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Strong, Fully Recyclable, and Thermoplastic Ultrahigh-Molecular-Weight Poly(tetramethyl glycolide)

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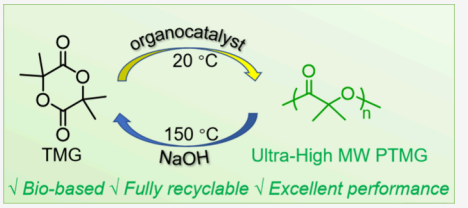
ABSTRACT: Advancing chemically circular, biobased polymers is essential for achieving a sustainable circular plastic economy. Poly(L-lactic acid) (PLLA) provides a renewable and chemically circular alternative to petroleum-based plastics, but its low strength and high gas permeability and high reactive C−H bonding at the α-position of the C═O group in PLLA limit its applicability. Poly(tetramethyl glycolide) (PTMG), an α,α'-dimethyl-substituted PLLA, shows promise as a circular polymer but suffers from inadequate tensile strength due to the low molecular weights produced by current uncontrolled anionic ring-opening polymerization methods. Here, we report the first effective living organopolymerization of the biorenewable tetramethyl glycolide (TMG) to synthesize ultrahigh-molecular-weight (M_n up to 1139 kg mol^{-1}) metal-free PTMG. The synthesized polymer exhibits improved tensile strength (ultimate strength of 80.0 MPa and modulus of 4.9 GPa), along with superior gas barrier and transparency properties relative to commercialized PLLA (M_n = 58.6 kg mol^{-1}), and it can be depolymerized to fully recover the monomer (quantitative TMG recovery) under mild conditions (using a catalyst at 150 °C).



INTRODUCTION

Plastic products are essential in modern life, but their linear life cycles and poor end-of-life management lead to environmental issues like waste buildup and resource depletion.[1−4] Closed-loop chemical cycling offers a solution by depolymerizing materials into their original monomers or oligomers for repolymerization.[5−20] Enhancing polymer sustainability can also be achieved by using bioderived monomers and feedstocks, particularly nonfood sources.[21] Poly(L-lactic acid) (PLLA), a bioderived polymer, is extensively utilized owing to its cost-effectiveness, processability, and advantageous properties.[22−28] However, the highly reactive C−H bonding at the α-position of the C═O group in PLLA poses a challenge for monomer recovery, leading to diastereoisomers, meso, and *D*,*D*-lactides that reduce the crystallinity and melting point of the regenerated PLLA.[22−24] To address the aforementioned issues, two strategies have been devised: the creation of efficient catalytic systems for depolymerization of PLLA under mild conditions and the removal of highly reactive C−H bonds. Thus, several families of catalyst systems for chemical recycling of PLLA have recently been developed, such as $Zn(OAc)_2$,[25] $Sn(Oct)_2$,[26] $ZnCl_2$/poly(ethylene glycol),[27] $Sn(Oct)_2$/glycerolethoxylate,[28] and [1,5-*a*]pyrid-3-yl)phenolate zinc.[29] Ninety-two percent yield and 99% selectivity with extreme activity of 2800 h^{-1} for the depolymerization of PLLA to LLA were accomplished by $Sn(Oct)_2$/glycerolethoxylate.[28] Additionally, the limited mechanical strength (ultimate strength ∼28 to 50 MPa, modulus ∼1 to 3 GPa) and high gas permeability of PLLA restrict its use in packaging applications.[30−34] These limitations and the desire to remove the C−H bond of PLLA have spurred research into modifying the chemical structure of lactic acid to develop alternative polymers with properties surpassing those of PLLA.

Geminal disubstitution of cyclic monomers effectively enhances both the chemical recyclability and performance of their polymers.[35−41] For instance, gem-dialkyl substitution at the α-position of poly(δ-valerolactone) (PVL) yields poly(α,α-dialkyl-substituted-δ-valerolactone) (PVL^{R2}), which demonstrates superior material performance and can be recycled to its lactone monomers under mild conditions.[35,36] This substitution raises the melting temperature (T_m) to 140 °C, a significant increase from the T_m of 57 °C of unsubstituted PVL. Similarly, gem-dialkyl substitution in the 3-hydroxybutyrate (3HB) monomer results in a polyester that is chemically recyclable and possesses intrinsic crystallinity and heat processability.[37] These findings indicate that gem-disubstitution enables closed-loop polymer recycling while enhancing the material properties.

