

Toward Circular Recycling of Polyurethanes: Depolymerization and Recovery of Isocyanates

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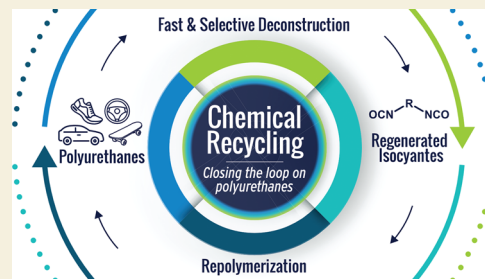
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ABSTRACT: We report a depolymerization strategy to nearly quantitatively regenerate isocyanates from thermoplastic and thermoset polyurethanes (PUs) and then resynthesize PUs using the recovered isocyanates. To date, chemical/advanced recycling of PUs has focused primarily on the recovery of polyols and diamines under comparatively harsh conditions (*e.g.*, high pressure and temperature), and the recovery of isocyanates has been difficult. Our approach leverages an organoboron Lewis acid to depolymerize PUs directly to isocyanates under mild conditions (*e.g.*, ~80 °C in toluene) without the need for phosgene or other harsh reagents, and we show that both laboratory-synthesized and commercially sourced PUs can be depolymerized. Furthermore, we demonstrate the utility of the recovered isocyanate in the production of second-generation PUs with thermal properties and molecular weights similar to those of the virgin PUs. Overall, this route uniquely provides an opportunity for circularity in PU materials and can add significant value to end-of-life PU products.

KEYWORDS: Polyurethane, depolymerization, isocyanate, chemical recycling, closed-loop, life-cycle management



INTRODUCTION

Polyurethanes (PUs) are a ubiquitous class of polymers that offers a wide range of accessible thermomechanical properties that can be tailored through the choice of monomers and additives used in synthesis and materials formulation.¹ PUs rank sixth in overall polymer production with a projected global market of \$73 billion by 2028.² Conventional PUs are polymerized from isocyanates, polyols/macrodioles, and a short-chain diol chain extender. Unfortunately, the production of PUs is associated with environmental and human health concerns, as the isocyanate monomers are prepared by reacting amines with phosgene, a highly toxic substance,³ and the most common diisocyanates used in PU synthesis, such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), are classified as carcinogenic, mutagenic, and reprotoxic compounds.⁴ Exposure to these chemicals has been linked to asthma, dermatitis, conjunctivitis, respiratory disorders, and acute poisoning.^{5,6} Despite these concerns, PUs are versatile materials that have been incorporated into everyday consumer products, such as footwear, refrigerators, foams, mattresses, carpets, furniture, adhesives, coatings, composites, automotive parts, and windmills, among other material targets.^{7–9}

The widespread use of PUs has led to the generation of large amounts PU waste (used products and post-production scraps), the majority of which is landfilled or incinerated.¹⁰ Recycling these waste streams into usable goods is challenging;^{11–15} current PU recycling strategies (*e.g.*,

mechanical or thermochemical recycling) have shown some promise, but none have shown substantial progress toward complete circularity.¹⁶ Mechanical recycling is the most common approach for PU recycling. For thermoplastics, mechanical recycling can include melt processing/remolding and/or dissolution and solvent casting.¹⁷ For thermosets or mixed thermoplastic/thermosets, mechanical recycling primarily consists of grinding scraps into granules, flakes, or powder and then rebonding for use as filler in new products.^{18,19} In both cases, compatibilizers or other additives are often employed to facilitate blending with virgin polymer, increasing the complexity and cost of the recycling process.²⁰ Additionally, the resulting second-generation outputs generally have inferior properties to virgin PUs and thus, are used in lower-value applications, such as carpeting and padding.¹⁹ Moreover, PU materials cannot be mechanically recycled indefinitely because their thermomechanical properties deteriorate significantly with each processing cycle, necessitating landfilling or incineration as the eventual end-of-life outcome.^{18,21}

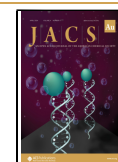
In contrast to mechanical routes, thermochemical recycling involves the depolymerization/deconstruction of used PU into

