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High chemical recyclability of vinyl lactone acrylic bioplastics

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The depolymerization selectivity of poly(methyl methacrylate) (PMMA) under thermolysis and dynamic vacuum is inherently limited by the repeat-unit structure, leaving much (~47%) of PMMA to fragment and carbonize to char. Here we show that renewable, high-performance alternatives to PMMA with vinyl lactone repeat units, poly(α-methylene-γ-butyrolactone) (PMBL) and poly(γ-methyl-α-methylene-γ-butyrolactone) (PγMMBL), unexpectedly depolymerize much more selectively and recover monomers with considerably higher yield and purity than PMMA (76% pure monomer isolated from PγMMBL) and are also devoid of char formation, leaving the residue as only the oligomers with a total mass balance. To uncover the origin of the unexpected high chemical recyclability of P(M)MBL, this study has ascertained their ceiling temperature (T_c) by density functional theory, trapped and analyzed both primary and tertiary macroradicals generated during the depolymerization, and probed the stability of macroradicals using Lewis acid additives and mixed plastic feeds. The evidence obtained through this study suggests that the much enhanced recyclability of P(M)MBL bioplastics relative to PMMA is not due to their differences in T_c values, but rather the linear ester and cyclic ester-imparted difference in stability and monomer-production roles of primary and tertiary macroradicals generated in the random chain scission processes.

Introduction

Synthetic polymers have become indispensable in our daily life and the global economy. From cling wraps used to prevent food from spoiling to aircraft and automobile parts for transportation, polymers are ubiquitous and vital. Most synthetic polymers, especially commodity vinyl-addition polymers such as polyethylene (PE), polystyrene (PS), and poly(methyl methacrylate) (PMMA), come with the cost of high chemical stability in terms of chemical recycling.[1–10] Though the high stability may be a desired property for certain practical applications at first glance, it makes such thermally and chemically robust synthetic polymers a burden to dispose of, in particular through chemical recycling to obtain their monomers for repolymerization to virgin-quality plastics, contributing to massive environmental pollution and infrastructural strain.[11–15]

The high stability of these polymers stems from the highly exergonic nature of their vinyl-addition polymerizations. The chain-growth polymerization of ethylene releases 22 kcal/mol chemical energy, giving rise to a thermodynamically highly stable PE with an extremely high bulk ceiling temperature (T_c) reaching 610 °C.[16] Note that T_c is defined as the temperature at which the polymerization and depolymerization reactions reach an equilibrium, thus serving as a measure of de/polymerizability, depending on whether the polymer or monomer is referred to. At a working temperature (T) below T_c, the monomer can be polymerized into the corresponding polymer as the thermodynamically more stable state, but at T above T_c the polymer is thermodynamically unstable and can revert back to its monomer (when the kinetic barrier is overcome). Thus, many challenges exist while developing methods to recycle these high T_c polymers, such as PE, for chemical recycling, including high energy inputs and multiple competing decomposition pathways of organic matter under such high T conditions. Hence, recent advances in recycling PE have, therefore, been focused on increasing depolymerization selectivity to oligomers that can be transformed into other useful products, rather than complete depolymerization of the polymer to the monomer.[17,18]

Medium range T_c polymers, such as PMMA with a T_c of 205 °C in 1.0 M or 296 °C in 9.35 M (bulk), still possess high stability (ΔH_p = -13.4 kcal/mol, ΔS_p = -28.0 cal/mol K),[16] but complete depolymerization can be achieved through exploitation of depolymerization mechanisms and setups. PMMA can undergo thermally induced depolymerization through two separate mechanisms, chain-end scission and random chain scission.[19–21] Chain-end scission is favored at lower temperatures, where a tertiary radical is generated at the end of the polymer chain and depolymerization proceeds from there. Random chain scission, on the other hand, is favored at higher temperatures, where two macroradicals, a tertiary and a primary radical, are generated at a random bond in the polymer backbone and both species can proceed to depolymerize, with the tertiary radical leading to more monomer production (Scheme 1).

