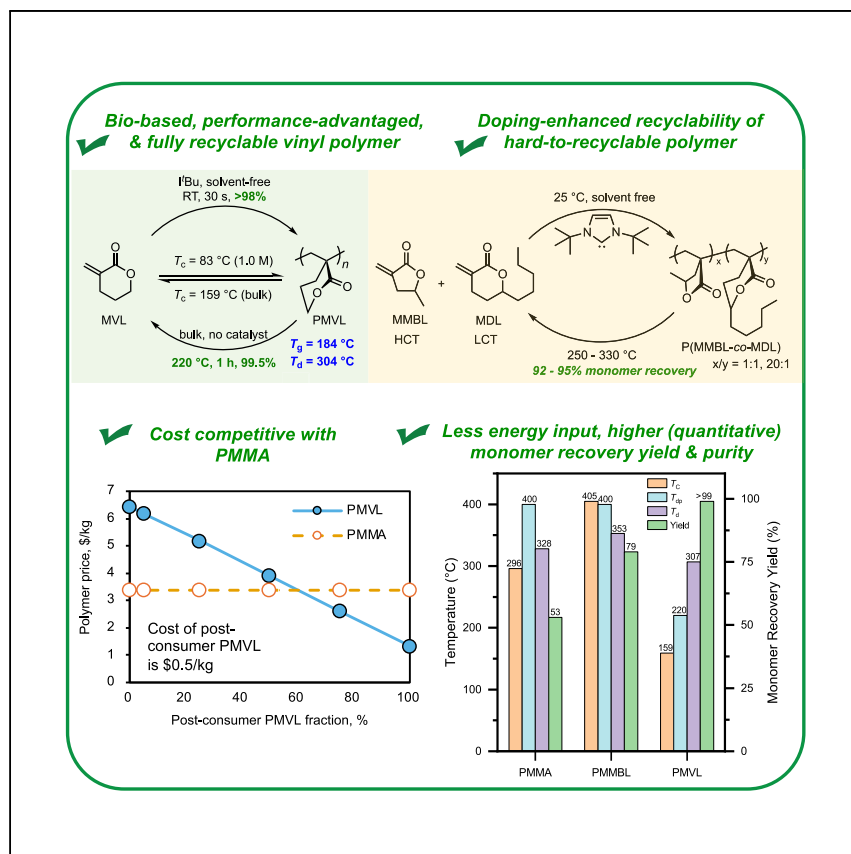


Article

Bio-based lactone acrylic plastics with performance and recyclability advantages



Gilsdorf et al. report bio-based lactone acrylics designed to enhance renewability and recyclability, which also exhibit several performance-advantaged properties, as compared to the petroleum-based incumbent. This can be accredited to the bio-privileged six-membered lactone ring pendent to the all-carbon vinyl polymer backbone.

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Highlights

Bio-based lactone acrylics exhibit both performance and recyclability advantages

Doping HCT polymer with an LCT one to form copolymer enhances depolymerizability

TEA and LCA guide reaction optimization for commercial viability of bio-acrylics



Article

Bio-based lactone acrylic plastics with performance and recyclability advantages

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SUMMARY

There is a drive to use bio-based feedstocks in polymers and engineer new materials for circularity. Here, we aimed to study bio-based, lower-ceiling-temperature alternatives to poly(methyl methacrylate) (PMMA) to achieve enhanced recycling and performance. We show that poly(α -methylene- δ -valerolactone) (PMVL) and poly(α -methylene- δ -decalactone) (PMDL), derived from the corresponding bio-based monomers MVL and MDL, exhibit five advantages compared to PMMA: exceptionally high polymerization rates under green conditions, near-quantitative bulk depolymerization to recover the monomer under mild conditions, enhanced solvent resistance and glass transition temperatures, atom-efficient reversible upcycling to advanced materials, and reduction of the temperature needed for recycling high-ceiling-temperature polyacrylates by forming copolymers doped with MDL. All advantaged properties can be accredited to the pendent lactone attached to the all-carbon backbone. Lastly, techno-economic analysis and life cycle assessment for producing PMVL from bio-based sources show that the production could be economically and environmentally competitive with PMMA under ambitious recycling scenarios that leverage the inherent recyclability of PMVL.

INTRODUCTION

Poly(methyl methacrylate) (PMMA), a transparent thermoplastic, is the most important member of the large α , β -conjugated polar vinyl polymer or acrylic family, a technologically important class of polymers in today's materials economy.¹ PMMA is found in a variety of applications, from automotive parts to electronic displays, optical fibers, and construction industries, valued at about \$1.2 billion in the US market (~\$4 billion globally) in 2022, and is expected to grow at a compound annual growth rate of 5.4% from 2023 to 2030.^{2,3} With this broad use comes a US annual supply chain energy cost of 110 PJ/year and US annual greenhouse gas emissions of 3.8 million metric tons/year (based on production volumes from 2017 to 2019).⁴ This broad relevancy and use calls for more sustainable production, use, and recycling of acrylic plastics, much like other commodity plastics produced globally that have an overall less than 10% recycling rate.^{5–8} In terms of depolymerizability, PMMA exhibits a ceiling temperature (T_c) of 205°C at a 1.0 M concentration or 296°C in bulk,⁹ which still requires a relatively high temperature to thermally shift the polymerization/depolymerization equilibrium to the monomer. Pyrolysis of PMMA has been studied extensively using different reactor configurations and molten metal (e.g., Pb, Sn) bath processes at temperatures above 400°C, demonstrating that bulk PMMA depolymerizes (by radical unzipping starting at 350°C) to MMA (>90 wt %)

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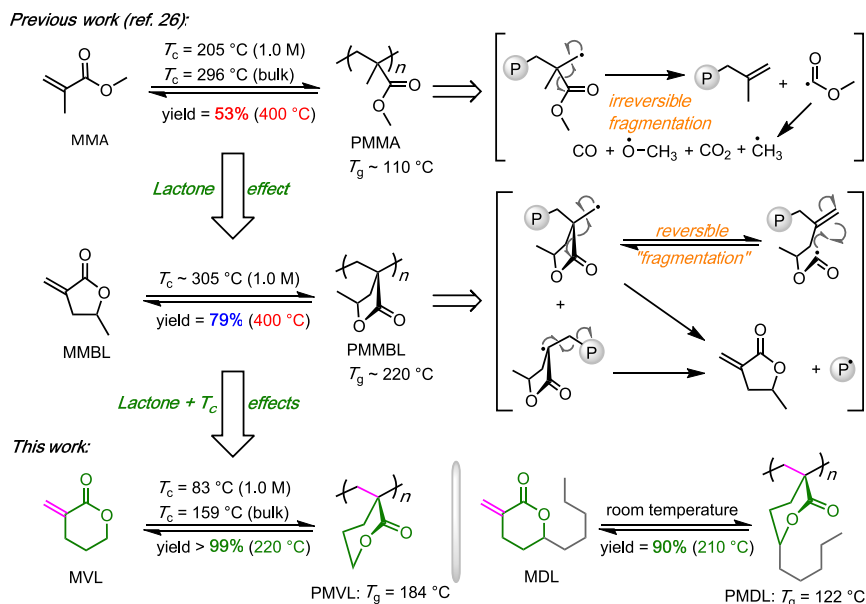


at 450°C.^{10–13} Given the high temperature required for PMMA thermal depolymerization, there has been a drive^{14,15} to develop catalytic strategies to reduce the energy input and increase the selectivity and bio-based alternatives that could exhibit similar or even superior properties to PMMA and more facile and selective depolymerization schemes back to the monomer.

