

Zinc-Mediated Allylation-Lactonization One-Pot Reaction to Methylene Butyrolactones: Renewable Monomers for Sustainable Acrylic Polymers with Closed-Loop Recyclability

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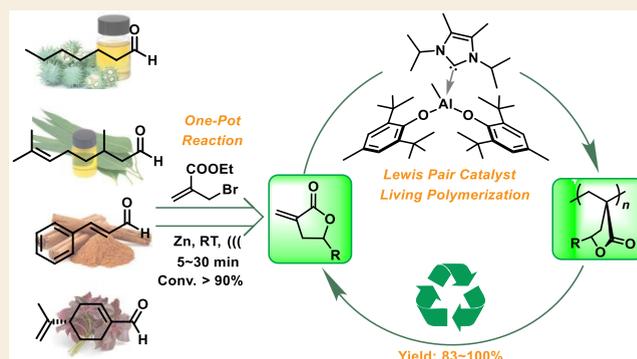
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ABSTRACT: Despite biomass-derived methylene butyrolactone monomers having great potential in substituting the petroleum-based methacrylates for synthesizing the sustainable acrylic polymers, the possible industrial production of these cyclic monomers is unfortunately not practical due to moderate overall yields and harsh reaction conditions or a time-consuming multistep process. Here we report a convenient and effective synthetic approach to a series of biomass-derived methylene butyrolactone monomers via a zinc-mediated allylation-lactonization one-pot reaction of biorenewable aldehydes with ethyl 2-(bromomethyl)acrylate. Under simple room-temperature sonication conditions, near-quantitative conversions (>90%) can be accomplished within 5–30 min, providing pure products with high isolated yields of 70–80%. Their efficient polymerizations with a high degree of control and complete chemoselectivity were enabled by the judiciously chosen Lewis pair catalyst based on methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) [MeAl(BHT)₂] Lewis acid and 3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I^tPr) Lewis base, affording new poly(methylene butyrolactone)s with high thermal stability and thermal properties tuned in a wide range as well as pendant vinyl groups for postfunctionalization. Through the development of an effective depolymerization setup (370–390 °C, ca. 100 mTorr, 1 h, a muffle furnace), thermal depolymerizations of these polymers have been achieved with monomer recovery up to 99.8%, thus successfully constructing sustainable acrylic polymers with closed-loop recyclability.

KEYWORDS: Sustainable polymer, Closed-loop recyclability, Biorenewable, Controlled/living polymerizations, Lewis pair polymerization, Postfunctionalization



INTRODUCTION

The current production and disposal of synthetic polymers follows a linear-economy model comprising a “fossil, take, make, use, dispose”, which not only rapidly depletes finite natural resources but also creates postconsumer polymer wastes causing both economic loss and negative environmental impacts.^{1–4} An important approach that holds great potential to combat the above crisis is the development of sustainable polymers^{5–7} that are generally derived from renewable feedstocks^{8,9} and exhibit closed-loop recyclability, in particular, through chemical recycling to their monomers (M) for repolymerization to virgin-quality polymers.^{10–13}

Acrylic polymers, such as poly(methyl methacrylate) (PMMA), are the industrially important thermoplastics. To replace these petroleum-based polymers with those derived from renewable resources, increasing attention has been paid to biomass-derived methylene butyrolactones, which are generally described as the cyclic analogue of methyl methacrylate (MMA).^{14–23} The most studied methylene butyrolactones include α -methylene- γ -butyrolactone (MBL,

also known as tulipalin A),^{15,16} γ -methyl- α -methylene- γ -butyrolactone (γ -MMBL),^{17–20} and β -methyl- α -methylene- γ -butyrolactone (β -MMBL)²¹ (Scheme S1). The rigid cyclic units in methylene butyrolactones can impart significant enhancements in the material properties of the resultant polymers as compared to PMMA [glass transition temperature (T_g): ~ 100 °C], with increased thermal and optical properties as well as resistance to solvent, heat, and scratching.¹⁴ For example, PMBL displays a high T_g of 195 °C,¹⁵ while P γ MMBL and P β MMBL exhibit even higher T_g values of 227 and 288 °C,²¹ respectively. More importantly, a recent study by Chen and co-workers has demonstrated that the thermal

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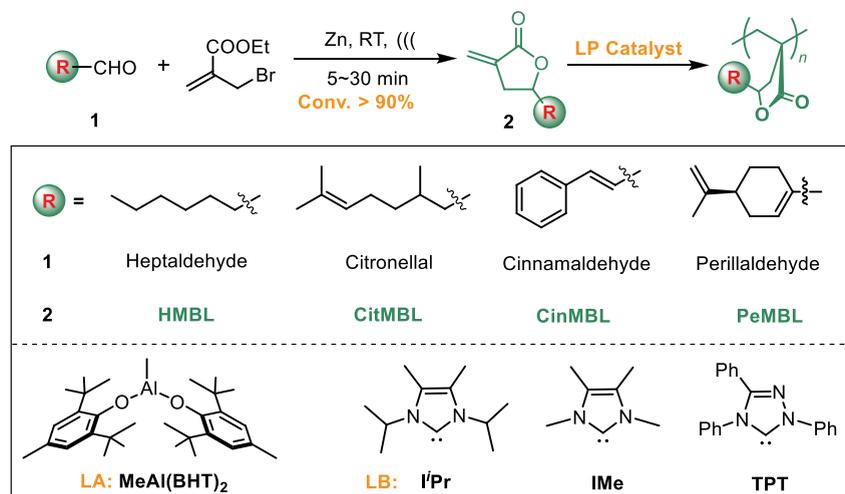
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Scheme 1. Synthetic Route to Methylene Butyrolactones from Biorenewable Aldehydes Via a Zinc-Mediated Allylation-Lactonization One-Pot Reaction as well as the Structures of Monomers, the Resulting Polymers, LA, and LBs Used in This Work