Utilizing fixed and fluid bed reactors to drive the reaction at temperatures exceeding 400 °C (typically at ~ 450 °C) that favors the random chain scission mechanism has been reported to depolymerize PMMA to methyl methacrylate (MMA) with high

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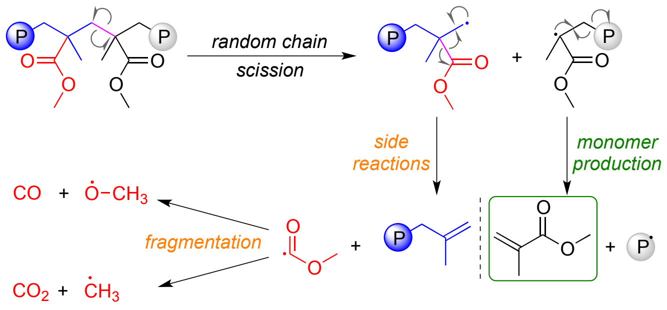
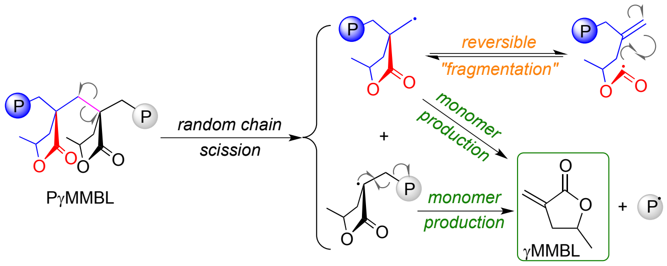


Scheme 1 Random chain scission mechanism of PMMA depolymerization.



Scheme 2 Proposed tethering effect of the lactone units within PγMMBL on enhancing depolymerization selectivity by suppressing fragmentation side reactions.

to quantitative conversions.[22–29] These more complex reactors were employed in order to reduce the PMMA's resonance time within the reactor and prevent the primary radical species from undergoing unproductive side reactions that would lower overall yield and purity of the recovered MMA. Recently, strides have even been made in controlled depolymerization of chloride-capped PMMA (PMMA-Cl) at low temperature (100 °C) catalyzed by a ruthenium(II) complex.[30] After reaching equilibrium monomer concentration at this temperature, ~5% MMA was released, but applying three evaporation cycles (thus four depolymerization processes) generated collectively ~15% MMA after 40 h. Performing this depolymerization at higher temperature (120 °C) began to experience side reactions.

There has been significant interest in developing renewable acrylic alternatives to the petroleum-based MMA.[31–33] These alternatives include biomass-derived, cyclic MMA analogs, such as α-methylene-γ-butyrolactone (MBL), β-methyl-α-methylene-γ-butyrolactone (βMMBL), and γ-methyl-α-methylene-γ-butyrolactone (γMMBL).[34–37] Although we have studied the polymerization of such biorenewable vinyl lactone monomers for almost a decade,[38–45] the depolymerizability of the resulting polymers, P(M)MBL, has not been investigated. This inactivity has been in part because of the current assumption that (M)MBL is more reactive than MMA, exhibits higher polymerizability, and leads to more thermodynamically stable P(M)MBL polymers with superior properties (e.g., solvent and heat resistance) to PMMA; thus, P(M)MBL was considered to be less depolymerizable and thus chemically recyclable. Here we report that the vinyl lactone repeat units in P(M)MBL prove to be critical in mitigating the side reactions encountered with the primary radical species produced by random chain scission processes. The understating of this beneficial feature is based on our working hypothesis that the five-membered lactone units tethered to the P(M)MBL backbone with two carbon-carbon linkages keep any alkoxycarbonyl radicals formed by β-scission in close proximity, which allows for facile, reversible primary radical "fragmentation" and reformation, overall suppressing side reactions and therefore increasing depolymerization yield and selectivity (Scheme 2). The combined experimental and density functional theory (DFT) studies described below present evidence to support this hypothesis.

Results and discussion

1. Thermally induced depolymerization of PMMA and P(M)MBL

As mentioned earlier, the bulk T_c of PMMA was reported to be ~300 °C, but that value does not mean one can readily depolymerize PMMA at this temperature. It is important to note that T_c values of polymers only indicate their thermodynamic stability relative to their monomer states in an equilibrium situation under given conditions (temperature, concentration, state). Once the polymer is out of the polymer–monomer equilibrium (i.e., the quenched, dead polymer chains), it will need to be *reactivated* and brought back to the equilibrium before depolymerization can take place at $T \geq T_c$. This activation could be a chain scission reaction to generate reactive intermediates or active species (e.g., a radical, cation, anion, coordination complex, etc.) by which de/polymerization can proceed, which could be achieved by thermolysis at T (much) greater than T_c or catalysis under milder conditions to overcome the kinetic (activation) barrier.