Poly(tetramethyl glycolide) (PTMG) is an optically nonactive polyester with superior thermal properties (T_g = 68 °C, T_m = 190 °C) compared to PLLA.[42−44] Its dimethyl-substituted PLA structure prevents racemization during depolymerization, making it a promising candidate for circular polymers. The dimethyl substitution in tetramethyl glycolide

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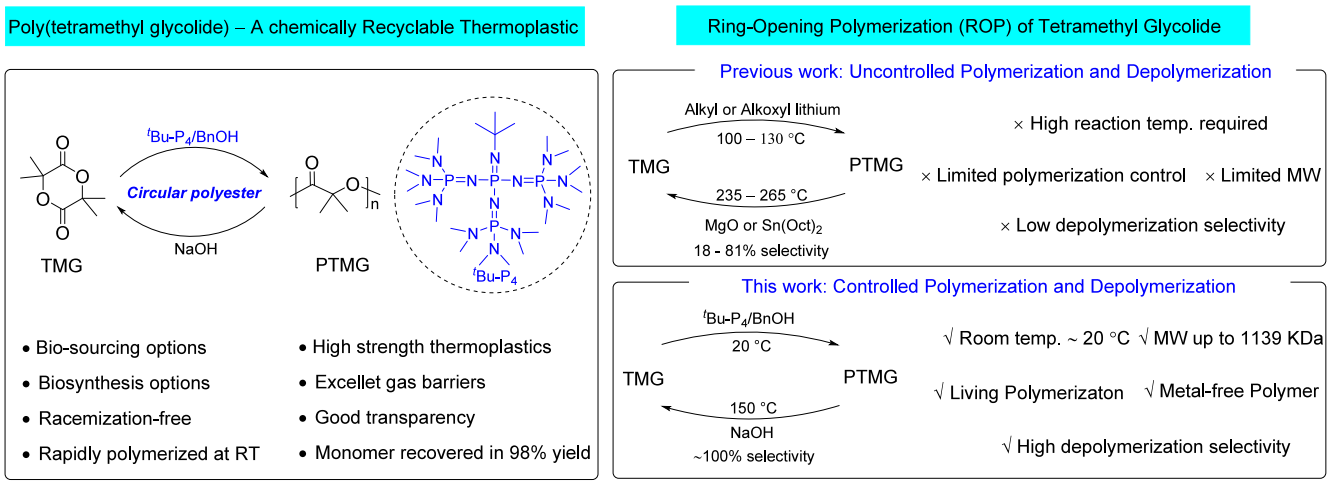
Scheme 1. Development of the Controlled TMG Polymerization System and PTMG Depolymerization System



(TMG) also obviously decreased its polymerization (thus greatly enhancing depolymerizability) with a lower ceiling temperature (T_c = 122 °C in 1 mol L^{-1} Figure S1) compared with the parent lactide (LLA, T_c = 343 °C in 1 mol L^{-1}).[45] Early work on PTMG suggested its biomass-base resources and potential applications (Scheme 1).[46−48] However, the significant depolymerization of PTMG poses challenges for achieving controlled ring-opening polymerization (ROP) of TMG under mild conditions and low catalyst loading. For example, polymerization of the bulk TMG at 120 °C using ^{t}BuLi as the catalyst with [TMG]/[^{t}BuLi] = 170 for 24 h gives an acceptable yield but affords poor molecular weight control and high metal residues in the formed polymer.[42] In addition, consistently obtaining high selectivity for depolymerization to TMG has remained challenging because the thermal degradation of PTMG is accompanied by elimination reactions. The depolymerization of the bulk PTMG at 283 °C recovered trace amounts of TMG (2.9%), producing methacrylic acid (57.1%) and recovering acetone (40%) are recovered.[42] Although the presence of tin ethylhexanoate $Sn(Oct)_2$ during thermal decomposition can enhance the selectivity of depolymerization to result in crude TMG (80.8%) with methacrylic acid (19.2%), these side reactions at high temperature (265 °C) are problematic and delimit the efficiency of chemical recycling to pure TMG.[42]