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monomers or other valuable small molecules that can potentially be repolymerized into virgin-grade products, yet none lead to recovery of all original starting components.^{12,13,22,23} The most common PU chemical recycling methods are hydrolysis, aminolysis, hydrogenolysis, and glycolysis,^{22,24} although other techniques that leverage transcarbamoylation/transurethanization reactions have been reported recently.^{12,13,23,25–27} Glycolysis is the most mature chemical recycling route, in which PU waste is deconstructed by reacting the polymer with an alcohol, typically a diol or triol (e.g., ethylene glycol or glycerol), at ~ 240 °C to form polyols that can be incorporated into second-generation PUs.^{28–32} However, the elevated reaction temperatures result in high energy intensity, and to achieve desirable performance metrics, the recycled polyol often needs to be mixed with a significant amount of virgin polyol.^{33,34} In hydrolysis, PUs are typically reacted with steam at >200 °C in the presence of a basic catalyst (e.g., sodium hydroxide), resulting in the formation of amines, polyols, and carbon dioxide.³⁵ Chemoenzymatic hydrolysis routes have been reported in an effort to explore enzymatic degradation pathways, and these approaches also result in the formation of diamines and polyols.³⁶ For aminolysis, the deconstruction of PUs is carried out using ammonia or aliphatic amines as the active agent with or without base (e.g., sodium hydroxide, potassium hydroxide); amines, polyols, ureas, and carbamates are the typical outputs,^{37–39} although a similar approach has been leveraged to upcycle PU foams into 3D-printing resins using *N,N*-dimethylformamide.⁴⁰ More recently, the catalytic hydrogenolysis of PU waste has been employed to deconstruct PU materials into the corresponding diamine and polyol fractions using external hydrogen, a base (e.g., potassium *tert*-butoxide), and transition-metal catalysts (e.g., Ir, Mn, Ru), especially transition-metal pincer complexes.^{41–43} Catalytic hydrogenolysis enables high product selectivity, but the use of high-pressure hydrogen hampers its scalability.^{41–43} Despite the considerable attention to PU recycling, only glycolysis has been applied on an industrial scale, and there have been no reports of chemical recycling techniques that enable the recovery of isocyanates, a key component for PU synthesis.⁴⁴ Previous literature has reported the use of catecholborane halides and boron halides for the deconstruction of small-molecule carbamates/diurethanes to the corresponding isocyanates via a base-catalyzed dehydrochlorination reaction followed by elimination of the catecholborane with the alcohol of the urethane in near-quantitative conversion,^{45–47} but this strategy has not been applied to PU deconstruction. Thus, a robust approach to generate and recover isocyanates from PU deconstruction is still needed to reduce the use of highly hazardous compounds, such as phosgene, and to unlock PU circularity.

Herein, we report the depolymerization of PU materials that enables the recovery of isocyanates with nearly quantitative conversion using an organoboron halide Lewis acid as the depolymerization agent under mild reaction conditions (Figure 1). The β -chlorocatecholborane-mediated depolymerization enables the recovery of isocyanates directly from PUs by breaking urethane/carbamate linkages and “capping” reactive alcohol groups to avoid recombination. Laboratory-synthesized and commercially sourced thermoplastic and thermoset polyurethanes comprised of aromatic and aliphatic isocyanates were depolymerized, and the recovered isocyanates were used to prepare second-generation PU materials with molecular

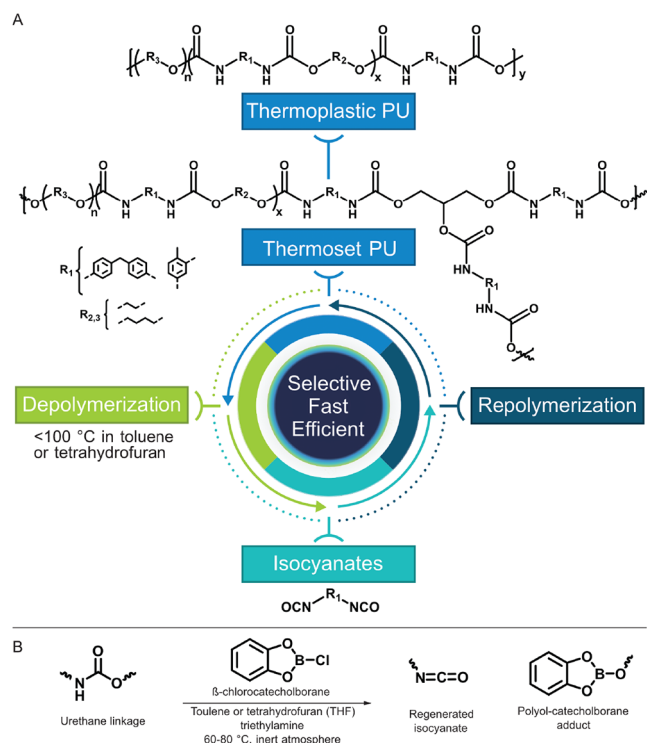


Figure 1. (A) Overview of PU depolymerization to isocyanates under mild conditions followed by repolymerization to second-generation materials. (B) β -chlorocatecholborane-mediated depolymerization of urethane linkages to form polyol/chain extender boranes and regenerated isocyanate.

weights and thermal properties commensurate with those of the virgin materials.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

Three thermoplastic PUs and two thermoset PUs were chosen for depolymerization experiments. PU1, a thermoplastic PU, was synthesized using MDI as the hard segment, poly(tetramethylene oxide) (PTMO) as the soft segment, and 1,4-butanediol (BDO) as the chain extender (Scheme S1 and Table 1). PU2, a thermoset PU, was synthesized in a similar fashion to PU1, except glycerol was substituted for some of the BDO to generate a crosslinked material (Scheme S1, Table 1). PU3 also was synthesized in a manner similar to PU1, except aliphatic hexamethylene diisocyanate (HDI) was substituted for aromatic MDI to assess the impact of isocyanate structure on depolymerization. Detailed synthetic protocols are provided in the Supporting Information. CPU1 (Estane 58 300, Lubrizol), an MDI- and polyether-based thermoplastic PU, and CPU2 (Scotch-Brite kitchen sponge, 3M), a thermoset PU foam, were purchased from commercial suppliers and stripped of additives prior to use as described in the Supporting Information. The molecular weight distributions (number-average molecular weights, M_n s; weight-average molecular weights, M_w s; dispersities, D_s) of the thermoplastic PUs were determined by gel permeation chromatography (GPC) (Table 1 and Figure S1), and differential scanning calorimetry (DSC) was conducted to assess the glass transition temperatures [T_g s] and crystallization/melting temperatures [T_c s; T_m s] as shown in Figure S1 and Table S1.