There are three general strategies that have been developed to enhance the chemical recyclability of PMMA, its analogs, or bio-based alternatives, aiming to lower the depolymerization temperature (T_{dp} ; i.e., decreasing energy input) and enhance the selectivity toward pure monomer recovery (i.e., suppressing side reactions during thermolysis to eliminate the need for additional purification). The first is to install a specific lower-energy end group (i.e., a weaker C–X bond) on the terminal end of the polymer chain so that the chain-end radical that triggers subsequent chain zipping or scissions can be initiated at lower temperatures. These methods rely on precision synthesis of polymers so that the end group has high fidelity, allowing for catalytic depolymerization,¹⁶ typically coupled with the use of dilute polymerization solutions to maximize monomer recovery (by lowering the T_c using concentration effects to shift the equilibrium to the monomer).^{17–23} These requirements render polymers made by alternative polymerization methods with not-well-defined chain-end groups essentially inert and also hinder the scalability of depolymerization when polymerization solutions are needed. The second strategy is to use analogous MMA structures that exhibit a low T_c (LCT), which renders intrinsic chemical recyclability into the polymer.²⁴ For example, bulk depolymerization of poly(ethyl cyanoacrylate), derived from LCT, highly reactive, super-glue monomer ethyl cyanoacrylate that requires special handling, can be performed at 210°C to achieve a monomer recovery yield of 92%.²⁵ However, side reactions were reported to still persist, akin to PMMA depolymerization, leading to carbonaceous material remaining in the reaction flask.

The third strategy, employed within this study, is to utilize the lactone ring (the cyclic form of the ester moiety) possessed in bio-based vinyl lactone polymers, such as α -methylene- γ -methyl- γ -butyrolactone (MMBL) (Scheme 1), which have been shown to enhance the bulk depolymerization selectivity to yield pure monomers in high to quantitative yields, by suppressing the small-molecule-forming side reactions (i.e., irreversible radical fragmentation) with the cyclic pendent group.^{26–28} Although this unique feature is advantageous, these monomers exhibit a higher T_c (HCT), thus requiring a high temperature of 400°C for efficient depolymerization.²⁶ Nonetheless, this approach is promising, as it adheres to the principles of the bio-based economy for developing bio-based polymers with performance-advantaged properties that harness the inherent chemical functionalities of the starting bio-feedstocks.²⁹

The above overview of the current three strategies highlights the advantages and limitations of each approach. We posit that, ideally, new acrylic plastics should be bio-based and exhibit advantages over the incumbent PMMA in both performance and end-of-life options, especially in chemical recyclability. In addition, the depolymerization should be performed with bulk polymer and achieve high selectivity and yield for pure monomer recovery, while the closed-loop (de)polymerization should be performed under energy-efficient conditions. Centering on this objective, we reasoned that the beneficial effects of selectivity- and property-enhancing lactone rings and LCT monomer structures of low energy input and higher monomer recovery yield could be synergistically coupled, rendering a bio-based acrylic plastic system possessing the above-stated desirable properties (Scheme 1). The lactone in the acyclic monomer structure is critical for enhancing both polymerization activity and performance over the linear analogs, and we hypothesized that an LCT lactone



Scheme 1. Comparison between PMMA and lactone-containing acrylics

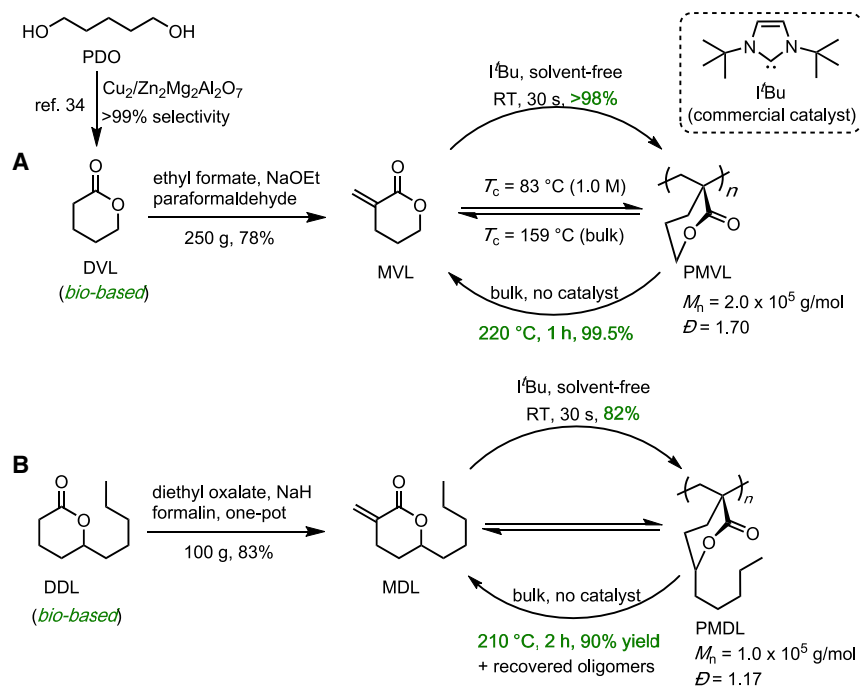
Outlined effects of the lactone incorporation that suppresses side reactions during thermolysis and the LCT-enabling six-membered lactone, δ -valerolactone (DVL; the ring highlighted in green), that lowers the depolymerization temperature and enhances selectivity to achieve quantitative monomer recovery with combined lactone and LCT effects. Note that the incorporation of the DVL in acrylic plastics increases the T_g (vs. PMMA) and recyclability to pure monomer recovery under even milder conditions (vs. PMMA and PMMBL), and the depolymerization can be performed with bulk polymer without specific end-group requirements.

acrylic monomer would render both a high polymerization rate and bulk depolymerization selectivity according to the hybrid monomer design.^{24,30,31} As shown in this work, α -methylene- δ -valerolactone (MVL)³² and α -methylene- δ -decalactone (MDL), two bio-based six-membered lactone-containing acrylic monomers (Scheme 1), meet the above stringent criteria and exhibit advantages in both enhancing the polymerization rate and bulk depolymerization selectivity to recover monomers in essentially quantitative yield under mild conditions. In addition, they exhibit advantages in enhancing physical properties or recyclability of HCT polymers and establishing atom-efficient reversible post-functionalization to advanced materials. Techno-economic analysis (TEA) and life cycle assessment (LCA) are employed to assess MVL scalability and sustainability in an industrial context to highlight the advantages of the chemically recyclable polymers and to identify areas of improvement needed for their application as consumer polymers.

RESULTS AND DISCUSSION

Advantages in exceptionally rapid organopolymerization

Prior to investigations into MVL and MDL, we examined their LCT linear analog, methyl ethacrylate (MEA), which exhibits a T_c of 20 °C at 1.0 M or 82 °C in bulk.^{33–35} Bulk depolymerization of the corresponding polymer poly(MEA) (PMEA) was indeed facile, recovering monomers in >95% yield at 265 °C and 50 mTorr in 1 h (Figures S1–S5; supplemental experimental procedures). However, PMEA (Figures S19 and S20) exhibits a relatively low glass transition temperature (T_g) of 65 °C (i.e., inferior to 110 °C of PMMA), and the polymerization was quite burdensome, requiring either extremely high pressures (for free radical polymerization) or exceptionally low temperatures and long reaction times (for anionic polymerization).