Identifying an effective catalyst to lower PTMG's depolymerization temperature would enable low-temperature depolymerization, minimizing completing reactions and facilitating a more selective, energy-efficient process for recovering high-purity TMG. Here, we identify potent organocatalysts for the living ROP of TMG, enabling the synthesis of metal-free ultrahigh-molecular-weight TMG materials with superior mechanical, gas barrier, and transparency properties compared to commercialized PLLA. Furthermore, we showcase the catalyzed and selective depolymerization of bulk PTMG at desirably mild conditions of 150 °C, enabling the complete recovery of pure TMG (Scheme 1).

RESULT AND DISCUSSION

Control in the ROP of TMG. Initial experiments at the ROP of TMG employed lanthanide and zinc complexes, including $La[N(SiMe_3)_2]_3$, $[La(OBn)_3]_x$, and $[Zn(OBn)_2]_x$, which are effective in coordination−insertion ROP of lactones (Table S2 runs 1−3).[49−51] Nevertheless, no polymer was synthesized within 24 h when the polymerization was performed at ambient or elevated temperatures in toluene or other common organic solvents. Potassium alkoxides were explored for the ROP of TMG. The CH_3OK/BnOH catalytic system ([CH_3OK]/[BnOH] = 1/1) effectively polymerized 100 equiv of TMG at 20 °C ([TMG]$_0$ = 1.0 M), achieving 81% conversion after 10 min to produce PTMG with number-average molecular weight (M_n) of 15.5 kg mol^{-1} and dispersity ($Đ$) of 1.34 (Table S2 run 3). The ^{t}BuOK/BnOH ([^{t}BuOK]/[BnOH] = 1/1) further enhanced polymerization activity, achieving 83% conversion in 8 min (M_n = 18.6 kg mol^{-1}, $Đ$ = 1.38) (Table S2 run 4). However, the potassium-alkoxide-catalyzed process is uncontrollable, yielding polymers with wide molecular weight distributions. Given the ability of organic bases to control the ROP of lactone[52−54] and the benefit of producing metal-free polymers, organic molecules were employed for the ROP of TMG. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), and *tert*-butylimino-tris(dimethylamino)-phosphorene (^{t}Bu-P_1, $^{MeCN}pK_a$ = 26.9) demonstrated inactivity in the ROP of TMG (Table S2 runs 6 and 7). Stronger basic 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi-(phosphazene) (^{t}Bu-P_2, $^{MeCN}pK_a$ = 33.5) was able to facilitate some monomer conversion (47%, 24 h) (Table S2 run 9). The P_4-phosphazene, 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis-[tris(dimethylamino)phos-phoranylid-enamino]-2λ^5,4λ^5-catenadi (phosphazene) (^{t}Bu-P_4), is among the strongest known neutral bases with $^{MeCN}pK_a$ of 42.7 for its conjugate acid in MeCN.[55] Leveraging its high Brønsted basicity, ^{t}Bu-P_4 has been combined with alcohol to create an effective metal-free initiator system for lactone or lactide polymerization, forming active weakly paired species [$RO^-\cdots{}^+H{}^t$Bu-P_4]$^-$ and initiating the ring opening of the monomer via the RO^- anion.[55] We investigated the ROP of TMG using the ^{t}Bu-P_4/BnOH catalytic system with [TMG]/[^{t}Bu-P_4]/[BnOH] = 200/1/1 in toluene at 20 °C ([TMG]$_0$ = 1.0 M). The ^{t}Bu-P_4/BnOH catalytic system effectively polymerized 200 equiv of TMG, achieving 93% conversion after 1 min. When the [TMG]/[^{t}Bu-P_4] ratio was increased to 6500:1, the ^{t}Bu-P_4/BnOH catalytic system also catalyzed the rapid ROP of TMG, which gave 98% monomer conversion within 10 min in toluene at 20 °C. The living feature of the ROP of TMG using ^{t}Bu-P_4/BnOH as a