In this context, previous studies showed that MMA yield from the thermally induced depolymerization of PMMA were maximal at 450 °C in fixed or fluidized bed reactors or in molten metal (Pb or Sn) baths.[23,26] These specialized setups are generally not accessible in laboratory settings and, in the case of using molten metal baths, can lead to toxic organometallic impurities in the recovered monomer that requires further purification. For the current comparative chemical recyclability study, we employed a more traditional glassware distillation apparatus that enabled the depolymerization experiments to be performed at relatively small laboratory scale under identical conditions. Therefore, typical synthetic glassware was employed as the depolymerization apparatus with a hemispherical heating mantle equipped with a thermocouple for heating. In contrast with flowing gas, vacuum was used and volatile products were distilled off of the reaction as they were produced. Under the current thermolysis/depolymerization conditions (400 °C, 50 mTorr, 3 h), however, the recovered MMA yield was only modest (53%, run 1, Table 1), leaving a substantial amount of char residue. In the glassware distillation apparatus, the polymer was in contact with the hot glass for extended periods of time, leading to the residue carbonizing and side reactions to proceed. Carbon monoxide, carbon dioxide, and highly reactive methyl and methoxy radicals could also be eliminated from the primary macroradical chain end (Scheme 1). These elimination products can lead to the production of a variety of undesirable products,[25] overall lowering the yield and also the purity of the recovered monomer in the distillate (Figure 1). This decrease in purity necessitates the need for further purification in order to obtain MMA suitable for repolymerization, which has been the case with the more specialized reactor setups as well.[25]

Table 1 Results of thermal depolymerization of acrylics. [a]

Run	Polymer (M_n, kDa) [b]	T_d, T_max (°C) [c]	Monomer recovery (%) [d]	Residue identity (%) [e]	Residue M_n (kDa) [b]
1	PMMA (44.8)	328 366	53 ± 4	Char (n.d.)	n.d.
2	PMBL (11.7)	341 419	65 ± 4	oligomer (~35)	1.50
3	PγMMBL (120)	353 444	76 ± 1	oligomer (~24)	1.60

[a] Conditions: 500 mg polymer sample, 400 °C, 50 mTorr, 3 h; n.d. = not determined. [b] number-average molecular weight (M_n) data were obtained by gel-permeation chromatography (GPC) in DMF against PMMA standards. [c] T_d is the decomposition temperature at 5% mass loss obtained from thermal gravimetric analysis (TGA) experiments and T_max is the maximum rate decomposition temperature. [d] Percent recovery was determined from the mass of the collected over two runs. [e] Residue was isolated by dissolution in chloroform before filtration and characterization by ^{1}H NMR and GPC analysis.

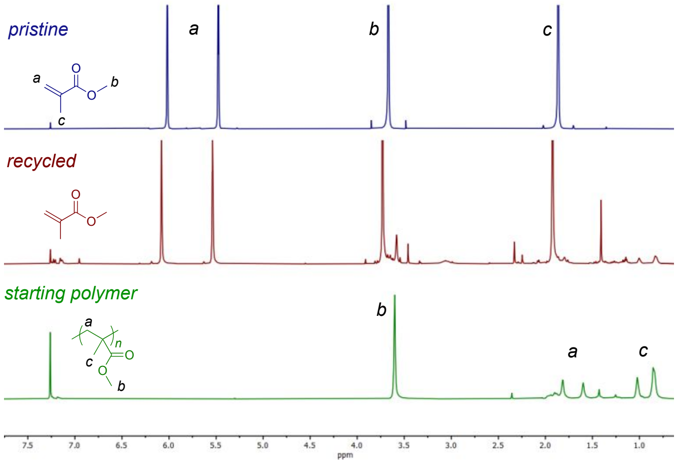


Figure 1 Stacked NMR ($CDCl_3$) spectra comparing pristine MMA with recycled MMA and starting PMMA used for depolymerization (slight chemical shift differences in recycled MMA due to presence of some contaminants).