Table 1. Macromolecular Details for Synthesized and Commercially Sourced PUs

sample	isocyanate	polyol	chain extender	type	M_n (g/mol) ^a	M_w (g/mol) ^a	\bar{D} (M_w/M_n)
PU1	MDI	PTMO	BDO	thermoplastic	14,700	30,700	2.1
CPU1	MDI	PTMO	BDO	thermoplastic	11,200	32,600	2.9
PU2	MDI	PTMO	glycerol/BDO	thermoset	-	-	-
CPU2	TDI	unknown	unknown	thermoset	-	-	-
PU3	HDI	PTMO	BDO	thermoplastic	6,800	12,900	1.9

^aCalculated from GPC in *N,N*-dimethylacetamide with 0.5 wt % LiBr using poly(methyl methacrylate) (PMMA) standards.

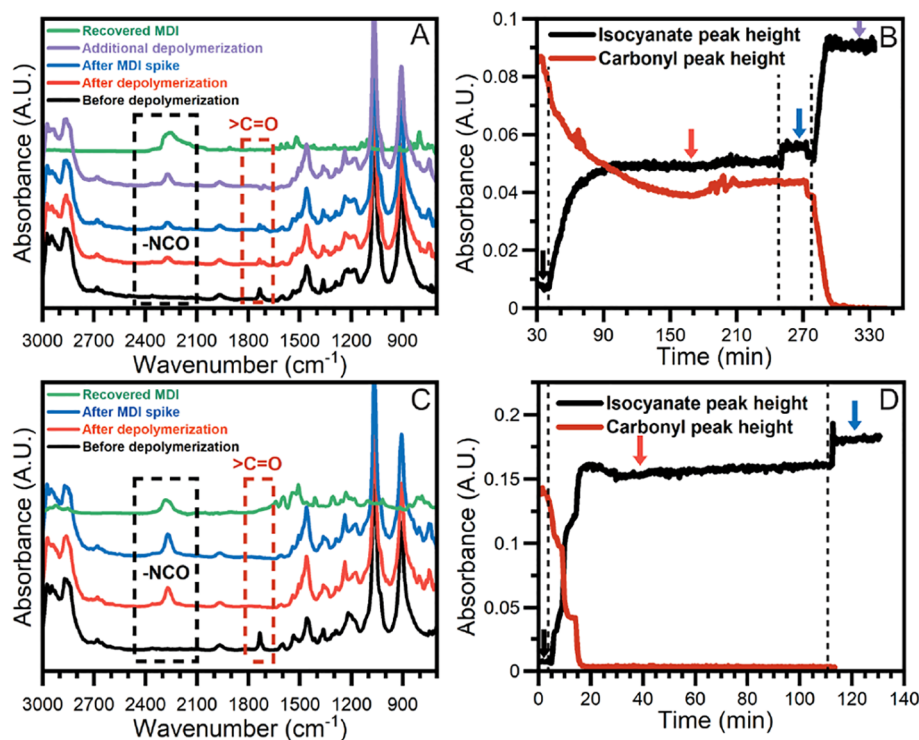


Figure 2. (A) ATR-FTIR spectra of the model thermoplastic (PU1) before depolymerization (black), after depolymerization (red), after isocyanate spiking (blue), after further depolymerization (purple), and after isocyanate purification (green). (B) Isocyanate (2270 cm^{-1}) peak height and urethane carbonyl (1733 cm^{-1}) peak height vs time with color-matched arrows to indicate the time points for the spectra in panel A. (C) ATR-FTIR spectra of the commercial thermoplastic (CPU1) before depolymerization (black), after depolymerization (red), after isocyanate spiking (blue), and after isocyanate purification (green). (D) Isocyanate (2270 cm^{-1}) peak height and urethane carbonyl (1733 cm^{-1}) peak height vs time with color-matched arrows to indicate the time points for the spectra in panel C. Spectra in panels A and C are offset vertically for clarity with the -N=C=O and carbonyl peaks indicated with dashed boxes, and the additions of β -chlorocatecholborane and the MDI standard are indicated by dashed lines in panels B and D.