depolymerization of PMBL and P γ MMBL can lead to a noticeable increase of pure monomer recovery [yield: γ -MMBL (76%), MBL (65%)], in sharp contrast to ~53% of the impure monomer recovery in the PMMA depolymerization under the same conditions (400 °C, 50 mTorr, 3 h, glassware distillation apparatus).²⁴ These thermal depolymerizations are proposed to proceed via tertiary and primary macroradicals formed by chain-end and random chain scissions, respectively.^{25–28} The enhanced depolymerization selectivity in PMBL and P γ MMBL should be attributed to the suppression of side reactions on account of the stabilization of highly reactive primary macroradicals by the lactone moiety that renders both primary and tertiary macroradicals to be productive in monomer formation, in comparison to PMMA depolymerization, where the monomer formation is mainly achieved by the tertiary macroradicals, while the unstable primary macroradicals are susceptible to undergoing side reactions to eliminate undesirable products (e.g., CO, CO₂, and methyl and methoxy radicals).²⁴

Despite biomass-derived methylene butyrolactones having great potential in substituting the petroleum-based methacrylate monomers for synthesizing the sustainable acrylic polymers with intriguing physical properties and enhanced depolymerization selectivity, the possibly industrial production of these cyclic monomers is unfortunately not practical because the currently adopted synthetic routes starting from itaconic acid (for MBL²⁹ and β -MMBL³⁰) and levulinic acid (for γ -MMBL^{31–33}) (Scheme S1) gave rise to moderate overall yields (typically ~50%) and required harsh reaction conditions (500 psi, 400 °C, γ -MMBL) or a time-consuming multistep process (β -MMBL). To realize the possibly industrial applicability of methylene butyrolactone-based polymers, it is highly desirable to develop a more convenient and effective synthetic process of these monomers. Herein, we report the zinc-mediated allylation-lactonization one-pot reaction for the highly efficient preparation of biomass-derived methylene butyrolactone monomers with high isolated yield (70–80%) under simple room-temperature sonication conditions (Scheme 1). Through the judiciously chosen Lewis pair (LP) polymerization catalyst and the development of an effective depolymerization setup, a series of new sustainable acrylic polymers with controlled

structures and closed-loop recyclability has been successfully constructed.

RESULTS AND DISCUSSION

Preparation of Methylene Butyrolactone Monomers and Establishment of Their Controlled Polymerizations by LP Catalyst

As described above, the currently adopted synthetic routes (Scheme S1) to methylene butyrolactone monomers generally encountered the challenges. Currently, the structural motif of methylene butyrolactone has been observed in more than 3000 known natural products with diverse useful biological activities, which has attracted broad interests from different research areas (e.g., natural product chemistry, biology, and pharmacology) to develop methodologies to construct relevant structures.^{34,35} The most convergent approach is the allylation-lactonization reaction (Scheme S1) by the addition of 2-(alkoxycarbonyl)allyl organometallic reagent made from boron, silicon, tin, zinc, nickel, indium, magnesium, ruthenium, chromium, etc. with an aldehyde and, subsequently, spontaneous cyclization.^{36–38} Recently, Williams and Ley et al. established a zinc-mediated allylation-lactonization one-pot reaction under a sonication condition at room temperature (RT), which provided a relatively simple and green method for constructing the structural motif of methylene butyrolactone.³⁸ In this work, we successfully applied this method to synthesize a series of biomass-derived methylene butyrolactones (Scheme 1), including γ -hexyl- α -methylene- γ -butyrolactone (HMBL), γ -(2,6-dimethylhept-5-en-1-yl)- α -methylene- γ -butyrolactone (CitMBL), γ -(*E*)-styryl- α -methylene- γ -butyrolactone (CinMBL), and γ -(-)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)- α -methylene- γ -butyrolactone (PeMBL), from one-pot reactions of ethyl 2-(bromomethyl)acrylate with biorenewable heptaldehyde, citronellal, cinnamaldehyde, and (-)-perillaldehyde, respectively, in the presence of zinc powder. Recently, ethyl 2-bromomethacrylate was reported to be synthesized by using ethyl acrylate as the starting material through two high-yield steps, including the conversion of ethyl acrylate into ethyl 2-(hydroxymethyl) acrylate via the reaction with paraformaldehyde in the presence of 1,4-

Table 1. Results of Methylene Butyrolactones by MeAl(BHT)₂-Based LP Catalytic Systems^a

run	LB	M	[M] ₀ /[LA] ₀ /[LB] ₀	[M] ₀	time (min)	Conv ^b (%)	M _n ^c (kg/mol)	<i>D</i> ^c	I* ^d (%)
1	TPT	HMBL	500:4:1	1.65	20	>99	295.1	1.18	30.8
2	IMe	HMBL	500:4:1	1.65	10	>99	66.1	1.20	137.7
3	IPr	HMBL	500:4:1	1.65	6	>99	120.1	1.12	76.0
4	IPr	HMBL	500:2:1	1.65	10	>99	191.1	1.02	47.6
5	IPr	HMBL	500:0:1	1.65	300	10			
6		HMBL	500:2:0	1.65	1440	0			
7	IPr	HMBL	350:4:1	1.65	1	>99	65.9	1.03	97.0
8	IPr	HMBL	800:4:1	1.65	180	>99	210.0	1.50	70.0
9	IPr	CinMBL	300:4:1	1.65	5	>99	72.6	1.05	92.0
10	IPr	CinMBL	300:4:1	0.83 ^e	10	>99	55.8	1.07	107.8
11	IPr	PeMBL	300:4:1	1.65	2	>99	68.6	1.10	95.6