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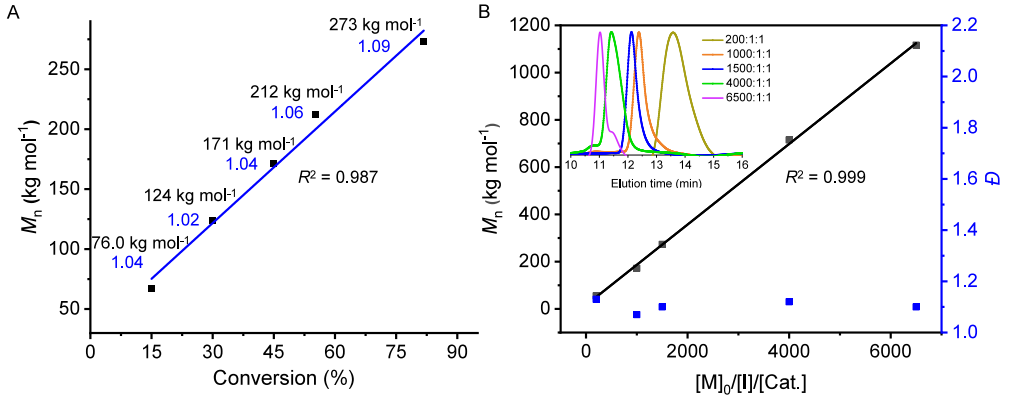

Figure 1. Evidence of the controlled polymerization of the TMG. (A) Graphs depicting M_n and $Đ$ of the PTMG in relation to monomer conversion in $[TMG]_0/[^tBu\text{-}P_4]_0/[BnOH]_0 = 2000/1/1$. (B) Graph depicting M_n and $Đ$ for the PTMG in relation to the $[TMG]_0/[^tBu\text{-}P_4]_0$ ratio. Inset: SEC curves for PTMG were produced at varying initial ratios $[TMG]_0/[BnOH]_0/[^tBu\text{-}P_4]_0$.

catalyst system was assessed by periodically analyzing reaction samples via size exclusion chromatography (SEC) to determine the M_n and $Đ$ values of the synthesized PTMG at different conversion stages. A clear linear correlation was identified between the increase in TMG conversion and PTMG M_n increase ($R^2 = 0.987$), with $Đ$ consistently ranging from 1.02 to 1.09 across all conversions (Figure 1A). The impact of the monomer feed on the resulting polymer M_n and the findings from chain extension experiments further confirmed the controlled nature of the ROP process. The M_n of PTMG increased progressively from 59.3 kg mol^{-1} ($Đ$ = 1.13) to 185 kg mol^{-1} ($Đ$ = 1.07), 297 kg mol^{-1} ($Đ$ = 1.09), 737 kg mol^{-1} ($Đ$ = 1.12), and 1139 kg mol^{-1} ($Đ$ = 1.10) with varying $[TMG]/[^tBu\text{-}P_4]$ ratios of 200:1, 1000:1, 1500:1, 4000:1, and 6500:1, respectively (Figure 1B). Furthermore, in a chain extension experiment, an additional 200 equiv of TMG was introduced to the polymerization mixture with a $[TMG]/[^tBu\text{-}P_4]$ ratio of 200:1. As expected, the M_n increased to 114 kg mol^{-1} with $Đ$ = 1.13, nearly doubling the initial M_n of 59.3 kg mol^{-1} and maintaining the same $Đ$ of 1.13 for PTMG from the initial addition (Figure 2). The three experiments detailed

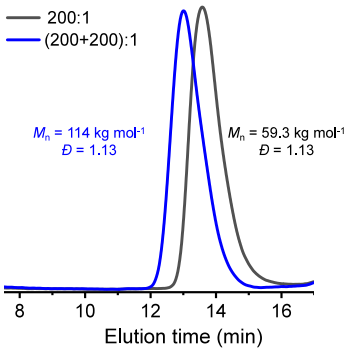

Figure 2. SEC curves for PTMG samples obtained by chain extension experiments.

above, involving the assessment of M_n and $Đ$ in relation to monomer conversion, tracking M_n and $Đ$ concerning monomer loading, and investigating chain extension, collectively indicate that the ROP of TMG catalyzed by $^tBu\text{-}P_4$/BnOH proceeds in a living manner.