PU Depolymerization

The laboratory-synthesized (PU1 and PU3) and commercially sourced (CPU1) thermoplastics were successfully depolymerized using β -chlorocatecholborane in the presence of triethylamine at $60\text{ }^\circ\text{C}$ in tetrahydrofuran (THF) according to the procedure described in the Materials and Methods section. The regeneration of MDI for PU1 and CPU1 was confirmed by *in situ* ATR-FTIR spectroscopy, and the -N=C=O stretch at $\sim 2270\text{ cm}^{-1}$ was prominent in both cases (Figure 2) and emerged almost immediately upon addition of β -chlorocatecholborane. The disappearance of the urethane carbonyl peak (1733 cm^{-1}) also was used to track depolymerization. Similarly, ATR-FTIR spectroscopy confirmed the formation of HDI in the depolymerization of PU3 (Figure S2), although the reaction proceeded slower than PU1 and CPU1. The *in situ* ATR-FTIR spectroscopy was leveraged to quantify the amount of isocyanate generated (*i.e.*, conversion) in each case using the heights of the -N=C=O stretch peaks (Figures 2B,D and S2B) and a standard addition

approach as described in the Materials and Methods section.^{48–50} Furthermore, consumption of urethane linkages in the polymer was quantified by the disappearance of the urethane carbonyl (1733 cm^{-1}) peak upon normalization. Depolymerization of PU1 resulted in the generation of MDI with $\sim 85\%$ conversion vs the theoretical maximum and urethane carbonyl disappearance of 100%, whereas CPU1 produced MDI with a conversion of 56 wt % vs the starting polymer mass with a 98% reduction in the urethane carbonyl peak (Table 2). The composition of CPU1 was unknown, and calculation of the conversion to isocyanate based on MDI content was not possible. PU3 had a low hard-segment content (8.5 wt %) and was only partially soluble in THF owing to its high crystallinity relative to the other thermoplastics (Figure S1B), leading to challenges with HDI quantification by ATR-FTIR spectroscopy — $>200\%$ conversion was calculated using the spiking method. However, the urethane carbonyl peak decreased by 78%, indicating successful depolymerization.

Table 2. Hard Segment Contents, Depolymerization Conversions, and Isolated Isocyanate Yields

sample	hard segment content (wt %)	conversion (%) ^a	conversion (%) ^b	isolated yield (%) ^c	yield basis
PU1	30.6	85	100	23	isocyanate content
CPU1	-	56	98	12	polymer weight
PU2	20.0	100	-	20	isocyanate content
CPU2	-	6.7	-	5	polymer weight
PU3	8.5	-	78	-	isocyanate content

^aDetermined via *in situ* ATR-FTIR spectroscopy using the method of standard addition. ^bDetermined by disappearance of urethane carbonyl (1733 cm⁻¹) peak. ^cDetermined gravimetrically after isocyanate purification by column chromatography.

Thermoset PUs are difficult to recycle by any of the common strategies, but the β -chlorocatecholborane-based depolymerization approach was applied to both a laboratory-synthesized (PU2) and a commercially sourced (CPU2) thermoset. The same depolymerization conditions (*i.e.*, excess β -chlorocatecholborane and triethylamine) were applied to both thermosets, but toluene was substituted for THF to enable a higher reaction temperature (80 °C vs 60 °C). Formation of the corresponding isocyanates was confirmed by *in situ* ATR-FTIR spectroscopy (Figure 3). The ATR-FTIR spectra exhibited the characteristic $\text{N}=\text{C}=\text{O}$ stretching peak, and the spiking quantification method used for the thermoplastic samples was applied to the thermosets to determine the conversion of PUs to isocyanates. Tracking the urethane carbonyl peak (1733 cm⁻¹) was not possible, because the thermosets were insoluble. PU2 depolymerization was quantitative (~100% conversion vs the theoretical maximum), and CPU2 conversion to TDI was 6.7 wt % on a polymer mass basis (Table 2). A series of photos from the depolymerization of CPU2 is shown in Figure 3E with the associated color dots indicating reaction times in Figure 3D. The sponge was clearly intact prior to the injection of the β -chlorocatecholborane, but it quickly degraded to form a homogeneous mixture shortly after the β -chlorocatecholborane was added.

The regenerated isocyanates from PU1, PU2, CPU1, and CPU2 were separated by flash column chromatography to obtain pure compounds, as described in the Materials and Methods section. All products were analyzed by ATR-FTIR spectroscopy, as shown in Figures 2 and 3 (panels A and C) for thermoplastics and thermosets, respectively. The crude reaction mixture for PU1 (depolymerized in a separate experiment using toluene to avoid NMR spectrum peak overlap with THF) was analyzed by ¹H and ¹³C NMR spectroscopy (Figures S3 and S4). Purified MDI and TDI samples also were analyzed by ¹H NMR spectroscopy as shown in Figure S5 (MDI samples: PU1, PU2, CPU1) and Figure S6 (TDI sample: CPU2) with spectra for pure standards shown for reference. The isolated MDI yields (*i.e.*, the gravimetric yields of pure isocyanates recovered after separation from the reaction product mixtures) for PU1 and PU2 were ~23% and ~20% of the theoretical maximum values, respectively (Table 2). For CPU1, ~58 mg of MDI was

isolated from 500 mg of starting PU material (12 wt % on a starting polymer basis), and for CPU2, TDI was isolated with <5 wt % yield on a starting polymer basis (Table 2). Significant losses during purification were not unexpected, as isocyanates are sensitive to moisture and can react with silica columns, but column chromatography was the most straightforward separation technique available. This approach may be infeasible at scale, and optimization of the purification process using other separations techniques could significantly improve yields. For instance, countercurrent chromatography^{51,52} could achieve similar separations without the need for reactive silica gel supports, or conventional distillation approaches could be applied in place of chromatography.