Scheme 2. Synthetic pathways to produce PMVL and PMDL from bio-based lactones

(A) MVL synthesis and its rapid organopolymerization to PMVL, which can be depolymerized back to MVL at 220°C in quantitative selectivity and yield to close the loop.
(B) MDL synthesis and its rapid organopolymerization to PMDL, which can be depolymerized back to MDL at 210°C.

Turning to lactone acrylic monomers, developing their efficient and cost-effective synthesis starting with a bio-based feedstock, such as δ -valerolactone (DVL) derived from bio-derived 1,5-pentanediol (PDO),^{36–38} is essential for potential industrial implementation of their derived acrylic plastics. Monomer MVL was typically prepared by aldol condensation of DVL with diethyl oxalate or ethyl formate, followed by reacting the resulting aldol with formaldehyde,^{32,39} and monomer MDL was synthesized from δ -decalactone, which can be derived from bio-based 6-acyl- α -pyrone,⁴⁰ using the same procedures (see [supplemental information](#)). Switching the base from sodium hydride to sodium ethoxide (NaOEt) reduced the pyrophoric hazards (Scheme 2), and the synthesis was further optimized through concurrent process modeling efforts (*vide infra*), by employing sodium carbonate instead of potassium carbonate due to the cost and solubility of the reagent in the aqueous workup of MVL.

MVL can be polymerized rapidly via conjugate addition polymerization initiated by a commercially available organic *N*-heterocyclic carbene (NHC), 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu).³⁹ This polymerization bears several hallmarks of a green process, namely, it employs an organic catalyst at ambient conditions, and it is solvent free, catalytic, rapid (in a few seconds), and essentially quantitative (Scheme 2A). This organopolymerization of MVL can readily afford high-molar-mass PMVL with number-average molar mass (M_n) up to $2.0 \times 10^5 \text{ g/mol}$ and dispersity (\mathcal{D}) of 1.70. In contrast, organopolymerization of MMA by an NHC is sluggish, achieving only 68% conversion even after 1 h.⁴¹ The substantially higher reactivity of MVL relative to MMA can be rationalized by its highly activated double bond (the methylene moiety highlighted in magenta in Scheme 1) that is *exo*-cyclic and in the *s-cis* conformation (and thus more sterically accessible), relative to the conjugated ester carbonyl of

the lactone (further activation by the electron-withdrawing group). Conversely, the double bond in MMA is more sterically hindered and less activated due to its linear structure that adopts both *s-trans* and *s-cis* conformations.

To demonstrate that the high depolymerizability of PMVL (*vide infra*) is inherent to its lactone ring and LCT but independent of chain ends, we also prepared PMVL employing simple, conventional free radical polymerization initiated by azobisisobutyronitrile (AIBN), which we found requires a longer reaction time (1 h).³² Worth noting here is that the polymerization by AIBN is carried out at 60°C (the temperature required to generate the radical initiator from AIBN) in bulk to achieve high conversions and thus high-molar-mass PMVL. LCT monomers like MVL require high monomer concentrations, most desirably in bulk, to achieve high conversion to polymer. Thus, the previously reported radical polymerizations using MVL solutions³² were not particularly effective, yielding only low-molar-mass PMVL that was isolated in low yields and appeared to be viscous. Our above-described bulk polymerization methods by ^tBu and AIBN were effectively applied to MDL, achieving similar polymerization results (Scheme 2B).

Advantages in physical properties and bulk depolymerization selectivity to recover pure monomer

Compared to PMMA, vinyl lactone polymers such as PMMBL are more solvent resistant and exhibit a much higher T_g due to the presence of the bulky lactone rings tethered to the polymer backbone.⁴² In this context, while PMMA is readily soluble in common organic solvents including toluene and acetone, PMVL is only soluble in selective chlorinated, polar solvents such as CH_2Cl_2 , CHCl_3 , and *N,N*-dimethylformamide. As expected, the rigidified polymer backbone in PMVL due to the DVL rings enhanced its T_g to 184°C, relative to the T_g of ~110°C for (atactic) PMMA. Incorporation of the plasticizing alkyl group (C_5H_{11}) in PMDL resulted in a lower T_g of 122°C relative to PMVL, highlighting the tunability in thermal properties of the lactone acrylic polymers. Conversely, both onset (5% weight loss) decomposition temperature ($T_{d,5\%} = 304^\circ\text{C}$) and maximum rate decomposition temperature ($T_{\text{max}} = 345^\circ\text{C}$) values of PMVL, determined by thermal gravimetric analysis (TGA), are about 20°C lower than those of PMMA, but these values are sufficiently high and suitable for thermal processing. As compared to PMVL, PMDL bearing the pentyl group on the DVL ring exhibits a slightly higher $T_{d,5\%}$ of 312°C and a similar T_{max} of 345°C.

LCT lactone acrylics PMVL and PMDL also showed advantages in selective depolymerization to recover pure monomer under milder temperatures. In contrast to bulk depolymerization of PMMA, which required a high temperature of 400°C and also suffered a low monomer recovery of 53% (due to competing thermal decomposition at high temperatures for HCT polymers),²⁶ PMVL and PMDL were depolymerized in bulk selectively at 220°C and 210°C, respectively, in a glass tube distillation reactor under vacuum for 1 h (Figure S18). Under these mild conditions, pure monomer was isolated in 99.5% and 90% yields for MVL and MDL, respectively (Figures 1 and 2). The recycled MVL (rMVL) can be repolymerized without further purification via free radical polymerization initiated by AIBN, yielding recycled PMVL in 98% isolated yield with an M_n of 5.0×10^4 g/mol, a D of 1.68, and thermal properties comparable to those of the virgin PMVL (Figures S23 and S24). The use of different initiating systems to polymerize MVL to PMVL, which can be depolymerized with similar selectivity and monomer recovery yield, highlights the end-group tolerance of the platform, enabling different polymerization techniques to be utilized without compromising the polymer's ability to efficiently depolymerize in mild conditions.

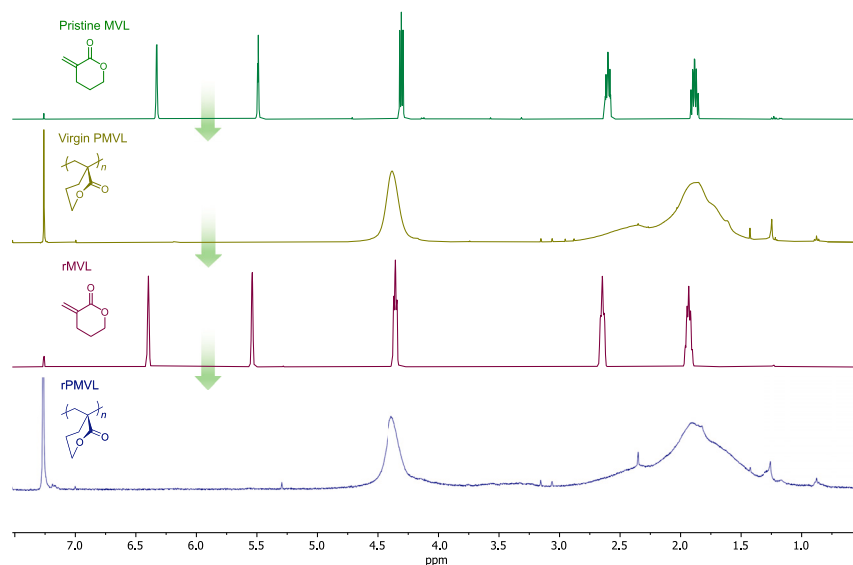


Figure 1. Demonstration of MVL closed-loop life cycle

Stacked ^1H nuclear magnetic resonance (NMR) spectra (CDCl_3) comparing pristine MVL, high-molar-mass virgin PMVL obtained by organopolymerization with I^tBu , rMVL recovered from depolymerization, and rPMVL obtained by free radical polymerization with AIBN, demonstrating closed-loop chemical recycling of PMVL.