^aConditions: temperature = 25 °C, toluene as the solvent. ^bMonomer conversion measured by ¹H NMR spectroscopy. ^cNumber-average molecular weight (*M_n*) and molecular weight distribution (*D* = *M_w*/*M_n*) determined by GPC at 40 °C in THF coupled with a multi(18)-angle light scattering detector and a refractive-index detector. ^dInitiation efficiency (*I**)% = *M_n*(calcd)/*M_n*(exptl) × 100, where *M_n*(calcd) = [MW(M)] × ([M]₀/[LB]₀) × conversion% + MW(end groups). ^eThe utilization of low monomer concentration is due to the relatively poor dissolvability of CinMBL in toluene.

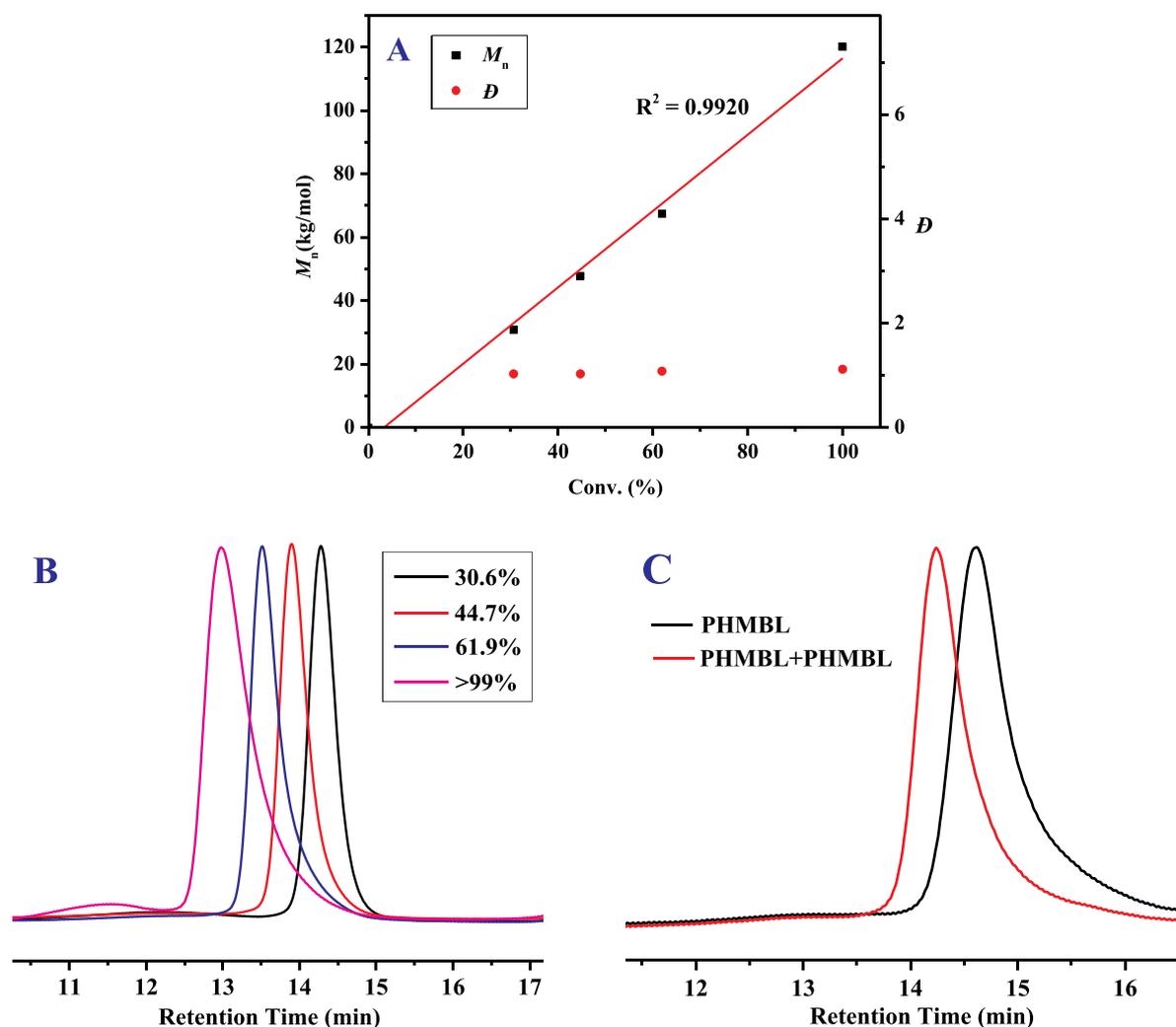


Figure 1. (A) Plots of *M_n* and *D* for the PHMBL vs monomer conversion (%) (Conv% = 30.6, 44.7, 62.0, >99%; *M_n* = 30.8, 47.8, 67.4, 120.1 kg/mol; *D* = 1.03, 1.03, 1.08, 1.12); (B) GPC curves for PHMBLs produced at different monomer conversions; (C) GPC curves of PHMBL samples obtained from chain extension experiment: *M_n* = 16.6 kg/mol, *D* = 1.04 (first batch); *M_n* = 26.2 kg/mol, *D* = 1.04 (second batch).