Alternative reagents and conditions also were evaluated for the depolymerization of CPU1. First, the impact of reaction temperature was assessed (Table S2), and depolymerization was consistently successful in toluene in the range of 50–100 °C, whereas no isocyanate was detected at 0 or 150 °C. It is worth noting that the 150 °C experiment was conducted in anhydrous *N,N*-dimethylacetamide owing to its higher boiling point vs toluene, and the *N,N*-dimethylacetamide could have catalyzed degradation of the isocyanate if it was formed during the reaction,^{53,54} leading to no detectable isocyanate recovery even if depolymerization/deconstruction was successful. A control experiment also was conducted that omitted triethylamine, and although some isocyanate was formed, the isolated yield was ~50% lower than that of the corresponding depolymerization with triethylamine present. These results indicate that the base likely plays a significant role in depolymerization by promoting the reaction itself and/or removing the HCl byproduct from the system as a triethylammonium chloride salt, enabling the reaction to proceed. Additionally, BCl₃ was substituted for β -chlorocatecholborane in the depolymerization of CPU1 to determine if other boron halide reagents could facilitate the depolymerization of PUs (Figures S7 and S8). The reaction generated isocyanate with an isolated MDI yield of ~4 wt % on a starting polymer basis (vs 12 wt % for the same reaction with β -chlorocatecholborane), but the conditions for this reaction were not optimized – thus, there likely is room for improvement. The impact of additives and dyes on depolymerization also was assessed with an unextracted CPU2 sample (Figure S9), and no isocyanate was formed in this case. Finally, the reactivity of the regenerated isocyanate in the crude reaction mixture for CPU1 was evaluated by adding *n*-butanol to the reaction mixture after depolymerization was complete (Figure S10 and Scheme S2). The *n*-butanol was successfully reacted with the isocyanate in the crude mixture to form a small-molecule diurethane, confirming the reactivity of the isocyanate in the crude mixture.

Overall, the conversions of PUs to isocyanates for the lab-made materials with relatively high isocyanate contents (PU1 and PU2) were determined to be nearly quantitative (85% and 100% vs the theoretical maximum values, respectively), and isocyanate generation for CPU1 and CPU2 was within the anticipated range (*i.e.*, high MDI content for CPU1 vs relatively low TDI content for CPU2). Conversion of urethane linkages, tracked by the disappearance of the urethane carbonyl peak (1733 cm⁻¹), was nearly quantitative in all cases it was possible to quantify (*i.e.*, thermoplastic depolymerization). The depolymerization reaction also was successful under a variety of conditions (*e.g.*, temperature, solvent, boron halide). However, quantification of conversion to isocyanates in