The main-chain structure of the isolated PTMG was verified through ^1H NMR spectra, which were employed to identify the polymer chain structure (Figure S2). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and ^1H NMR spectroscopy were employed to identify the polymer chain ends. The MALDI-TOF MS data revealed a series of molecular ion peaks to linear PTMG with BnO/H as the chain ends, denoted as BnO−$[TMG]_n$−H (Figure 3). The structure aligns with the ^1H NMR analysis of the synthesized polymer. The ^1H NMR spectra revealed prominent signals at 1.53 ppm for the proton of the main chain ($-[C(=O)CMe_2O]_n-$) and minor signals at 7.33 and 5.13 ppm corresponding to the chain-end groups (BnO/H) (Figure S2). These findings align with the mechanistic scenario depicted in Figure 4, which describes initiation pathways through the BnO− anion generated by the deprotonation of BnOH by $^tBu\text{-}P_4$.

Thermal, Mechanical, and Gas Barriers Properties of PTMG. The PTMG exhibited a typical T_m of 184 °C and a T_g of 71 °C (Figure S3), which are higher than that of typical PLLA (T_g ~54 to 59 °C, T_m ~159 to 178 °C).[31−34] Thermal gravimetric analysis (TGA) indicates that the onset thermal decomposition temperature ($T_{d,5\%}$) of PTMG was influenced by its molecular weight. As the molecular weight increased from 5.3 to 1139 kg mol^{-1}, the $T_{d,5\%}$ value of PTMG rose from 272 to 289 °C (Figures S4−S6). The PTMG with M_n = 129 kg mol^{-1} has a strength σ_B = 41.5 ± 0.2 MPa and a modulus E = 3.2 ± 0.2 GPa. Raising the PTMG M_n to 332 kg mol^{-1} improved σ_B and E values to 62.6 ± 1.9 MPa and 3.9 ± 0.08 GPa, respectively. Further increasing the PTMG M_n to 1139 kg mol^{-1} improved both σ_B and E values to 65.5 ± 2.1 MPa and 4.2 ± 0.05 GPa, respectively. Overall, the ultrahigh-molecular-weight PTMG exhibits mechanical properties (σ_B ~66 MPa, E ~4.2 GPa, ε_B ~2%) that are favorable compared to commercialized PLLA materials (M_n = 58.6 kg mol^{-1}, σ_B ~49 MPa, E ~3.2 GPa, ε_B ~4%)[31−34] (Figure 5A, Table S8). Although PLLA with a molecular weight equivalent to that of PTMG (1139 kg mol^{-1}) may also exhibit mechanical properties comparable to that of ultrahigh-molecular-weight PTMG, this polymer has not yet been reported. However, PTMG (ε_B ~2%) is a slightly more brittle polymer than commercialized PLLA (ε_B ~2 to 4%) (Figure 5A, Table S8). Excitingly, after further heat treatment, the strength and modulus of PTMG reach 80.0 ± 2.1 MPa and 4.9 ± 0.1 GPa, respectively, which are obviously better than typical PS (σ_B ~30 to 60 MPa, E ~2.4 to 3.2 GPa, ε_B ~1 to 4%).[56] The PTMG specimen underwent tension film mode dynamic