The lack of high selectivity for MMA reformation in PMMA depolymerization under the current long-residence-time conditions can be attributed to the structure of the repeat units within the polymer. As the primary macroradical chain end is well understood to have limited ability to produce monomer and instead eliminate radicals that inhibit the tertiary macroradical from producing monomer,[25] we hypothesized that structural alteration of the pendant group to a cyclic ester (lactone) rather than a linear ester present in PMMA would enable the primary macroradical to produce monomer by blocking elimination side reactions (Scheme 2). Indeed, under identical depolymerization conditions, PMBL depolymerization achieved notably increased monomer recovery by 12% relative to PMMA, while carbonizing of the residual polymer was completely avoided and instead sublimation of oligomeric residue (with complete mass balance) was observed (run 2, Table 1). Note that extending the reaction time beyond 3 h resulted in no further increase in the recovered monomer yield, due to concomitant sublimation of macroradicals once reaching low enough molecular weight, which effectively halted further depolymerization. Accompanying the greater yield of monomer recovery was also the increased purity of the recovered monomer, although it's still not spectroscopically pure by nuclear magnetic resonance (NMR) spectra (Figure 2A). Apparently, the lactone pendant groups within the polymer repeat units decrease the proliferation of side reactions, effectively preventing carbonization. Excitingly, depolymerization of PγMMBL exhibited not only a further increase in monomer recovery yield by 23% relative to PMMA (76%, run 3, Table 1), but also a drastic increase in monomer purity to recover *spectroscopically pure monomer* γMMBL (Figure 2B). The remaining balanced mass was for the recovered, not yet fully depolymerized oligomers. This further enhanced depolymerization selectivity towards monomer formation relative to PMBL could be attributed to the methyl group on the γ-position of the lactone ring that imparts more stability due to hyperconjugation, which further stabilizes the primary macroradicals and allows for more productive monomer formation and suppression of side reactions. Worth noting here is that, as the recovered residue was the incompletely depolymerize oligomeric residue in the depolymerization of P(M)MBL, not the intractable carbonized char in the case of PMMA, it presents a possibility to design a more effective depolymerization setup to achieve quantitative monomer recovery in the chemical recycling of P(M)MBL.

2. DFT calculations to estimate T_c values of PMBL and PγMMBL

An alternative hypothesis for the much-enhanced chemical recyclability of bio-based P(M)MBL vs. PMMA is due to reduced T_c values for P(M)MBL, which would render monomer production more favorable. To provide evidence to either support or dispute this alternative hypothesis, we performed DFT calculations to estimate T_c values for PMBL and PγMMBL as their experimental values are currently not available and difficult to measure experimentally. Included also in this DFT study are PMMA to establish an empirical relationship between the computed ΔH_p and ΔS_p values and literature values, and a new vinyl lactone polymer poly(α-ethylidene-γ-butyrolactone) (PEBL) designed with a low T_c for more energy-efficient chemical recycling, thus establishing a broader data set for comparisons amongst high to lower T_c acrylic polymers.

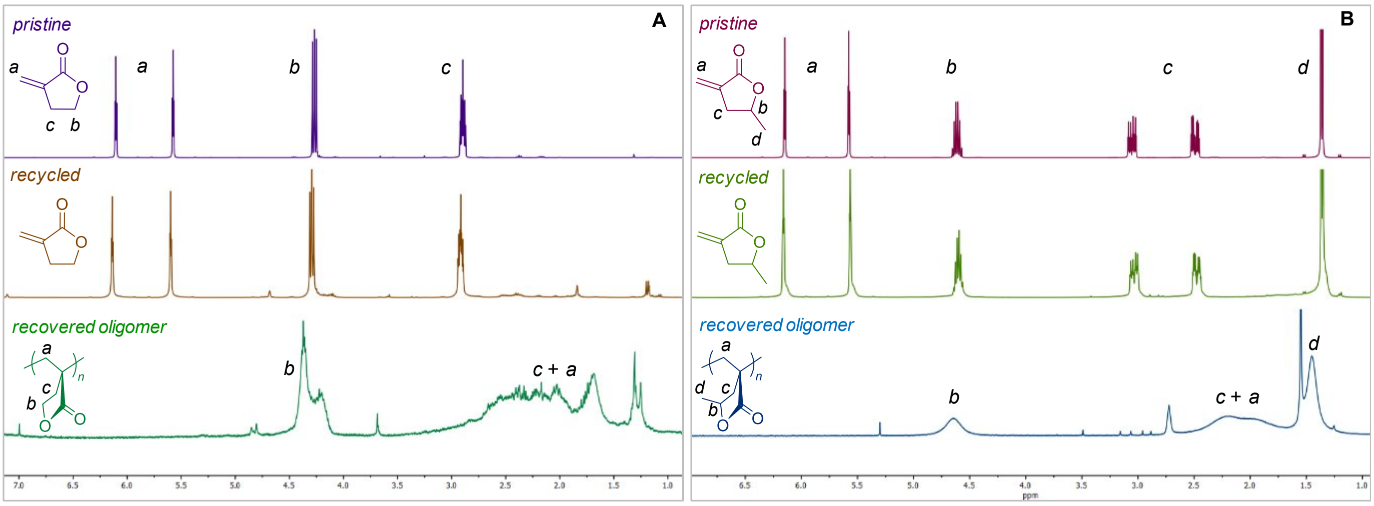


Figure 2 Stacked NMR ($CDCl_3$) spectra of **A**) PMBL recycling to form MBL and oligomeric residue and **B**) PγMMBL recycling to form pure γMMBL and oligomeric residue. In both cases the total mass balance was achieved for the recovered monomer and oligomers.