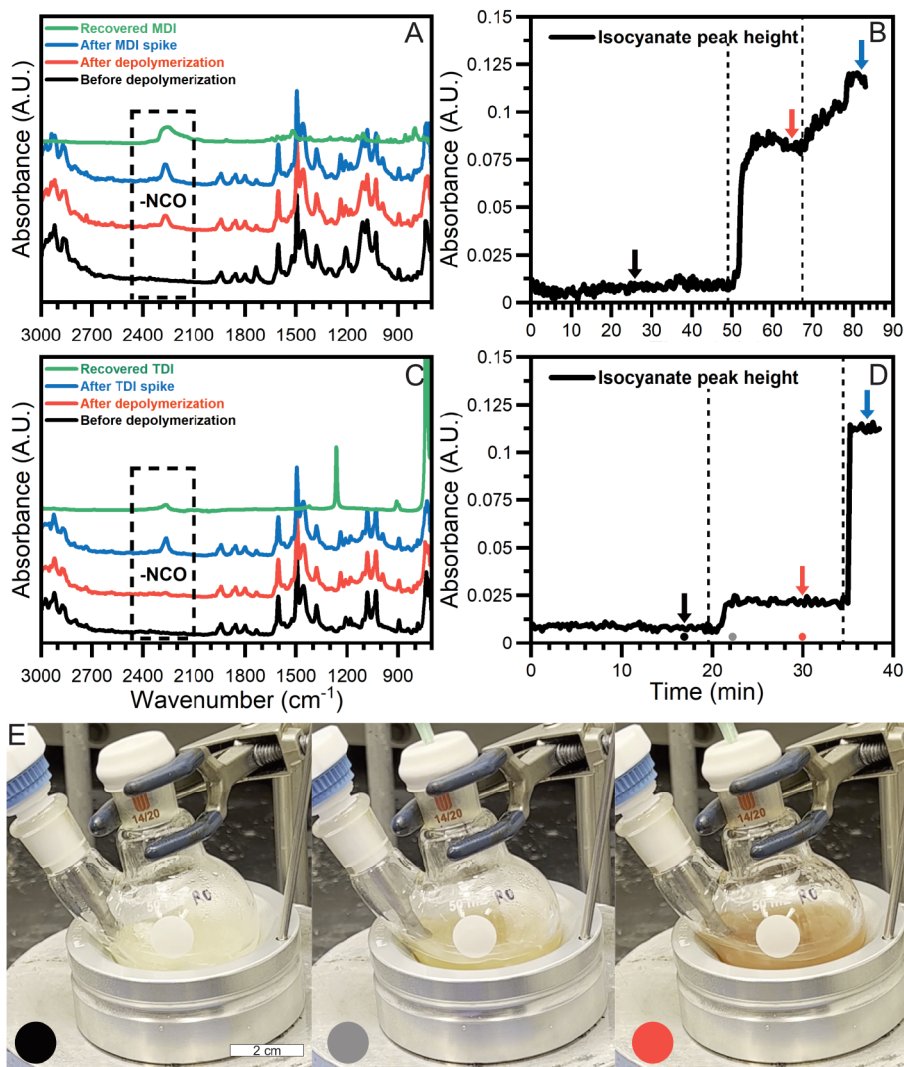


Figure 3. (A) ATR-FTIR spectra of the model thermoset (PU2) before depolymerization (black), after depolymerization (red), after isocyanate spiking (blue), and after isocyanate purification (green). (B) Isocyanate (2270 cm^{-1}) peak height vs time with color-matched arrows to indicate the time points for the spectra in panel A. (C) ATR-FTIR spectra of the commercial thermoset (CPU2) before depolymerization (black), after depolymerization (red), after isocyanate spiking (blue), and after isocyanate purification (green). (D) Isocyanate (2270 cm^{-1}) peak height vs time with color-matched arrows to indicate the time points for the spectra in panel C. Spectra in panels A and C are offset vertically for clarity with the $-N=C=O$ peaks indicated by a dashed box, and the additions of β -chlorocatecholborane and the MDI/TDI standards are indicated by dashed lines in panels B and D. (E) Photographs of the CPU2 depolymerization reaction mixture with colored circles indicating the reaction time in panel D (see the Supporting Information for a video of the depolymerization reaction for CPU2).

samples with lower hard segment contents proved more challenging with ATR-FTIR spectroscopy. For instance, the calculated conversion for CPU2 was highly variable with a relative standard deviation of 15.5%, and the conversion for PU3 was calculated as $>100\%$. The method relied on a linear detector response (*i.e.*, Beer–Lambert Law) and assumed a constant molar absorptance and path length. The calculations also relied on the assumption of a negligible change in sample volume. Thus, the high variability in low isocyanate samples likely can be attributed to a low signal-to-noise ratio and/or non-linear detector response at low analyte concentrations.^{48,49}

Two additional noteworthy findings from these depolymerization experiments were the impact of additives on depolymerization and the differences between the thermoplastic and thermoset samples. For the unstripped sample of CPU2, no isocyanate was detected, even when a larger-than-normal excess of β -catecholborane was used. Thus, thorough

removal of additives could be a critical step for implementing this depolymerization strategy. It is anticipated that nucleophilic additives, such as phenolic or aminic antioxidants, may be the most prominent depolymerization inhibitors;⁵⁵ however, given the myriad of additives present in commercially sourced PU samples, it is difficult to determine which additives are most likely to inhibit depolymerization without further investigation. Additional studies to determine the impacts of individual additives (*e.g.*, antioxidants, processing aids, polymerization catalysts, dyes, flame retardants) could elucidate the most problematic compounds and guide future efforts to apply these findings to post-consumer PU waste streams. Another key aspect for scale-up and implementation of this depolymerization method is understanding transport in thermoset materials. In comparison to the fully soluble thermoplastic samples that reacted almost immediately upon the addition of β -chlorocatecholborane, there was a delay on

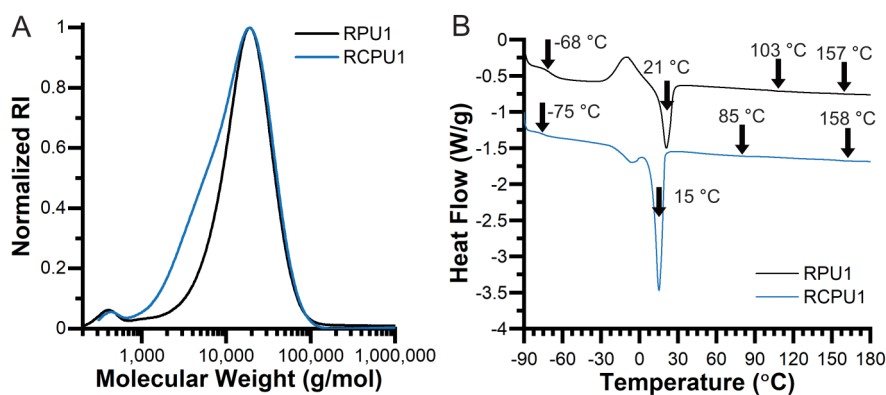


Figure 4. (A) GPC chromatograms of second-generation PUs prepared from recovered MDI (RPU1 – black, RCPU1 – blue). GPC was conducted with *N,N*-dimethylacetamide with 0.5 wt % LiBr as the solvent, and molecular weights were calculated relative to a series of PMMA standards. (B) DSC thermograms (exotherm up) of resynthesized polymers RPU1 (black) and RCPU1 (blue). Thermograms are shifted vertically for clarity, with transitions labeled.

