastomers that (1) can be bio-derived, (2) have a feasible end-of-life recycling pathway, and (3) maintain desirable utility. We showed that not only were P4MCL and P4PrCL TPUUs competitive with a commercially available polyester TPU, Elastollan®, but additionally, the fully amorphous nature of P4MCL and P4PrCL affords distinct elasticity advantages over semi-crystalline PCL, which is currently used in commercial formulations as a SS. After use, the TPUU films herein were chemically recycled to monomer with ease using $ZnCl_2$ as the catalyst, and recovered monomers were successfully used to prepare a new generation of materials with properties similar to the previous generation. Finally, thermodynamic analyses were used to approximate $\Delta H_p, \Delta S_p,$ and T_c values towards greater fundamental understanding of these sustainable materials of tomorrow.

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Supporting Information

Characterization and synthetic details; kinetic studies and molar mass of entanglement (M_e) determination for P4PrCL; characterization of P4MCL. PMCL, P4PrCL and PCL telechelic diols by ^{1}H NMR, SEC, TGA and DSC; characterization of TPUUs by ATR-FTIR, SEC, TGA, DSC, DMTA, SAXS, and WAXS; additional tensile properties and hysteresis for TPUUs; preparation of a P4MCL TPU prepared using 1,4-BD as chain extender and a thermoset P4MCL TPU; a 4-month composting study performed on the P4MCL-5k-29%HS TPUU; reaction condition and yield data for chemical recycling in a reactive distillation set-up including mass spectra for recovered monomers; SEC, tensile properties, and hysteresis testing for TPUUs prepared with recycled monomers; additional thermodynamics of polymerization info including Van't Hoff analysis assuming $[M]_{ss}$ = 1 M and ΔH_p determination from heat of combustion values.

Data Access Statement

The data from this study are openly available in the Data Repository for University of Minnesota (DRUM) at 10.13020/05ek-6k60.

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