Table 2 Results of DFT calculations performed on lactone acrylic polymer systems

Entry	Polymer	Estimated [a] ΔH_p (kcal/mol)	Estimated [a] ΔS_p (cal/mol K)	Estimated T_c (°C) [b] at 1.0 M	Estimated T_c (°C) [b] in Bulk [M]
1	PγMMBL	-17.3	-30.0	305	405 (9.36 M)
2	PMBL	-15.9	-25.3	354	502 (11.4 M)
3	PEBL	-8.6	-29.2	23	80 (10.7 M)

[a] ΔH_p and ΔS_p are the averages of BP86/SVPD calculations on oligomer series adjusted using PMMA correction factors described in the main text. [b] T_c values were calculated using the equation: $T_c = \Delta H_p/(\Delta S_p + R\ \mathrm{Ln}\{[M]\})$, where ΔH_p and ΔS_p are enthalpy and entropy changes of polymerization, R is the idea gas constant, and [M] is monomer concentration.

These relatively inexpensive DFT calculations were carried out at the BP86/SVPD[45–47] level to calculate enthalpy and entropy changes of polymerization, ΔH_p and ΔS_p, for each polymer with the ultimate goal of establishing a method for estimating/predicting acrylic polymers' T_c values. This estimation was done by averaging the ΔH_p and ΔS_p values between each successive oligomer up to the tetramer (Table S2†), where the beginnings of chain-entanglement and favorable intra-chain interactions were observed. The raw averages overestimate the stability of these structures for a well-studied polymer, PMMA, by -9.01 kcal/mol and -29.4 cal/mol K for ΔH_p and ΔS_p, respectively, which was subsequently used to adjust the averages for the polymer series as reported in Table 2. Specifically, for ΔH_p corrections a subtraction of 9.01 from the raw averages was applied, whereas for ΔS_p corrections, a division of the raw averages by 2.05 was applied. This hybrid correction method was shown to work the best on the basis of fitting the DFT calculations results against the full set of experimental data at various [M] concentrations (Fig. S1†) for our previously studied ring-opening polymerization of MBL.[48] While the accuracy of these estimations could be improved in the future by modeling and incorporating more vinyl polymers with known ΔH_p and ΔS_p values and experimenting with more expensive basis sets and functionals, the computationally estimated bulk T_c values of P(M)MBL (~400 °C for PγMMBL and ~500 °C for PMBL) are considerably higher than that PMMA (~300 °C), thus ruling out the alternative hypothesis that the much enhanced depolymerization selectivity of P(M)MBL relative to PMMA is due to their more favorable (lower) T_c values than PMMA. Note that the order of estimated T_c values of MBL > γMMBL > MMA is consistent with the observed reactivity and polymerizability trend following the same order.

3. Trapping macroradicals during PγMMBL depolymerization

To further shed light on the surperior depolymerization seletivity of PγMMBL, radical trapping studies were performed. The experiment was conducted such that the depolymerization of the PγMMBL prepared by the Lewis-acid catalyzed group-transfer polymerization (GTP) with known end groups (Figure 3) was initiated before being quenched with a potent radical trap, galvinoxyl, which traps the macroradicals and allows for analysis by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure 3). The presence of trapped tertiary macroradical was apparent from Figure 3, in addition to the undepolymerized PγMMBL chains, indicating that the depolymerization of PγMMBL followed a similar mechanism proposed for the PMMA depolymerization (Schemes 1 and 2). The results of this radical trapping experiment also suggest that the tertiary macroradical species formed in the depolymerization are more stable, as it is