Table 3. Composition and Molecular Weight Distributions of RPU1 and RCPU1

sample	isocyanate source	isocyanate	polyol	chain extender	M_n (g/mol) ^a	M_w (g/mol) ^a	\bar{D} (M_w/M_n) ^a
RPU1	PU1	MDI	PTMO	BDO	12,000	20,800	1.7
RCPU1	CPU1	MDI	PTMO	BDO	8,100	17,700	2.2

^aCalculated from GPC in *N,N*-dimethylacetamide with 0.5 wt % LiBr using poly(methyl methacrylate) (PMMA) standards.

the order of ~10–30 s for the thermoset samples. This effect was not unexpected and likely can be attributed to slower transport in the swelled polymer matrix, but it could have an even greater impact for samples that are larger/thicker, less porous (*i.e.*, not foams), more densely crosslinked, or less swollen by a given solvent system. Thus, an in-depth assessment of transport limitations in PU depolymerization could be critical for processing real PU waste streams.

Second-Generation PU Synthesized Using Recovered MDI/TDI

Recovered isocyanates from PU1 and CPU1 were used to synthesize second-generation PUs (RPU1 and RCPU1; see Table S3) that mimicked the composition of PU1 (recycled diisocyanate with fresh PTMO as macrodiol and BDO as chain extender). These samples were chosen because their high isocyanate content enabled the production of enough recycled isocyanate to synthesize second-generation materials on a smaller scale. The conversion of the recovered isocyanates and –OH functional groups to urethane linkages was confirmed by ATR-FTIR spectroscopy – in both cases, the –N=C=O stretching peaks disappeared, and characteristic urethane peaks reappeared. GPC was used to measure the molecular weight distributions of the resynthesized PUs, and M_n s (relative to PMMA standards) were 12,000 g/mol ($\bar{D} \sim 1.7$) and 8,100 g/mol ($\bar{D} \sim 2.2$) for RPU1 and RCPU1, respectively (Figure 4A and Table 3). The thermal characteristics of the resynthesized PUs were assessed by DSC (Figure 4B and Table S4). RPU1 and RCPU1 exhibited soft segment T_g s of –68 and –75 °C, soft segment T_m s of 21 and 15 °C, and hard segment T_g s of 157 and 158 °C, respectively, in comparison to –73 °C, 17 °C, and 156 °C for PU1 (Figure S1B). RPU1 also exhibited a second hard segment T_g at 103 °C, and RCPU1 appeared to have a small hard segment T_m or other phase transition at ~85 °C.⁵⁶ A close-up DSC thermogram highlighting the hard segment transitions for RPU1 and RPU2 is shown in Figure S11.

The comparable molecular weights and thermal characteristics for the recycled PUs indicate that the β -catecholborane-based recycling approach can be used to successfully prepare second-generation materials with thermomechanical properties that are equivalent to those of virgin PUs. Third-generation PUs were not explored in this work, but it is expected that multiple polymerization–deconstruction–repolymerization cycles could be performed without a loss of recycled polymer quality. Additionally, the development of a process to recycle the β -chlorocatecholborane and recover the polyol/chain extender components would vastly improve the sustainability of this depolymerization approach and provide a pathway toward a fully circular life cycle for conventional PU materials.

CONCLUSION

A new approach for the depolymerization and regeneration of thermoplastic and thermoset PU materials has been applied to both laboratory-synthesized and commercially sourced PUs. The method uses a relatively inexpensive organoboron Lewis acid as the depolymerization agent and directly produces isocyanates with nearly quantitative conversions under mild reaction conditions (<100 °C and ambient pressure). The regenerated isocyanates were recovered and used to synthesize second-generation PUs with molecular weights and thermal properties similar to the virgin PUs. Overall, this advanced/chemical recycling method provides a route toward circularity for conventional PUs and could reduce the need for the production of new isocyanates from environmentally harmful and highly toxic petrochemical feedstocks.

MATERIALS AND METHODS

Materials

A list of all chemicals and materials can be found in the Supporting Information.

PU Synthesis, Pretreatment, and Characterization

All synthesis, pretreatment, and characterization methods can be found in the [Supporting Information](#).