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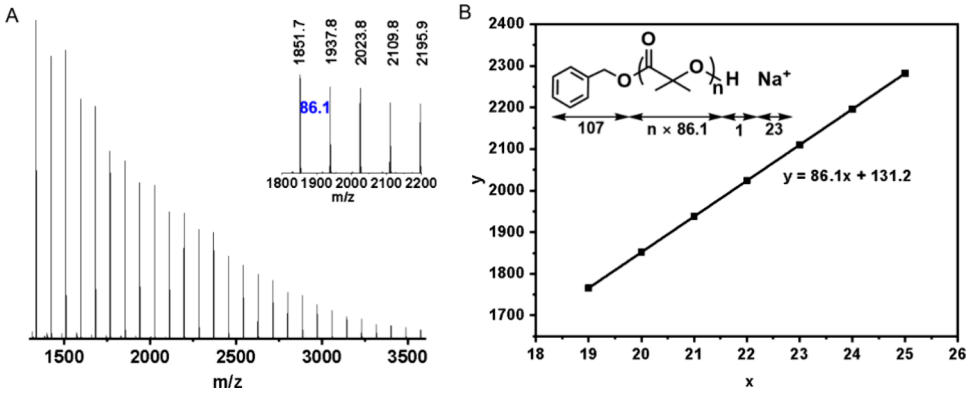

Figure 3. Characterization of linear PTMG using MALDI-TOF MS analysis. (A) MALDI-TOF MS of PTMG obtained with [TMG]/[^{t}Bu-P$_4$]/[BnOH] = 15/1/1. (B) Graph depicting the relationship between mass/charge ratio (m/z) values (y) vs the theoretical count of TMG repeat units (x) for PTMG.

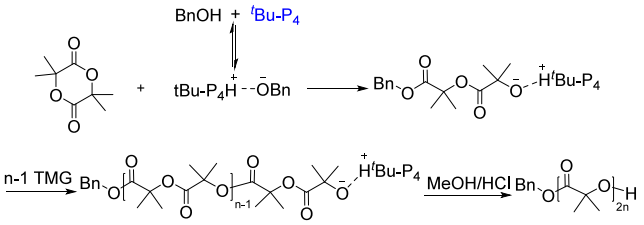

Figure 4. Proposed mechanism for the ROP of TMG using ^{t}Bu-P$_4$/BnOH.

mechanical analysis (DMA). The DMA curve of PTMG exhibited a notably high storage modulus (E') of 2.2 GPa in the glassy phase. After the glass-transition region, marked by a T_α value of 94 °C (determined by the peak of tan δ, the E''/E' ratio), E' was reduced by about 2 orders of magnitude (Figure 5B).

As PTMG outperforms commercialized PLLA mechanically and thermally, we also examined its transport properties to evaluate its suitability for packaging applications. Commercialized polyethylene terephthalate (PET), PLLA, and poly(butyleneadipate-*co*-terephthalate) (PBAT), frequently utilized in the packaging, were concurrently analyzed as references. Commercialized PET, PLLA, and PBAT demonstrated a moderate to high barrier to oxygen permeation with oxygen permeability (P_{O2}) values of 0.14 ± 0.04, 0.21 ± 0.01, and 1.00 ± 0.07 Barrer, respectively. The PTMG demonstrated a significantly higher barrier to oxygen permeation, with a P_{O2} value of 0.12 ± 0.01 Barrer, which is lower than those of commercialized PET,[57] PLLA,[57] and PBAT.[57] The PTMG also exhibits a significantly lower water-vapor transmission rate (WVTR) value (1.63 ± 0.11 g mm m^{-2} per day) compared to those of PBAT (4.52 ± 0.33 g mm m^{-2} per day) and PLLA (2.04 ± 0.07 g mm m^{-2} per day). These findings indicate that PTMG is a viable alternative to commercialized PLLA for packaging applications due to its superior mechanical, barrier, and thermal properties (Figure 6).

Considering the importance of transparency for packaging materials, we investigated the optical properties of PTMG and common optical materials including commercialized PMMA, polystyrene (PS), and PLLA. Using an ultraviolet−visible-near-infrared spectrophotometer (UV−vis-NIR) on a 200 μm thin film sample, we observed transmittance values ranging from 92 to 95% in the 400−1000 nm region, with an overall transmittance of T% = 93% (Figure 7). The transparency of PTMG is the same as that of commercialized PLLA. This level