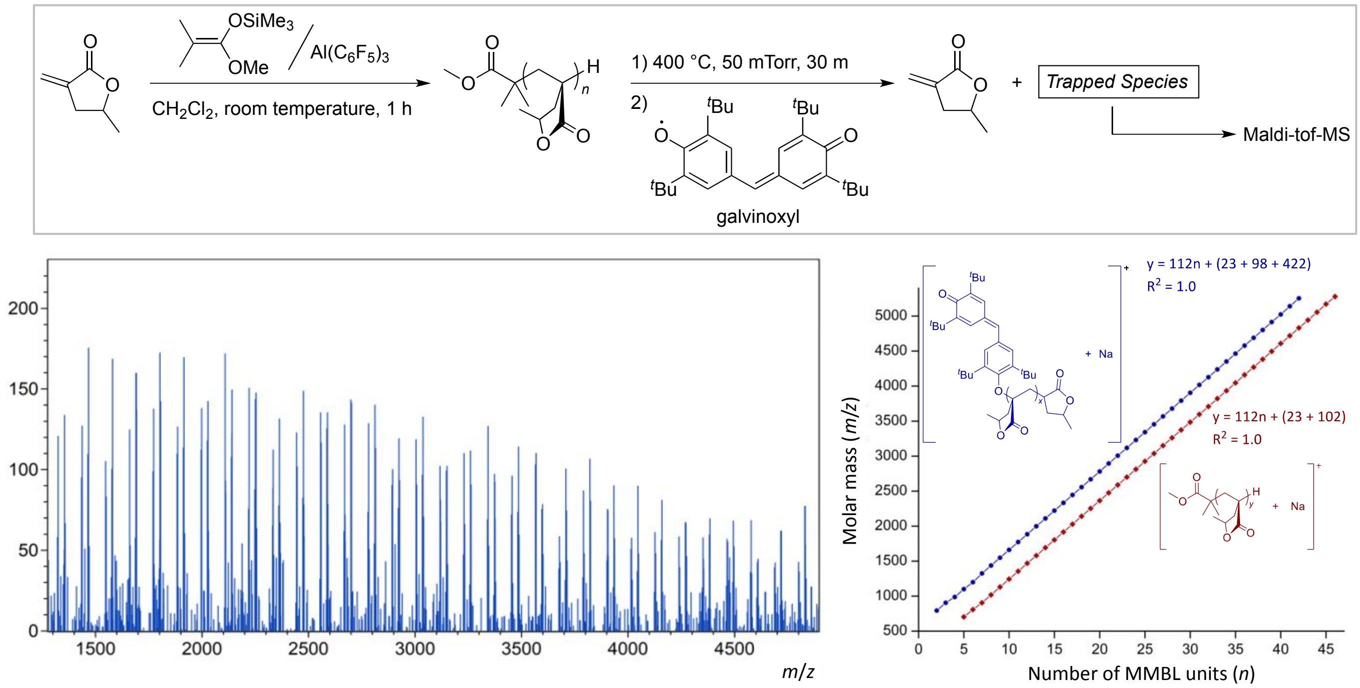


Figure 3 MALDI-TOF MS spectrum and chain-end analysis of polymer residues from depolymerization of PγMMBL synthesized by GTP.