The enhanced chemical recyclability of PMVL and PMDL not only enabled a lower T_{dp} relative to PMMA but also resulted in a much higher selectivity and yield for pure monomer recovery (Figure 3), which is attributed to both the LCT and the pendent lactone structure. The lower T_c allows for lower temperatures to be used for depolymerization, while the lactone pendent group further prevents or suppresses side reactions (e.g., irreversible radical fragmentation) from occurring by ensuring that no or negligible small-molecule radical species can be eliminated. It is noteworthy that although both T_c and T_d relate to the polymer thermal stability, they are different. Specifically, the T_c defines the relative thermodynamic stability of polymer vs. monomer: at a temperature below the T_c , the polymer is more stable than the monomer, and vice versa. However, polymers can still be thermally stable, once kinetically trapped (the quenched polymer chain from the polymerization reaction), at a temperature far exceeding the T_c , as the “dead” chain must be reactivated or cleaved at a temperature that is a function of bond type, which defines T_d , before depolymerization can take place to revert to the monomer. Hence, T_c is purely a thermodynamic parameter (e.g., independent of catalyst), while T_d has to do with both thermodynamic (onset temperature or energy required to break a bond) and kinetic (rate, thus catalyst-dependent) parameters of the system.

It is worth noting here that the PMVLs produced from NHC-initiated conjugate addition and free radical polymerization methods showed no difference in their depolymerization activity and selectivity. This important result indicates that the depolymerization of PMVL is not dependent on a specific polymerization method or the installation of specific end groups. Previously, enhanced depolymerization of acrylic plastics was completely reliant on how the polymer was synthesized, as the specific end groups installed on the terminal end of the polymer chains are the key species required in the specific depolymerization mechanism.^{18,19,21–23} These results further demonstrate advantages of redesigned, LCT acrylic plastics for establishing

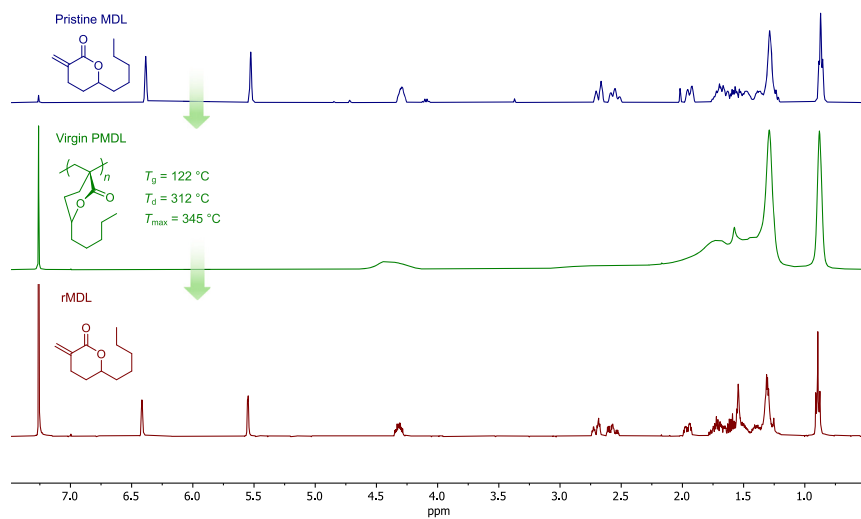


Figure 2. Demonstration of MDL closed-loop life cycle

Stacked ^1H NMR spectra (CDCl_3) comparing pristine MDL, virgin PMDL obtained by organopolymerization with t^{Bu} , and rMDL recovered from depolymerization, demonstrating closed-loop chemical recycling of PMDL.

closed-loop chemical recycling in an energy-efficient and selective manner and exhibiting broader applicability to various (de)polymerization methods.

Advantages in enabling atom-efficient reversible upcycling and enhancing recyclability of HCT polymers

Considering the fact that the ester moiety in PMVL is covalently tethered to the backbone of the repeating unit, we further posited that a PMVL ionomer would have a distinct advantage over a PMMA ionomer in that the transformation does not involve any carbon loss (methoxy elimination occurs with PMMA upon treatment with a base) and the transformation leaves the additional pendent hydroxyl group from the ring opening of the lactone (Scheme 3). Because of this unique structural feature of PMVL, it should also render circularity (i.e., virgin PMVL to the ionomer and back) of this post-functionalization via simple acid/base treatment. Hence, formation of the PMVL ionomer was explored by opening only a fraction of the lactone rings along the polymer chain. Indeed, a water-soluble ionomer can be readily produced upon treatment of PMVL with aqueous NaOH at 80°C . As predicted, the resulting ionomer showed a two-step decomposition profile with two separate T_{max} values of 349°C and 454°C on the TGA thermogram (Figure S25), which correspond to the fractions of the retained PMVL and ring-opened ionomer, respectively, highlighting thermal stability enhancement by 105°C via ionomer formation. Based on the TGA characterization, the weight fraction of the ionomer in the resulting copolymer was calculated to be $\sim 40\%$. Neutralization of the copolymer ionomer with HCl can partially revert it back to PMVL with about 26% remaining as the ionomer. This partial reversibility could be attributed to a reaction between the free hydroxyl groups and the carbonyl groups on other monomer units.

Additionally, we reasoned that DVL-containing LCT vinyl monomers such as MDL could enhance the depolymerizability of HCT monomers such as MMBL in the form of LCT/HCT copolymers via the doping effect. To this end, copolymerization of MMBL and MDL was performed to assess if the depolymerization of PMMBL could be improved by incorporating the LCT monomer units within the polymer chain.

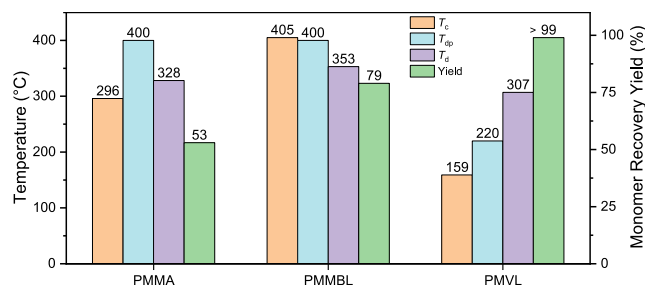


Figure 3. Comparison of the recyclability of PMMA and bio-based acrylics

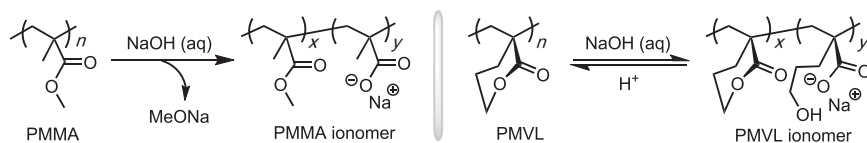
Comparisons of monomer recovery yield among three representative acrylic plastics with their T_c (orange), T_{dp} (blue), T_d (purple), and isolated monomer yield (green) values, highlighting the importance of coupling the LCT with the six-membered lactone ring in PMVL for achieving quantitative monomer recovery under mild conditions.