diazabicyclo[2.2.2]octane (DABCO) at RT (yield = 93%), which was followed by a bromination reaction (yield = 90%) (Scheme S1).^{56,57} It is worth pointing out that ethyl acrylate is

the downstream chemical of 3-hydroxypropionic acid, which is available from sugar and was classified recently by the United States Department of Energy as one of the top 10 biomass-

derived compounds best suited to replace petroleum-derived chemicals.⁵⁸ Therefore, ethyl 2-bromomethacrylate also has the potential as a biomass-derived compound from a renewable source. Noteworthy is that near-quantitative conversions of aldehydes into methylene butyrolactones can be achieved within just 5–30 min of sonication at RT [HMBl: Conv = 90.0% (5 min), CitMBl: Conv = 91.0% (5 min), CinMBl: Conv = 92.2% (30 min), PeMBl: Conv = 92.6% (10 min)]. After flash column chromatography, pure monomers were obtained with a high yield of 70–80% (Figures S1–S8).

The rapid and efficient preparation of methylene butyrolactone monomers with different substituents at the γ -position would offer a promising opportunity to sustainable acrylic polymers with the physical properties tuned in a wide range. Although various polymerization techniques have been employed or developed to polymerize methylene butyrolactones, such as radical,¹⁵ anionic,^{16,20} group-transfer,^{17,18} zwitterionic,¹⁹ and coordination²¹ polymerizations, controlled polymerizations of these monomers are scarce and not well-established relative to their linear analogue of methacrylates due to the much more active exocyclic double bond as a result of the ring strain and the fixed *s-cis* conformation enolate.¹⁴ Lewis pair polymerization (LPP),^{39–43} an emerging polymerization technique catalyzed by Lewis pair (LP), has been shown to be an effective strategy for polymerizing polar vinyl monomers (e.g., MMA, MBl, and γ -MMBl),^{44–47} thanks to a synergistic/cooperative monomer activation by both Lewis acid (LA) and Lewis base (LB). We hypothesized that the efficient and controlled polymerizations of these methylene butyrolactones (HMBl, CitMBl, CinMBl, PeMBl) synthesized in this work could be achieved if an LP catalytic system could be judiciously chosen via balancing the Lewis acidity, Lewis basicity, and steric effects.

In the initial study, sterically encumbered methylaluminum bis(2,6-*di*-*tert*-butyl-4-methylphenoxide) [MeAl(BHT)₂, Scheme 1], a privileged LA that has been utilized for controlled/living LPPs of various methacrylates and polar divinyl monomers^{48–51} as well as efficient LPPs of biomass-derived polar vinyl monomers,^{47,52–55} was first selected to construct LP catalysts with N-heterocyclic carbenes (NHCs, Scheme 1) for the polymerization of HMBl at RT. When keeping [HMBl]₀/[MeAl(BHT)₂]₀/[LB]₀ at a fixed ratio of 500:4:1, different NHCs, including 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (TPT), 1,3,4,5-tetramethyl-2-ylidene (IMe), and 3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I^tPr), were all active toward HMBl polymerization, with the activity following the order of TPT < IMe < I^tPr (Table 1, Runs 1–3). This order is in fact proportional to the nucleophilicity of NHC. Besides serving as a nucleophilic initiator to determine the activity and initiation efficiency, NHC also plays an important role in constructing a contact ion pair between an imidazolium-initiated chain end and an enolaluminate species during the propagation stage to affect both activity and the controllability of polymerization when relatively nonpolar toluene is used as the solvent.³⁹ Among three NHCs evaluated, MeAl(BHT)₂/I^tPr renders the best control of the polymerization, as evidenced by the lowest dispersity of the resultant polymer (\mathcal{D} = 1.12) and the acceptable initiation efficiency (I^* = 76.0%). In contrast, the lowest I^* (30.8%) in MeAl(BHT)₂/TPT-mediated LPP should be attributed to the weakest nucleophilicity of TPT that hampers the conjugate-addition initiation. Switching to MeAl(BHT)₂/IMe-mediated LPP led to the broadest \mathcal{D} (1.20)

and a high I^* value that was over 100.0% (137.7%), presumably due to the contact ion pair formed by the sterically less-demanding IMe, which cannot effectively suppress the termination and chain transfer to monomer²⁰ side reactions. As a result, both MeAl(BHT)₂/TPT and MeAl(BHT)₂/IMe LP catalysts led to the deviation from a controlled/living polymerization.

The living nature of MeAl(BHT)₂/I^tPr catalyst can be clearly confirmed by the observation of a linear growth of PHMBl M_n with the increase of monomer conversion (Figure 1A) as well as the gradual shift of gel permeation chromatography (GPC) curves of these PHMBl samples to the higher molecular weight (MW) region accordingly with narrow and unimodal distributions (\mathcal{D} : 1.03–1.12) maintained during the polymerization (Figure 1B). The successful chain extension polymerization of HMBl achieved by MeAl(BHT)₂/I^tPr can further confirm the living nature of this LPP. After the first batch of HMBl (100 equiv) was completely converted into PHMBl, the polymerization was immediately resumed once another batch of HMBl (100 equiv) was added. The GPC curve of PHMBl produced by the chain extension experiment showed a narrow and unimodal distribution without a detectable low MW tail (Figure 1C). Moreover, as shown in Figure 2, matrix-assisted laser