General Procedure for PU Depolymerization

PU1 (500 mg, 1.22 mmol urethane linkages) was added to a round-bottom flask with 12 mL of anhydrous THF and stirred for ~30 min at ~60 °C. Triethylamine (0.5 mL, 3.59 mmol) was added to the flask, and a solution of β -chlorocatecholborane (235 mg, 1.52 mmol) in 5 mL of anhydrous THF was added dropwise to the polymer solution. The addition was paused after two-thirds of the β -chlorocatecholborane solution was added, and the $-\text{N}=\text{C}=\text{O}$ peak was allowed to stabilize for several minutes. Then, the remaining β -chlorocatecholborane solution was added dropwise. In most cases, the $-\text{N}=\text{C}=\text{O}$ signal did not increase further, indicating that the maximum conversion was reached for the sample. If the $-\text{N}=\text{C}=\text{O}$ signal continued to increase, additional β -chlorocatecholborane was added in anhydrous THF, and the resulting mixture was held at 60 °C until the reaction was complete, as determined by *in situ* ATR-FTIR spectroscopy (*i.e.*, the $-\text{N}=\text{C}=\text{O}$ peak height stabilized after all of the β -chlorocatecholborane was added).

Product Characterization by In Situ FTIR Spectroscopy

The regeneration of isocyanates (conversion) was quantified by *in situ* ATR-FTIR spectroscopy using the method of standard addition.^{48,49} Once the $-\text{N}=\text{C}=\text{O}$ peak height reached a stable value during the depolymerization, a small amount (ca. 20–100 mg) of pure isocyanate was added to the reaction mixture in ~1 mL of the reaction solvent (THF or toluene). The step-change in the detector response was used to backcalculate the amount of isocyanate formed. This approach relied on two key assumptions: (1) the detector response was linear with respect to isocyanate concentration (*i.e.*, follows Beer–Lambert law), and (2) the volume, molar absorption coefficient, and path length remained approximately constant. The absorbance at a given wavelength is given by eq 1:

$$A = \epsilon lc \quad (1)$$

in which A is the absorbance, ϵ is the molar absorption coefficient, l is the path length, and c is the concentration of the absorbing species (*i.e.*, isocyanates). Assuming negligible volume change, constant absorption coefficient, and constant path length gives eq 2:

$$A_0 = am_0 \quad (2)$$

in which a is a coefficient capturing the molar absorption, path length, and sample volume, and m_0 is the mass of isocyanate formed in the depolymerization. Thus, by spiking in a known amount of pure isocyanate in a small volume of solvent, the absorbance after the addition of the pure isocyanate is given by eq 3:

$$A_{\text{spike}} = a(m_{\text{NCO}} + m_{\text{spike}}) \quad (3)$$

The ratio of eq 3 and eq 2 gives eq 4:

$$\frac{A_{\text{spike}}}{A_0} = 1 + \frac{m_{\text{spike}}}{m_0} \quad (4)$$

Solving for m_0 gives eq 5:

$$m_0 = \frac{m_{\text{spike}}}{\frac{A_{\text{spike}}}{A_0} - 1} \quad (5)$$

Isocyanate Purification by Column Chromatography

For experiments in which isocyanates were isolated for quantification, the spiking method was not used, as it would bias the isolated yields. Instead, the reaction mixture was filtered, and the solvent was removed by rotary evaporation at 50 °C to yield a crude product mixture. The regenerated isocyanate was separated by flash column chromatography (Biotage Selekt) using an EtOAc/hexanes solvent system (12 v/v% EtOAc in hexanes) and a silica gel column (Biotage Sfar).

ASSOCIATED CONTENT

Data Availability Statement

All data are available in the main text or the Supporting Information.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.4c00013>.

Supplementary Text; synthesis of PUs from MDI, PTMO, and a chain extender (Scheme S1); reaction of MDI with *n*-butanol to form a butyl diurethane (Scheme S2); GPC traces of starting thermoplastic PUs and DSC thermograms (Figure S1); ATR-FTIR spectra of the model thermoplastic PU3 (Figure S2); ¹H NMR (Figure S3) and ¹³C NMR (Figure S4) spectra for the crude PU1 reaction mixture and pure MDI; ¹H NMR spectra of recovered MDI from PU1, CPU1, and PU2 (Figure S5) and of recovered TDI from CPU2 (Figure S6); ATR-FTIR spectrum of CPU1 after depolymerization with BCl₃ (Figure S7); ¹H NMR spectrum of the crude product after depolymerization with BCl₃ (Figure S8); depolymerization of an unextracted sample of CPU2 to determine the impact of dyes and additives on depolymerization (Figure S9); ATR-FTIR spectra of the butyl diurethane synthesis from the CPU1 crude product mixture (Figure S10); zoomed-in DSC thermogram showing the hard segment transitions for RPUI and RCPUI (Figure S11); thermal transitions of PU1, CPU1, and PU3 (Table S1); CPU1 depolymerization reactions with β -chlorocatecholborane and triethylamine (Table S2); conditions used in the re-synthesis of polyurethanes using recovered isocyanates (Table S3); thermal transitions of RPUI and RCPUI (Table S4) (PDF)

Video of the depolymerization reaction for CPU2 (MP4)

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Notes

The authors declare no competing financial interest.

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