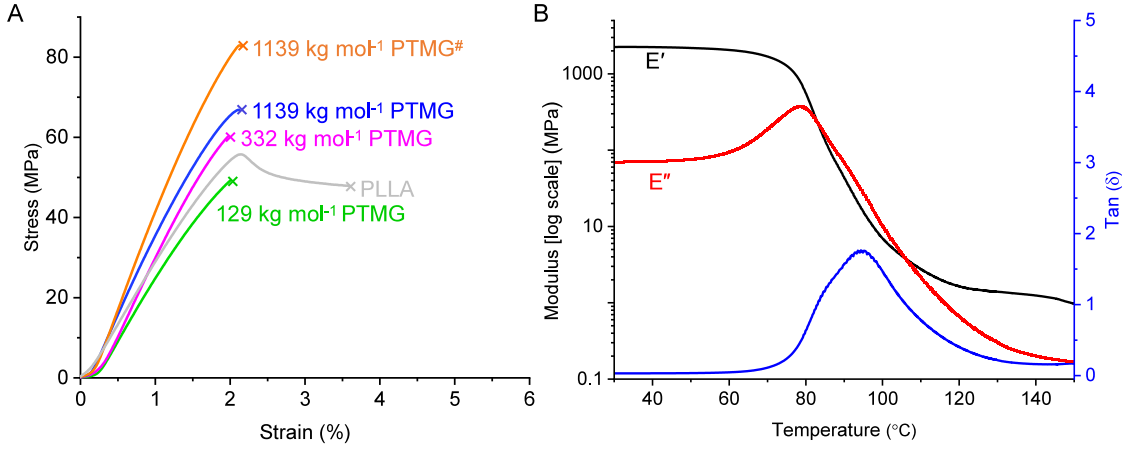

Figure 5. Static and dynamic mechanical properties of the PTMG. (A) Representative stress−strain curves measured by tensile testing of PTMG (5.0 mm min^{-1}, ambient temperature) over a molecular weight range (M_n = 129, 332, and 1139 kg mol^{-1}) compared to commercialized PLLA (M_n = 58.6 kg mol^{-1}). Fracture points are denoted with ×. Only selected samples are shown here for clarity. The samples were crystallized isothermally at 100 °C for 2 h (marked by #). (B) DMA curves of the PTMG in tension film mode with parameters set at 0.1% strain, 1 Hz frequency, and a temperature increase of 3 °C min^{-1} (M_n = 1139 kg mol^{-1}, Table S3 run 6).

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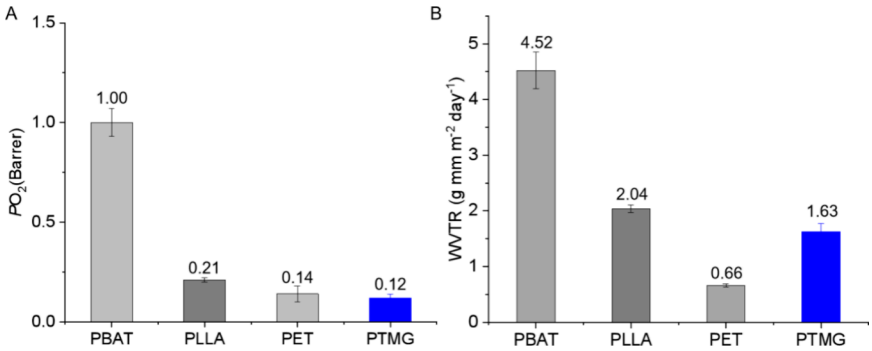

Figure 6. Transport properties of PTMG relative to commercialized PET, PLLA, and PBAT. (A) Oxygen permeability plots. (B) WVTR plots. Error bars correspond to the standard deviation of the three replicates. PTMG, M_n = 332 kg mol^{-1}; PLA, M_n = 58.6 kg mol^{-1}; PBAT, M_n = 22.6 kg mol^{-1}; PET, viscosity η = 0.83 mPa·s.