Random copolymers were readily prepared by conjugate addition polymerization of mixed monomer solutions with different (molar) feed ratios (MMBL:MDL = 1:1, 20:1) and subsequently depolymerized. The copolymer P(MMBL_{0.5}-co-MDL_{0.5}) from the 1:1 ratio was depolymerized in bulk at 210°C with a collective monomer recovery yield of 95%, whereas the copolymer P(MMBL_{0.95}-co-MDL_{0.05}) from the 20:1 copolymer was depolymerized at 330°C with a monomer recovery yield of 92% (Figure 4). These results showed that the presence of MDL decreases the activation energy of depolymerization, therefore allowing for lower temperatures to be used. More interestingly, even with MDL incorporation as low as 5%, the PMMBL T_{dp} was lowered by 70°C while synergistically increasing monomer recovery yield by over 10%. These results indicate that the limiting factor in the HCT polymer depolymerization is the high-energy random-chain scission required of high temperatures and that the LCT polymer exhibits an advantage in lowering the energy input (temperature) for depolymerization and increasing selectivity for monomer recovery (suppressing competing thermal decomposition).

Economic and environmental outlook of bio-based, circular lactone acrylic polymers

Given the performance-advantaged features of PMVL and PMDL, it is important to understand the economics and environmental impacts of the production processes for these circular polymers. To that end, a process model for MVL production, polymerization to PMVL, and depolymerization of post-consumer PMVL to obtain rMVL was developed in Aspen Plus V12 (Aspen Plus®) and used as the basis for TEA and LCA (Figure 5). Details of the process configurations (Figures S33–S37), design assumptions (Table S1), cost summaries (Tables S2–S5), and operating conditions are described in the supplemental information.

The PMVL manufacturing facility was modeled at 40,000 metric tons per year in the base case scenario, which aligns with the size of an average PMMA production plant. A simplified process flow diagram for this facility is shown in Figure 5. The base case scenario includes DVL production, MVL production, PMVL polymerization, and salt decomposition, whereas the recycling scenario (*vide infra*) includes the aforementioned process areas in addition to PMVL depolymerization (shown within the dashed blue boundary in Figure 5). The plant operations begin with the production of DVL via the dehydrogenation of PDO over a CuZnAl catalyst with a yield of 96%. Synthesis of MVL from DVL is then carried out in two steps: first, DVL is mixed with ethyl formate and a solution of NaOEt with diethyl ether at room temperature to form sodium enolate; second, the enolate is mixed with paraformaldehyde and



Scheme 3. Comparison between PMMA and PMVL ionomer formation

Comparison between irreversible and reversible post-functionalization of PMMA and PMVL, respectively, in the case of ionomer formation.

sodium carbonate solution to produce MVL at a single-pass yield of 70%. The unreacted sodium enolate is separated from MVL and recycled to increase the overall MVL yield to 97%. The polymerization of MVL is subsequently initiated by AIBN, with toluene acting as the solvent to reduce the viscosity of the mixture. A combination of chloroform and methanol is used to terminate the polymerization reaction, and the PMVL is purified by evaporating the solvent and chloroform mixture. In addition to the base case scenario, we considered a future recycling scenario in which post-consumer PMVL is depolymerized to rMVL (dashed blue box in Figure 5). The bulk depolymerization of PMVL to rMVL is performed under high temperature and vacuum with a yield of 99.5%. In the recycling scenario, rMVL is used to offset the production of virgin MVL at the facility (i.e., to maintain an overall facility production rate of PMVL of 40,000 metric tons per year).

For the base case scenario, the total capital investment (CAPEX) for virgin PMVL production is estimated at \$86 million with a total installed cost of \$45 million (Figure 6A; Table S7). The process areas that contribute most to the total installed cost are DVL production (63%) and MVL production (14%) stemming from the packed bed reactors, compressors, and distillation columns to purify the coproduct and recycle the solvents and unreacted substrates. The ease of polymerization and usage of low-boiling-point solvents result in PMVL polymerization accounting for only 1% of the total installed cost.

The annual operating expenses (OPEXs) are anticipated to be \$242 million (Figures 6B; Table S8), with the majority of the costs deriving from the purchase of PDO at \$81.5 million (30%, purchased at \$1.92/kg)⁴³ and NaOEt at \$79 million (29%, purchased at \$3.00/kg).⁴⁴ The other raw materials used in the process, including paraformaldehyde and ethyl formate, contribute \$73 million to OPEXs (28%). Smaller contributions (<5%) come from solvent makeups, utilities for heating and cooling, and electricity (Figure 6B). Notably, the operating cost contribution from the polymerization process area accounts for less than 3% of the total OPEXs, as the solvents and reagents exhibit low boiling points, allowing for facile recovery via evaporation. The process coproducts, hydrogen, ethanol, and excess sodium carbonate, account for \$33 million in revenue, which offsets 13% of the OPEXs (Figure 6B).

Based on these CAPEX and OPEX estimates, the minimum selling price (MSP) of PMVL is predicted to be \$6.43/kg (Figures 6C; Table S9). For comparison, the 5-year US average price (2016–2020) of virgin PMMA from fossil fuels is \$3.12/kg. Univariate sensitivity analysis for the base case scenario highlights that the major drivers of the PMVL MSP are the bio-based PDO and NaOEt costs (Figure 6D). Since the purchase prices for these feedstock chemicals are taken from literature rather than historical market data, they bear high uncertainty. Less impactful variables explored in this analysis include DVL yield, methanol loading in the polymerization step, and total CAPEX, highlighting the dominance of feedstock chemicals in the overall economics.

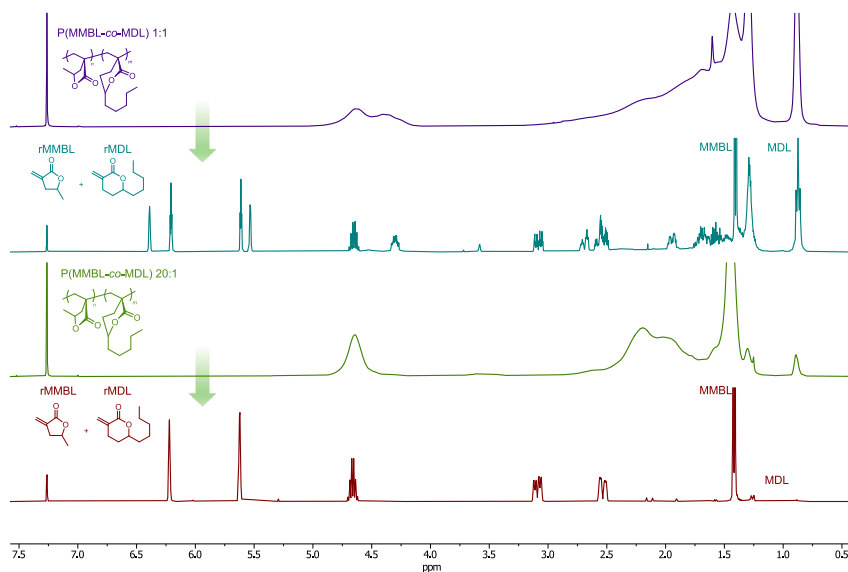


Figure 4. Demonstration of P(MMBL-co-MDL) copolymer recycling

Stacked ^1H NMR spectra (CDCl_3) comparing HCT/LCT copolymer P(MMBL-co-MDL) obtained by organopolymerization with $t\text{Bu}$ in two different molar ratios and the comonomers recovered from their depolymerizations.