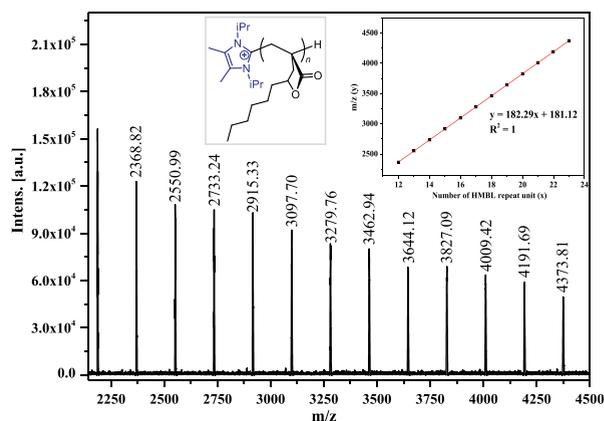


Figure 2. MALDI-TOF MS spectrum of PHMBl produced by MeAl(BHT)₂/I^tPr and a plot of m/z values (y) vs the number of PHMBl repeat units (x) for molecular ion peaks.

desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) of the low-MW PHMBl sample only showed one set of molecular ion peaks, which was attributed to linear PHMBl with a H-terminated chain end derived from a quenching process and I^tPr imidazolium-initiated chain end formed by the conjugate addition of I^tPr LB onto LA-activated HMBl monomer. Such a chain-end structure further demonstrates that MeAl(BHT)₂/I^tPr-catalyzed LPP proceeds in a living manner through an exclusive chain initiation without a backbiting termination side reaction.

It is worth pointing out that increasing the MeAl(BHT)₂/I^tPr ratio from 2:1 to 4:1 not only brought about a noticeable increase of activity but also was critical for rendering the polymerization with high I^* (Table 1, Run 3 vs 4). The utilization of abnormal 4 equiv of LA should be on account of sterically more demanding structures of current methylene butyrolactone monomers, relative to MMA, MBl, and γ -MMBl, which require additional LA for fully activating the

monomer and stabilizing the active propagation species to achieve an efficient and controlled polymerization. The attempt to polymerize HMBL by I^*Pr LB or $MeAl(BHT)_2$ LA alone was unsuccessful, which resulted in sluggish or inactive polymerization (Table 1, Runs 5–6), revealing the importance of bimolecular cooperative activation. When the $[HMBL]_0/[MeAl(BHT)_2]_0/[I^*Pr]_0$ ratio was decreased from 500:4:1 to 350:4:1, a fast and controlled polymerization was observed, which consumed all monomer in just 1 min and afforded PHMBL with a very low \bar{D} of 1.03 at a near-quantitative I^* value of 97.0% (Table 1, Run 7). High- M_n PHMBL up to 210.0 kg/mol can be readily prepared by employing a low catalyst loading ($[HMBL]_0/[MeAl(BHT)_2]_0/[I^*Pr]_0 = 800:4:1$, Table 1, Run 8) despite having a relatively broad \bar{D} of 1.50.

Noteworthy is that the $MeAl(BHT)_2/I^*Pr$ LP catalyst can also promote controlled polymerizations of the other biomass-derived methylene butyrolactones (CitMBL, CinMBL, PeMBL, Table 1, Runs 9–11). At the $[monomer]_0/[MeAl(BHT)_2]_0/[I^*Pr]_0$ ratio of 300:4:1, these polymerizations occurred rapidly with quantitative monomer conversions accomplished within 2–10 min, producing poly(methylene butyrolactone)s with predictable M_n s, low \bar{D} values (1.05–1.10, Figures S9–S11), and near-quantitative I^* values (92.0–107.8%). The living nature of the LPP of PeMBL was clearly evidenced by MALDI-TOF MS (Figure 3), which indicated

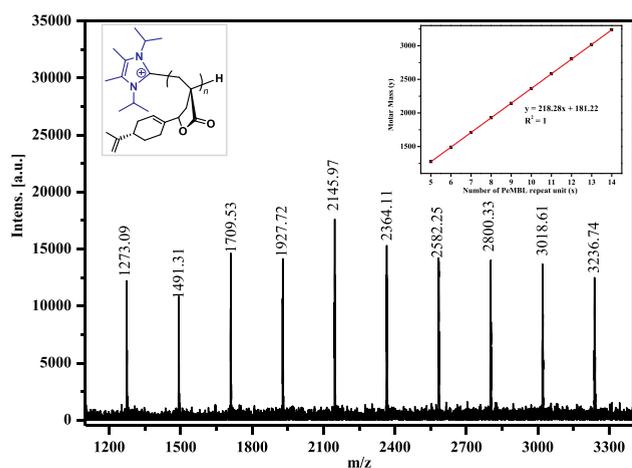


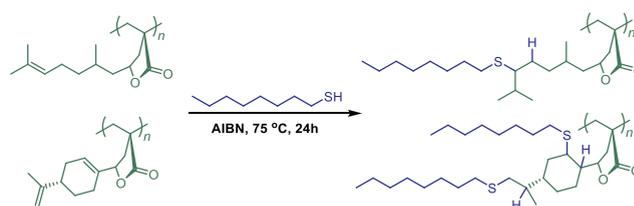
Figure 3. MALDI-TOF MS spectrum of PPeMBL and plots of m/z values (y) vs the number of PPeMBL repeat units (x) for molecular ion peaks.

exclusive chain initiation and undetectable chain termination. Moreover, NMR measurements (Figures S12–S19) of the obtained polymers confirmed that LPPs of these methylene butyrolactones proceed through a chain-growth mechanism by a conjugate addition of an α -methylene double bond, rather than through the ring-opening process of a five-membered lactone ring. The resultant polymers exhibited different dissolvability, depending on the substituents at the γ -position of monomers: PHMBL and PCitMBL are soluble in toluene, while PCinMBL and PPeMBL are insoluble. When switching to polar solvents (e.g., CH_2Cl_2 , $CHCl_3$, THF, DMF), good dissolvability of these new polymers can be observed.