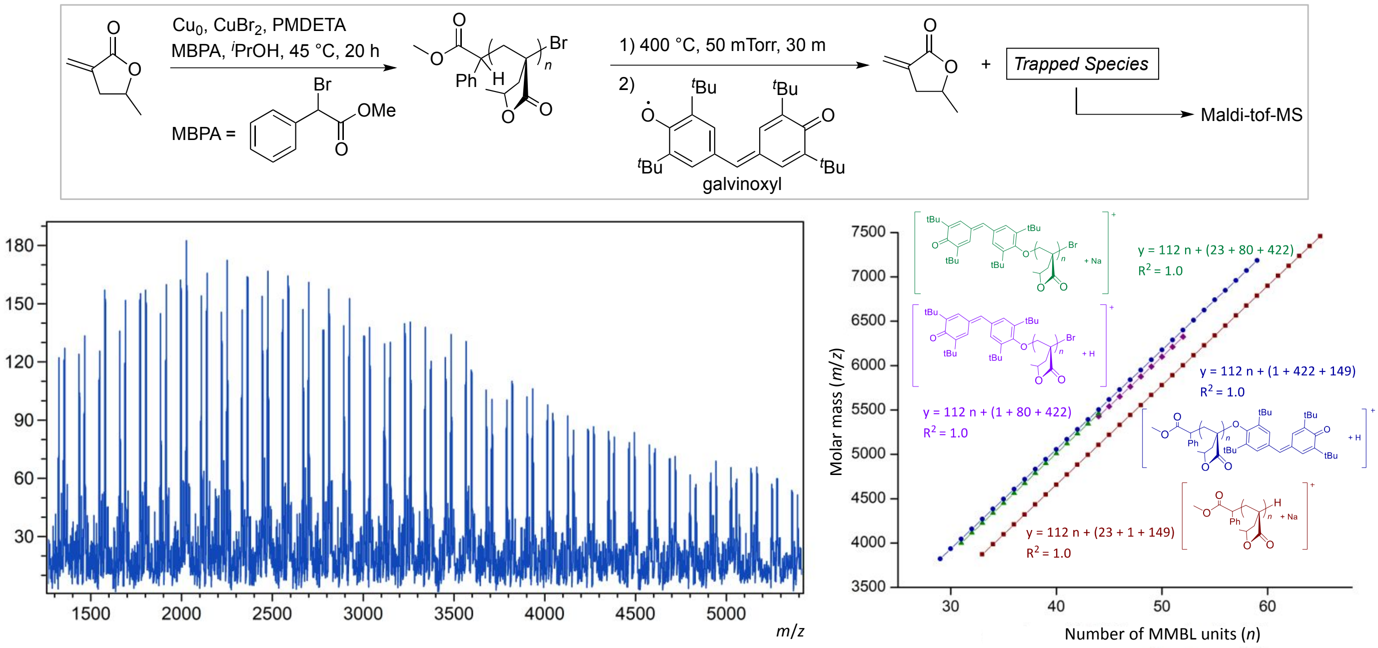


Figure 4 MALDI-TOF MS spectrum and chain-end analysis of polymer residues from depolymerization of PγMMBL synthesized by ATRP.

persistent enough to be quenched, whereas the primary macroradical species were too transient or the concentration is too low to be trapped for detection. This interesting result could be attributed to the stabilization of the highly reactive primary macroradical leading to more facile depolymerization, rendering the tertiary macroradical less productive, a scenario that is in stark contrast to that of PMMA depolymerization.

To detect primary macroradicals during the PγMMBL depolymerization through radical trapping experiments, we performed another study on the PγMMBL sample prepared by atom-transfer radical polymerization (ATRP). The quenched polymer carries bromide chain ends that were utilized to increase radical concentration *in situ* during the depolymerization to enable the persistence of the macroradicals. Trapping these radicals with galvinoxyl allowed for analysis of the trapped species with MALDI-TOF MS to reveal the identity of the species. The results depicted in Figure 4 indeed confirmed the presence of both primary and tertiary macroradicals, thus allowing for a more complete picture of the mechanism of depolymerization as shown in Scheme 2. In another radical trapping experiment, Cu^0 and $CuBr_2$ were added to the depolymerization of PγMMBL-Br to further increase radical concentration before quenching. This procedure enabled detection of an additional trapped species with two hydrogen end-groups (Figure S5), resulted presumably from hydrogen abstraction of other chains by the highly reactive primary macroradical.

4. Probing the stability of macroradicals in PγMMBL depolymerization

As both the tertiary and primary macroradicals generated in the depolymerization were successfully trapped and then observed in the MALDI-TOF spectra, we hypothesized that their stability could be modulated through addition of additives. First, destabilization of the primary macroradical via addition of Lewis acids would render the depolymerization to behave similarly to that of PMMA. As a result, the destabilization of the primary macroradical would allow for proliferation of side reactions, handing the monomer production roll back to the tertiary macroradical, overall decreasing monomer yield and purity while increasing carbonization. Lewis acids have recently been employed to facilitate the depolymerization of various renewable polyesters.[49,50] They catalyze the reaction by coordinating to the carboxyl groups and enable attack from more electron rich carboxyl groups. Therefore, we hypothesized that a Lewis acid would coordinate to the most electron rich carboxyl group in the lactone pendant groups of the PγMMBL, namely, the lactones closest to the primary macroradical chain end, which would enable the destabilization of the primary macroradical. Under the current standard conditions (400 °C, 50 mTorr, 3 h), the depolymerization of PγMMBL (M_n = 22.8 kDa) in the presence of Lewis acids such as $FeCl_3$ (0.05 – 0.1 mol% loading) and $ZnCl_2$ (1 – 5 mol% loading) noticeably lowered the monomer recovery yield to 20 – 37% for $FeCl_3$ and 10 – 46% for $ZnCl_2$. The purity of the recovered monomer was also negatively impacted. This finding appears to support the above hypothesis that primary macroradicals are the majority monomer producing units in the depolymerization.

To further probe the stability of the primary macroradicals derived from the PγMMBL depolymerization, we conducted mixed-feed depolymerization experiments (Table 3). We hypothesized that if either of the primary and tertiary macroradical species were in contact with other synthetic polymers, carbonization and side reactions would proliferate due to the macroradicals reacting with the other polymers. This, however, was not the case and carbonization was only observed in mixtures with PMMA (entry 1, Table 3) and PMBL (entry 2, Table 3), where the PMMA residue carbonized and the PγMMBL residue sublimed. This observation was attributed to the difference in T_c between the two polymers, where PMMA began to depolymerize first and PγMMBL after, leading to no inhibition in monomer production and rather, an increase in monomer production from PMMA due to the PγMMBL acting as mechanically fluidized reactor bed. When mixed with PS, PET [poly(ethylene terephthalate)], and PE, monomer production was either completely unhindered (entry 3, Table 3) or monomer was trapped in the viscous polymer melt (entries 4 and 5, Table 3), and no carbonization was observed. Interestingly, with mixtures of PMBL and PγMMBL, both polymers showed decreases in monomer production (entry 2, Table 3). This finding could be attributed to the similar reactivity of each polymer's macroradicals causing the quenching of PγMMBL macroradicals with PMBL macroradicals which lead to carbonization.