As demonstrated in this work, the depolymerization of PMVL is achievable at high temperatures and low pressures without catalyst or solvent, suggesting its potential compatibility with a circular plastics economy. To understand the economic impacts of a future recycling scenario, we assumed that post-consumer PMVL can be secured through existing collection and sortation infrastructure. As price data are unavailable for post-consumer PMVL, we assume a price of \$0.50/kg, and sensitivity analysis is carried out to assess the impact of this variable on the MSP. The average 2019 market prices for waste plastics (poly(ethylene terephthalate) [PET], high-density polyethylene [HDPE], polypropylene [PP], linear low-density polyethylene [LLDPE], poly(vinyl chloride) [PVC], and polystyrene [PS]) range from \$0.1 to \$0.7/kg. The impact of using rMVL at various fractions (i.e., the mass fraction of PMVL that results from rMVL) is shown in Figure 6E, with costs decreasing as more rMVL is used. This trend results from offsetting the high costs of production for virgin MVL with the relatively low costs of rMVL; the contributions of the depolymerization process to the overall CAPEX and OPEX are only \$0.2 and \$1–\$10 million per year (depending on the fraction of post-consumer PMVL), respectively (Tables S6 and S11–S13). At a recycling rate of ~60%, the PMVL MSP is estimated to become competitive with the PMMA market price. Since both the cost of PMVL collection and the volumes of post-consumer recyclate are unknown, multivariate sensitivity analysis was conducted varying the fraction of recycled PMVL content (0–1) and the price of recycled PMVL (\$0/kg to \$1/kg) (Figure 6F). For post-consumer PMVL prices less than \$0.50/kg and a recycling rate of 50%, the estimated MSP decreases by up to 39% (>\$3.9/kg); for a high cost of recovery of \$1/kg, a recovery of at least 75% would be required for the MSP of PMVL to be comparable with PMMA.

As highlighted through this economic analysis, reducing the costs associated with MVL synthesis is crucial to reducing the MSP of PMVL. Alternatively, other routes to produce DVL from bio-based sources such as tetrahydrofuran and furfuryl alcohol could be explored to understand if costs can be further decreased via cheaper feedstock materials and/or higher yields.⁴⁵ Another key area for process

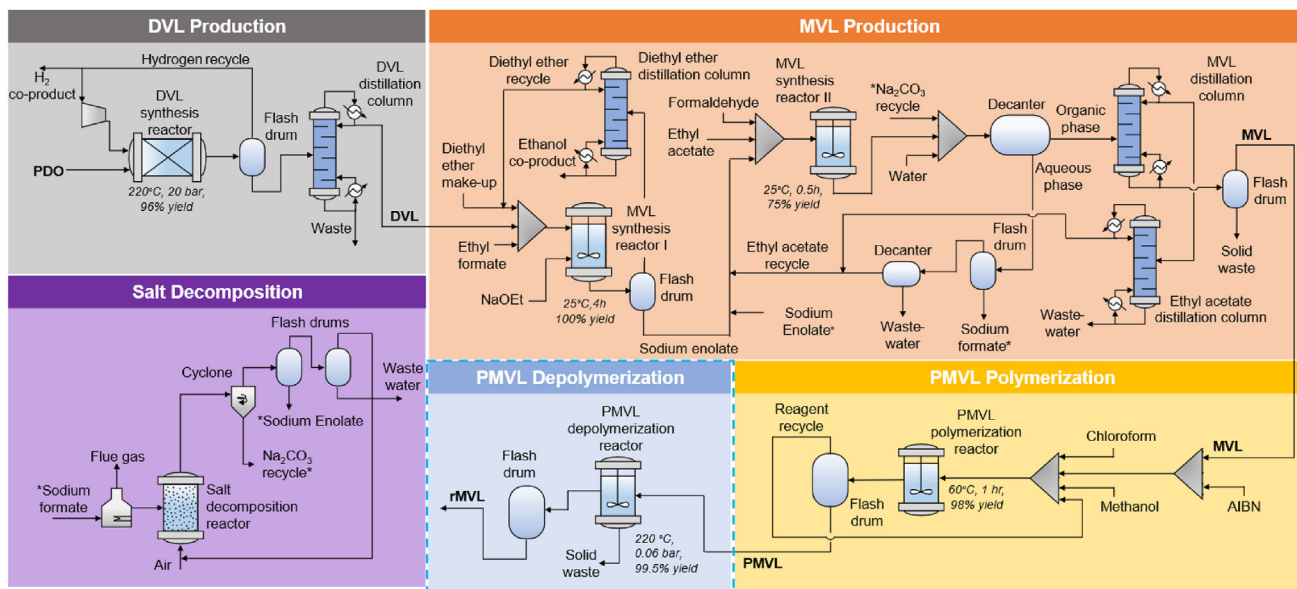


Figure 5. Process flow diagram for PMVL production and recycling

DVL production: this area includes the packed bed reactor to convert the PDO feedstock first to DVL. The product stream is distilled to purify DVL. **MVL production:** DVL is mixed with ethyl formate, NaOEt, and diethyl ether to produce sodium enolate. The products are separated via flash and subsequent distillation; ethanol is produced as a coproduct. The enolate undergoes a reaction with formaldehyde to produce MVL and sodium formate in the presence of ethyl acetate. An aqueous solution of sodium carbonate is added, and a decanter is used to separate the organic and aqueous phases. MVL is purified from the organic phase via distillation. The aqueous phase containing the salt is evaporated and sent to the salt decomposition step. **Salt decomposition:** the sodium formate mixture is pyrolyzed to form sodium carbonate. The volatiles are condensed and recycled to the MVL production step. **PMVL polymerization:** MVL produced undergoes polymerization with AIBN as the initiator and toluene as the solvent (to avoid the mixture becoming too viscous). A mixture of chloroform and methanol is used to terminate the polymerization reaction. **PMVL depolymerization:** PMVL is depolymerized (shown within the dashed blue border) under high temperature and vacuum to produce rMVL, which can be mixed with virgin MVL to produce PMVL. The detailed process flow diagrams with labeled streams and a corresponding table of stream compositions of each process section are included in [Figures S33–S37](#).

improvement lies in decreasing the ratio of H₂:PDO (16:1 M basis) required in the synthesis of DVL, which increases reactor and compressor costs. This could be achieved by coupling the dehydrogenation of PDO to DVL with the hydrogenation of ethyl levulinate to γ -valerolactone, thereby utilizing H₂ and energy released from the reactions. This coupled reaction would decrease net operational costs and generate another valuable bio-based coproduct.⁴⁶ Furthermore, increasing the recycled content of PMVL to 60% was shown to have substantial promise in decreasing the MSP of PMVL production, highlighting the compatibility of this polymer in a circular economy. However, the 60% recycling rates required to make PMVL production competitive with PMMA are beyond the 1%–15% recycling rates for plastics in the US today, indicating the need for a wide range of solutions to increase the recovery of PMVL.⁴⁵

To explore the environmental impacts of PMVL, the life cycle inventory for PMVL was derived from the process model discussed above ([Table S15](#)). Inventories for biomass-derived furfural⁴⁷ and PDO⁴³ were obtained from the literature. Hydrogen, sodium carbonate, and ethanol coproducts were assumed to replace conventional manufacture of these materials and therefore to reduce life cycle impacts via negative credits. Ecoinvent v.3.8 was used for background data (US specific if available, otherwise global). The LCA was conducted with Brightway 2.8 software using the ReCiPe Midpoint Hierarchist methodology.⁴⁸ The standard deviations were estimated using log-normal uncertainty distributions available in the ecoinvent