Intriguingly, completely chemoselective polymerizations of CitMBL, CinMBL, and PeMBL have been achieved, where the α -methylene double bond conjugated with the carbonyl moiety

is selectively polymerized, while the vinyl group at γ -position remains unreacted [Figures S14–S19, $(CH_3)_2C=CH-$ in PCitMBL: δ 5.07 ppm (1H NMR), δ 131.40, 124.35 ppm (^{13}C NMR); $-CH=CH-$ in PCinMBL: δ 6.67, 6.15 ppm (1H NMR), δ 128.70, 126.85 ppm (^{13}C NMR); $>C=CH-$ and $CH_2=C<$ in PPeMBL: δ 5.82, 4.72–4.76 ppm (1H NMR), δ 149.17, 133.34, 125.53, 109.11 ppm (^{13}C NMR)]. These pendant vinyl groups attached to every repeating unit on the main chain thus provide a convenient approach to functional or advanced acrylic polymers. For instance, postfunctionalization can be efficiently realized upon the utilization of a thiol–ene “click” reaction. Using α,α' -azobis(isobutyronitrile) (AIBN) as a thermal radical initiator, the reaction of PCitMBL or PPeMBL with 1-octanethiol at 72 °C for 24 h enabled the quantitative conversion of the pendant vinyl groups into the corresponding thioether groups (Scheme 2), as confirmed by

Scheme 2. Post-Functionalization of PCitMBL and PPeMBL by a Thiol–Ene Click Reaction



the disappearance of the vinyl group signals and the appearance of the signals for the newly formed thioether group at 2.47 ppm in 1H NMR spectra (Figures S20 & S21). Compared to PPeMBL, the GPC curves of postfunctionalized polymer PPeMBL-SR shifted to the higher MW region, while a narrow and unimodal distribution was retained (Figure S23). In addition, the disappearance of the $C=C$ stretching vibration (PCitMBL: 1673.42 cm^{-1} , PPeMBL: 1643.13 cm^{-1}) can further confirm the successful post-functionalization (Figures S24 & S25).

Thermal Properties of Poly(methylene butyrolactone)s and Their Thermal Recycling Behavior

Thermal properties of poly(methylene butyrolactone)s were examined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The second heating scans of DSC curves are depicted in Figure 4 (top). It was found that the glass transition temperatures (T_g s) can be tuned in a wide range from 84 to 206 °C, which were enhanced with an increase in the rigidity of the substituents at the γ -position, following the order of PCitMBL (84 °C) < PHMBL (123 °C) < PCinMBL (203 °C) < PPeMBL (206 °C). It is worth noting here that PCinMBL and PPeMBL exhibited higher T_g values than that of PMBL (195 °C)¹⁵ but a slightly lower value than that of $P\gamma$ MMBL (227 °C).²¹ As shown by TGA analysis (Figure 4, bottom), the current poly(methylene butyrolactone)s all exhibited high thermal stability with high onset degradation temperatures (T_d values, defined by the temperatures of 5% weight loss) ranging from 273 to 342 °C and high maximum degradation temperatures (T_{max} s, measured by the derivative TGA curves) ranging from 362 to 448 °C (Table 2). Except PPeMBL, which showed a two-step degradation profile ($T_{max1} = 362.84$ °C, $T_{max2} = 448.32$ °C), all other poly(methylene butyrolactone)s displayed a sharp, one-step degradation profile.

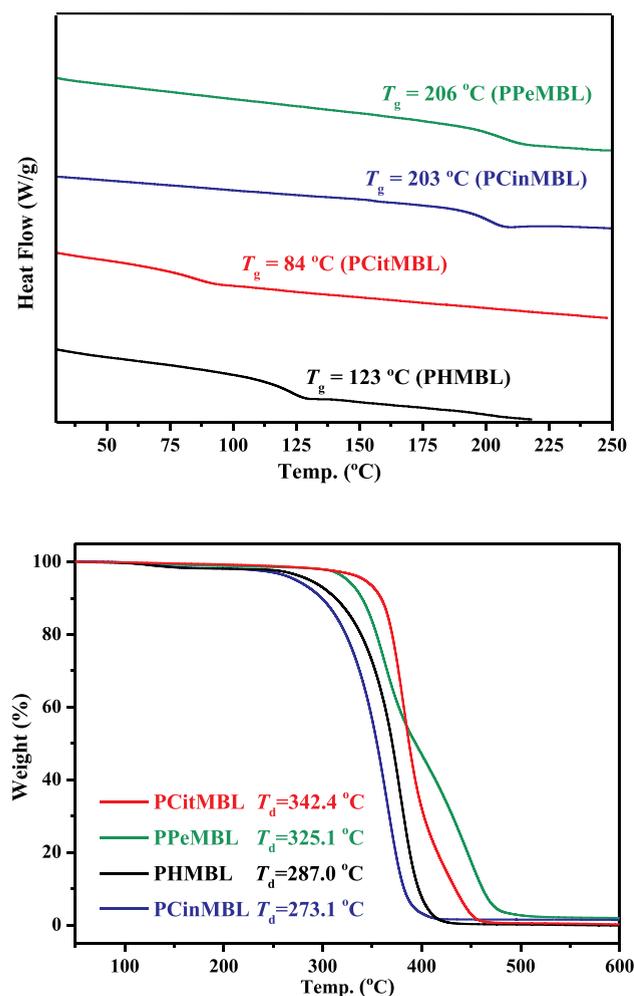


Figure 4. DSC (top) and TGA (bottom) curves for PHMBL (Table 1, run 7), PCitMBL (Table 1, run 9), PCinMBL (Table 1, run 10), and PPeMBL (Table 1, run 11).