Table 3 Chemical recycling of PγMMBL from mixed plastic feeds

Entry number	Polymer additive [a]	γMMBL yield (%)	Additive monomer yield (%)
1	PMMA	74	67
2	PMBL	52	52
3	PS	74	-
4	PET	49	-
5	PE	44	-

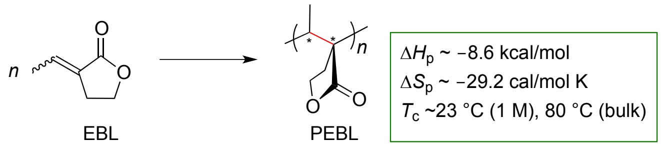
[a] Conditions: 1/1 weight mixed feed, 500 mg PγMMBL and 500 mg polymer additive, 400 °C, 50 mTorr, 3 h.

Conclusions

In summary, the results obtained from this comparative chemical recyclability study demonstrated that, under the current depolymerization conditions (400 °C, 50 mTorr, 3 h) without using specialized reactor setups, the depolymerization of PMMA recovered ~53% of the impure MMA, leaving ~47% of PMMA to carbonize into intractable char. In sharp contrast, the depolymerization of vinyl lactone acrylic bioplastics, especially PγMMBL, led to recovery of the pure monomer γMMBL in 76% isolated yield. Importantly, the depolymerization is devoid of carbonization, and the residue is that of incompletely depolymerized oligomers with a total mass balance. Hence, it is conceivable that, with a more effective depolymerization setup or recycling of the oligomers, achieving quantitative monomer recovery with high monomer purity in the chemical recycling of P(M)MBL is feasible.

Multiple experiments and DFT calculations were designed to help understand the origin of their sharp chemical recyclability differences between these two types of acrylic plastics, namely PMMA with open, linear ester pendant groups, and P(M)MBL with closed, cyclic ester (lactone) pendant groups. DFT calculations estimated that both PMBL and PγMMBL actually have considerably higher T_c values than PMMA (by 200 and 100 °C, respectively), thus ruling out the hypothesis that the enhanced recyclability of P(M)MBL is due to their more favorable T_c features. Next, the evidence accumulated through trapping and analysis of macroradicals generated during the depolymerization, as well as probing the stability of macroradicals using Lewis acid additives and mixed feed plastics, suggests that the difference in selectivity for monomer production between PMMA and P(M)MBL is due to the linear ester and cyclic lactone-imparted difference in stability and monomer-production roles of primary and tertiary macroradicals generated in the random chain scission process. In the case of PMMA depolymerization, tertiary macroradicals lead to more monomer production, while the unstable, highly reactive primary macroradicals undergo unproductive side reactions, lowering the overall yield and purity of the recovered MMA. In contrast, the stabilization of the highly reactive primary macroradicals provided by the lactone moiety in the case of P(M)MBL renders both primary and tertiary macroradicals to be productive in monomer reformation, thus suppressing the side reactions for reforming the pure monomer.

As vinyl-addition polymers, the bulk T_c's of PMMA (~300 °C) and PγMMBL (~400 °C) are still high, requiring high energy input for their chemical recycling. It is known that substituting the α-methyl group in PMMA with the ethyl group led to low T_c acrylic polymer, poly(methyl ethacrylate) (PMEA),[51,52] with a reported bulk T_c of only 82 °C, thus drastically lowering the T_c of the acrylic polymer by more than 200 °C relative to PMMA. For the lactone-bearing acrylic polymer, introducing of the methyl group to the exocyclic methylene moiety predicted a novel low T_c (80 °C) vinyl lactone acrylic bioplastic, PEBL (Scheme 3). Coupled with the macroradical stabilizing lactone function, the low T_c PEBL could be readily recyclable under relatively mild conditions to recover monomer in high selectivity and purity. Experimentation to materialize this potential is underway.



Scheme 3 Predicted low T_c vinyl lactone acrylic polymer PEBL that could be depolymerized under mild conditions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Table of Content Entry for

High chemical recyclability of vinyl lactone acrylic bioplastics

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Synopsis: Despite having higher thermostability than petroleum-based acrylic plastic poly(methyl methacrylate), biomass-derived vinyl lactone acrylic bioplastics can be depolymerized to their monomers in a simple distillation apparatus with greater selectivity, yield and purity than their petroleum counterpart.