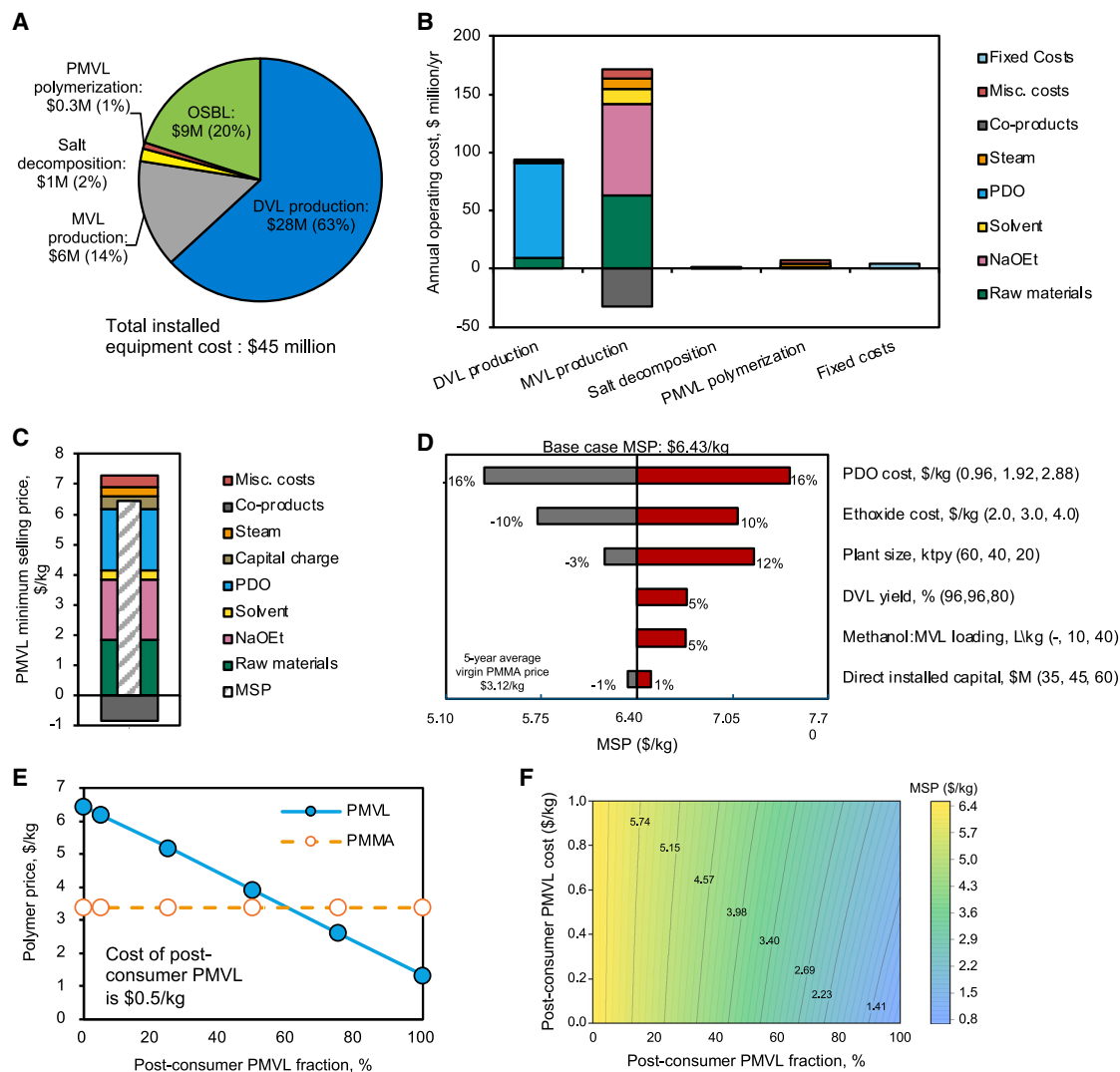


Figure 6. Techno-economic analysis of PMVL production and recycling

(A) Capital cost breakdown by area for each process section with a total capital investment of \$86 million. This includes a 25% contribution assumed from the outside battery limits investment, which consists of additional capital expenditure including piping and instrumentation required to integrate the over-the-fence utilities into the plant.

(B) Annual operating expense by process section. Fixed costs include fixed variable expenses toward labor, maintenance, and property and insurance taxes. Miscellaneous costs include utilities like cooling water and natural gas for the operation of the facility.

(C) Minimum selling price (MSP) breakdown of PMVL.

(D) Tornado plot showing the percentage of change in MSP for a univariate sensitivity analysis for scenario 1. The range explored for each variable is shown in parentheses, with the left number representing the lower bound (results shown as gray bars), the middle number showing the base case value, and the right number showing the upper bound (results shown as dark red bars).

(E) MSP of polymer as a function of PMVL recovery, assuming the cost of post-consumer PMVL is \$0.5/kg.

(F) Multivariate sensitivity analysis for the effects of the market price of recycled PMVL and recycled PMVL fractions on the MSP of PMVL.

database and Monte Carlo analysis performed with 1,000 iterations. All impacts were assessed for a functional unit of 1 kg of product on both a cradle-to-gate (PMVL or PMMA production only) and a cradle-to-grave (PMVL or PMMA production and recycling or disposal) basis.

Across most assessed categories, the cradle-to-gate environmental impacts of PMVL are 1.6 to 1,100 times higher than those of PMMA (Figure 7A; Table S14). Land