Table 2. Results of Thermal Depolymerization of Acrylic Polymers^a

run	polymer	T_{max} (°C)	temp (°C)	yield (%)
1	PHMBL	377	310	17.4
2	PHMBL		330	34.0
3	PHMBL		370	99.8
4	PCitMBL	385	370	78.4
5	PCitMBL		390	93.8
6	PCinMBL	366	370	85.1
7	PCinMBL		390	93.6
8	PPeMBL	363 and 448	390	83.0

^aConditions: 50 mg of polymer sample, ca. 100 mTorr, 1 h.

Taking advantage of the one-step degradation profile, we hypothesized that the thermal recyclability of PHMBL, PCitMBL, and PCinMBL should be feasible if suitable conditions and setups were developed. In this study, a muffle furnace equipped with a temperature-controlled instrument and a glass container connected to a cold trap and vacuum was employed for a thermal recyclability experiment (see the Supporting Information). Once the bulk polymer in the glass container is depolymerized or degraded during the heating, the formed volatile products would be distilled off under the

vacuum and captured by the cold trap for further analysis. We first evaluated the thermal recyclability of PHMBL via heating at different temperatures under ca. 100 mTorr for 1 h. At the temperature of 310 °C (23 °C above T_d), only a small amount of yellowish liquid can be found in the cold trap, while a substantial amount of polymer was left in the glass container. Without any purification, the obtained liquid was weighted and analyzed by a ¹H NMR spectrum and a gas chromatography–mass spectrometer (GC-MS), which revealed that thermal depolymerization occurred during the heating and that pure HMBL monomer was formed despite a low yield of 17.4% (Table 2, Run 1). When the temperature was raised to 330 °C, a noticeable enhancement of monomer recovery to 34.0% was observed (Table 2, Run 2). Noteworthy is that thermal depolymerization at 370 °C not only rendered the quantitative monomer recovery (Table 2, Run 3) but also afforded the recycled monomer in a spectroscopically pure state (GC-MS: purity = 95.7%, Figures 5 and S26), which thereby demonstrates the complete thermal recyclability of the PHMBL. More importantly, this recovered monomer in the cooling trap can be repolymerized directly without any additional purification or drying, which achieved the same activity and similar I^* under the same conditions ($[HMBL]_0/[MeAl(BHT)_2]_0/[I^*Pr]_0 = 500:4:1$, 6 min, Conv > 99%, $I^* = 78.5\%$) as well as produced a polymer with an M_n of 115.9 kg/mol and a \bar{D} of 1.14 that is very close to those of the virgin polymer ($M_n = 120.1$ kg/mol, $\bar{D} = 1.12$, $I^* = 76.0\%$, Table 1, Run 3).

Compared to PHMBL, a higher temperature of 390 °C was necessary to achieve near-quantitative monomer recovery in the thermal depolymerizations of PCitMBL and PCinMBL (Table 2, Run 4 vs 5, Run 6 vs 7, Figures S27 & S28). Strikingly different from these three poly(methylene butyrolactone)s, heating PPeMBL at 390 °C for 1 h led to a decreased monomer recovery of 83.0% accompanied by relatively low monomer purity (Table 2, Run 8, Figure S29), which might be related to its two-step degradation profile in the TGA analysis. In contrast to previous thermal depolymerizations of PMMA (~53%, impure), PMBL (65%), and P γ MMBL (76%) using glassware distillation apparatus,²⁴ the reason for the improved monomer recovery and purity in the current study is twofold: (1) the stabilization of highly reactive primary macroradicals by the lactone moiety, which suppresses undesirable side reactions and renders both primary and tertiary macroradicals to be productive in monomer formation²⁴ and (2) the development of a more effective depolymerization setup, which avoids the formation of intractable char and the sublimation of oligomeric residue.

CONCLUSIONS

In summary, a series of biomass-derived methylene butyrolactone monomers (HMBL, CitMBL, CinMBL, and PeMBL) have been synthesized in this work via a zinc-mediated allylation-lactonization one-pot reaction of biorenewable aldehydes with ethyl 2-(bromomethyl)acrylate under simple room-temperature sonication conditions. This convenient and effective synthetic method enables near-quantitative conversions (>90%) accomplished within 5–30 min, providing the pure products with high isolated yields of 70–80%. Among the LP catalysts evaluated, MeAl(BHT)₂/I^{*}Pr has been demonstrated to be the best catalyst for the efficient and controlled/living polymerizations of these monomers, affording new poly(methylene butyrolactone)s with high thermal stability

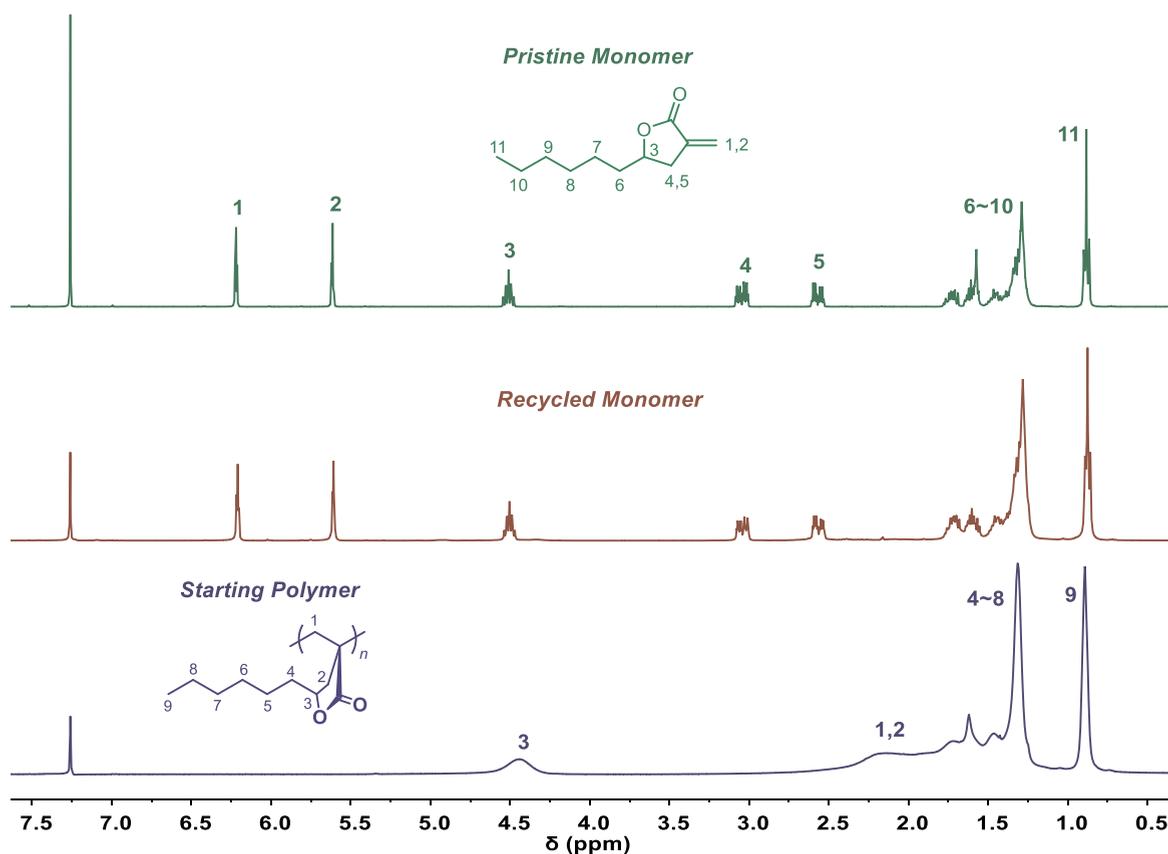


Figure 5. Overlays of ^1H NMR spectra (RT, CDCl_3): (top) pristine HMBL monomer; (middle) recycled HMBL monomer; (bottom) starting PHMBL used for depolymerization.

and thermal properties tuned in a wide range (T_g : 84–206 $^\circ\text{C}$). In addition, this catalyst also can mediate completely chemoselective LPPs of CitMBL, CinMBL, and PeMBL to produce vinyl-functionalized polymers that can undergo postfunctionalization via a thiol–ene click reaction. It is worth pointing out that, despite free NHCs (e.g., $i\text{Pr}$) being sensitive to the air and moisture, recent reports showed that CO_2 -protected NHC adducts are readily formed by the reaction of virtually all types of NHCs with CO_2 , and their thermolabile property leads to the reformation of free NHCs via decarboxylation,^{59–61} which not only provides an opportunity to overcome the disadvantage of susceptible (free) NHCs but also can act as thermally latent precatalysts for initiating polymerizations at industrial-relevant conditions. Through the development of an effective depolymerization setup (370–390 $^\circ\text{C}$, ca. 100 mTorr, 1 h, a muffle furnace), thermal depolymerization of these polymers has been achieved without the formation of intractable char and the sublimation of oligomeric residue. In particular, the thermal depolymerizations of PHMBL, PCitMBL, and PCinMBL back into their monomers are quantitative (99.8%) or near-quantitative (94%) with spectroscopical purity, thus demonstrating the complete thermal recyclability of these polymers. Overall, we anticipate that the rapid and facile preparation of methylene butyrolactone monomers with different substituents at the γ -position would offer a promising opportunity to form new sustainable acrylic polymers with closed-loop recyclability and intriguing physical properties tuned in a wide range.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acspolymersau.2c00001>.

Materials, reagents, experimental details including the general procedures for monomer synthesis, polymerization, thermal depolymerization, and post-functionalization via the thiol–ene click reaction, characterizations, comparison of previous work on the synthesis of MBL, β -MMBL, γ -MMBL from itaconic acid and levulinic acid as well as synthetic mechanism to methylene butyrolactones from biorenewable aldehydes via zinc-mediated allylation-lactonization one-pot reaction in this work, ^1H and ^{13}C NMR spectra for methylene butyrolactone monomers and corresponding poly-(methylene butyrolactone)s, GPC curves of PCitMBL, PCinMBL, and PPeMBL polymers, ^1H and ^{13}C NMR spectra, GPC curves, and FT-IR spectra for postfunctionalized polymers, GC-MS chromatogram of recovered monomer, and thermal recyclability of PCitMBL, PCinMBL, and PPeMBL polymers (PDF)

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Notes

The authors declare no competing financial interest.

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