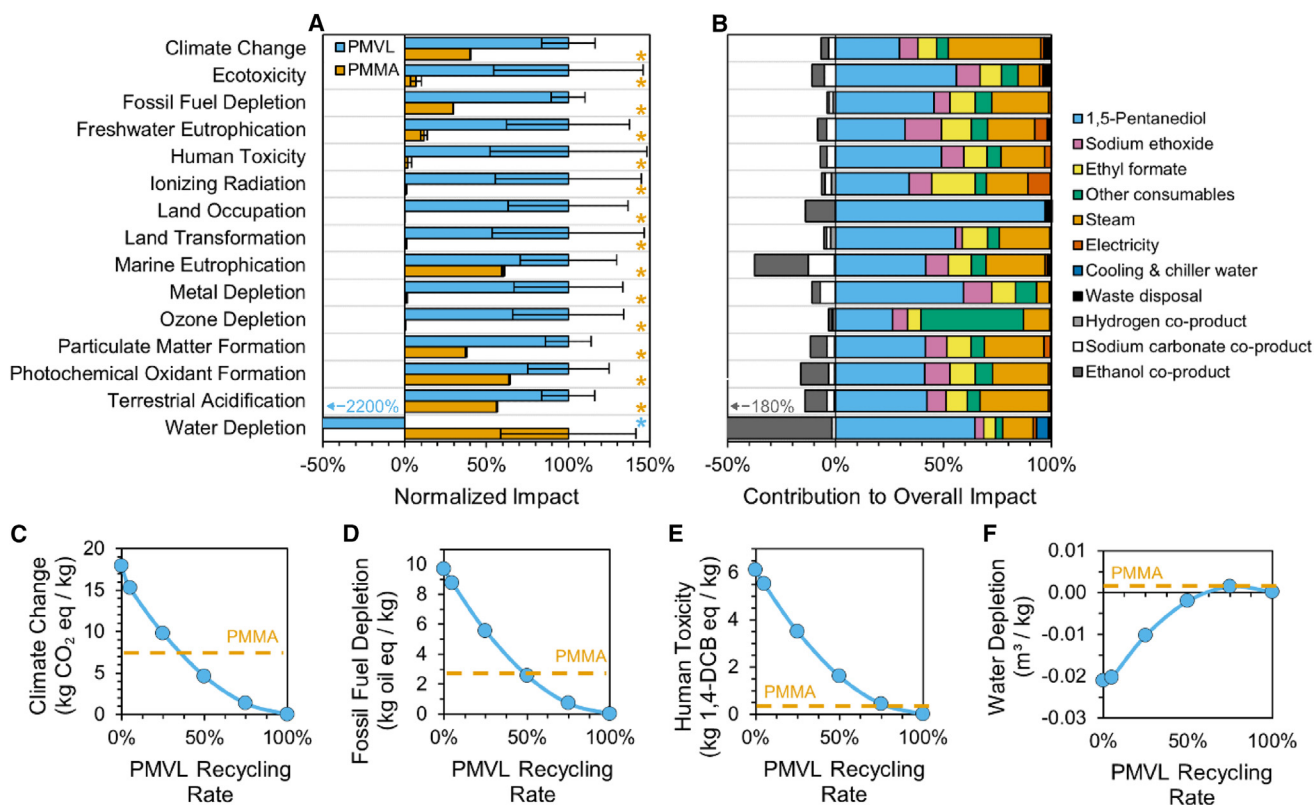


Figure 7. Life cycle assessment of PMVL

(A) Comparison between the cradle-to-gate life cycle impacts of PMVL and PMMA. The lowest environmental impact for each category is labeled with a colored asterisk. The error bars indicate standard deviations calculated from in-built uncertainty data in ecoinvent and Monte Carlo analysis with 1,000 iterations.

(B) Contribution of synthesis process components to the life cycle impacts of PMVL. “Other consumables” include diethyl ether, paraformaldehyde, ethyl acetate, toluene, chloroform, methanol, AIBN, and natural gas.

(C–F) The effect of increasing PMVL recycling rate on cradle-to-grave (C) climate change, (D) fossil fuel depletion, (E) human toxicity, and (F) water depletion. The PMVL results are normalized by the number of lifetimes that could be achieved by continuously recycling the polymer at the same rate (e.g., a 75% recycling rate results in a lifetime of 4, while a 25% recycling rate results in a lifetime of 1.33). The PMMA baselines include impacts associated with PMMA production and disposal by 90% landfill and 10% incineration with energy recovery (no recycling is assumed).

occupation, which considers land that is in use for a defined time period, is particularly high for PMVL (1,100 times that of PMMA) due to the bio-mass resources required for PDO production. PMVL also exhibits negative water depletion. The low water depletion value is due to credits from ethanol coproduction; conventional ethanol fermentation requires significant water input for the growth of the corn and sugar feedstocks.

Similar to the economic outlook presented above, most of the assessed life cycle impacts of PMVL originate from MVL synthesis (Figure 7B; Table S16). PDO, NaOEt, ethyl formate, and electricity contribute 26%–97%, 1%–17%, 1%–20%, and 1%–10%, respectively, to all environmental impacts. Steam—79% of which is used for MVL synthesis and 21% for polymerization—is also a major contributor at 1%–43% of all environmental impacts. Some of these impacts could be minimized through key process innovations, such as the development of manufacturing routes from less energy-intensive bio-based feedstocks than furfural/PDO, and heat integration to minimize steam and cooling water consumption.

Leveraging the inherent recyclability of PMVL will also be crucial for decreasing environmental impacts (Figures 7C–7F and S38; Table S17). In general, recycling PMVL

reduces overall life cycle impacts because the depolymerization process is less intensive than MVL synthesis. This cradle-to-grave LCA includes impacts associated with PMVL synthesis and depolymerization, normalized over the multiple lifetimes that could be obtained by recycling the original polymer continuously at a set rate (e.g., a 75% recycling rate would result in 4 lifetimes),⁴⁹ and does not include collection and sorting steps that would be required to recycle this polymer in a real-world scenario. A recycling rate of 50% could enable PMVL to exhibit lower climate change, fossil fuel depletion, land transformation, marine eutrophication, particulate matter formation, photochemical oxidant formation, terrestrial acidification, and water depletion than PMMA. Increasing the rate further to 100% would enable PMVL to have equivalent or lower life cycle impacts than PMMA across all 15 assessed metrics. Both of these scenarios are optimistic, as only 1%–15% of plastic waste is currently recycled in the US, depending on the polymer type.⁵⁰

Overall, this study has shown that the bio-based acrylic PMVL polymer exhibits the highlighted five advantages relative to the petroleum-based incumbent PMMA, all of which can be accredited to the presence of the bio-privileged six-membered DVL ring in the monomer MVL and corresponding polymer PMVL structures. First, the highly activated exocyclic double bond in MVL, as a result of the constrained *s-cis* conformation by the conjugated ester carbonyl of the lactone, renders its exceptional organopolymerization rate under desired solvent-free and ambient conditions, achieving quantitative monomer conversion to high-molar-mass PMVL in seconds. Second, the rigid lactone ring tethered to the polymer's all-carbon backbone provides PMVL with more solvent resistance and a much higher T_g . Third, the coupling of the selectivity-enhancing lactone and the LCT monomer structure, also due to the presence of the six-membered lactone that links the α -substituent and ester alkyl group, brings about the highly selective bulk depolymerization to recover monomer in an essentially quantitative yield under mild (220°C) conditions. Fourth, this high depolymerization selectivity is independent of polymerization mechanisms and thus chain-end groups, and this strategy can also be applied to enhance recyclability of HCT polymers via doping with the LCT lactone-acrylic comonomer. Fifth, taking advantage of the reversibility of lactone's ring opening and closing under base and acid conditions, respectively, PMVL can undergo reversible post-functionalization to advanced materials such as ionomers for achieving atom-efficient reversible upcycling of PMVL. It should be possible to enable other types of atom-efficient upcycling via the ring opening of the DVL ring in PMVL upon treatment with a variety of nucleophiles such as alcohols and amines. These five characteristics of PMVL, particularly its selective polymerization and depolymerization, will be crucial for lowering the costs and environmental impacts associated with MVL synthesis from PDO. TEA and LCA show that, without recycling and at current experimental conditions, PMVL costs two times the market price of PMMA and exhibits environmental impacts that are 1.6–1,100 times higher than PMMA. However, implementing 50%–60% recycling could enable cost and environmental competitiveness across most assessed metrics, highlighting the advantage inherent to chemical recyclability of circular polymers.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Requests for further information should be directed to and will be fulfilled by the lead contact, Eugene Y.-X. Chen (eugene.chen@colostate.edu).

Materials availability

This study did not generate new unique materials.

Data and code availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the [supplemental information](#). The Aspen model inputs and outputs are available upon request.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2024.101938>.

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AUTHOR CONTRIBUTIONS

E.Y.-X.C. conceived the idea and designed the experiments. R.A.G., E.R.C., and R.R.G. designed and carried out the experiments. A.A., T.U., A.S., and G.T.B. performed TEA and LCA studies. R.A.G., E.R.C., A.A., T.U., and A.S. cowrote the manuscript, G.T.B. and E.Y.-X.C. edited the drafts, and all authors participated in data analyses and discussions and read and edited the manuscript. G.T.B. and E.Y.-X.C. directed the project.

DECLARATION OF INTERESTS

R.A.G., E.R.C., and E.Y.-X.C. are inventors on a US provisional application submitted by Colorado State University Research Foundation, which covers the herein described polymers. G.T.B. is a member of the *Cell Reports Physical Science* editorial advisory board.

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