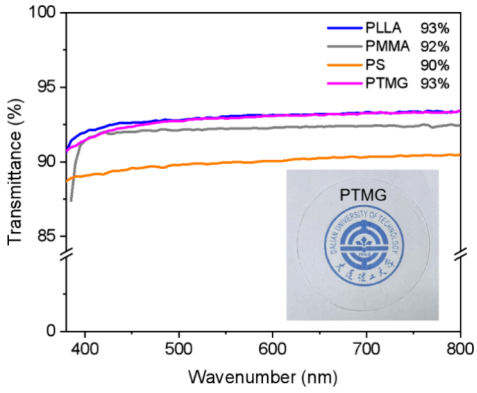

Figure 7. Ultraviolet−visible-near-infrared spectrophotometer (UV−vis-NIR) of amorphous PTMG compared to commercialized PLLA, PS, and PMMA. Transparent thin films with a thickness of approximately 200 μm.

of transparency rivals that of commonly used transparent commodity plastics like amorphous PMMA (T% = 92%) and PS (T% = 90%).

Chemical Recycling of PTMG. The chemical recyclability of the PTMG was assessed through high-temperature thermolysis and catalyst-assisted chemolysis at lower temperatures. As indicated by its low T_c of 122 °C (1.0 M), PTMG should be readily recyclable back to its monomer once the activation barrier is overcome. Indeed, heating PTMG (M_n = 26.6 kg mol^{-1}) in a sealed autoclave at 300 °C (T_{max}, the maximum rate decomposition temperature) for 2 h resulted in only trace amounts of TMG (3%) and produced a large amount of methacrylic acid (97%) (Table 1 run 1, Figure S13). Therefore, it is essential to develop a catalyzed depolymerization process that lowers the depolymerization temperature and prevents the β-H elimination reaction, thereby enabling the selective recovery of monomers with high yield and purity. Phosphomolybdic acid (PMA), an economical and recycled catalyst, has demonstrated effectiveness in the depolymerization of polyesters and was initially applied to the depolymerization of PTMG.[50] The depolymerization was conducted using a sublimation device. Mixing low-molecular-weight PTMG (M_n = 26.6 kg mol^{-1}) with 2.0 mol % PMA at 180 °C under reduced pressure (0.08 Torr) produced a colorless liquid after 4 h (20% conv.). The resulting liquid contained no TMG, only small amounts of methacrylic acid and complex impurities (Table 1 run 2, Figure S14). Subsequently, Lewis acids $ZnCl_2$, $Zn(CH_3COO)_2$, $LaCl_3$, and $[La(OBn)_3]_x$ were

Table 1. Depolymerization Results of PTMG Catalyzed by Various Catalysts at Varied Temperatures[a]

run	cat.	T (°C)	conv. (%)	[TMG]/[methacrylic acid]/[acetone][b]
1		300[c]	>99[c]	3/97/0
2	PMA	180	20	
3	$ZnCl_2$	200	0	
4	$ZnCl_2$/PEG	200	0	
5	$Zn(CH_3COO)_2$	180	76	2/0/98
6	$LaCl_3$	180	0	
7	$[La(OBn)_3]_x$	200	97[c]	100/0/0
8	Na_2CO_3	200	0	
9	^{t}BuOK	200	0	
10	DBU	200	5[d]	
11	TBD	180	56[e]	[d]
12	NaOH[f]	150	64 (98[g])	100/0/0

[a]The depolymerization reactions were conducted using 5 mol % catalyst, 4 h, and PTMG (M_n = 26.6 kg mol^{-1}). [b]Determined by ^{1}H NMR spectroscopy. [c]2 h. [d]The liquid obtained contains methacrylic acid and unknown impurity. [e]The liquid obtained contains methacrylic acid, TMG, and unknown impurity. [f]2 wt % NaOH. [g]20 h.

used for the depolymerization of PTMG. When PTMG (M_n = 26.6 kg mol^{-1}) was mixed with 2.0 mol % $ZnCl_2$ at 200 °C under reduced pressure, no depolymerization occurred after 4 h (Table 1 run 3). Considering that polyethylene glycol (PEG) can improve the catalytic depolymerization ability of $ZnCl_2$, a $ZnCl_2$/PEG system was also tried, but the depolymerization reaction still did not occur at 200 °C after 4 h (Table 1 run 4). When $Zn(CH_3COO)_2$ was used as the catalyst, a liquid mixture (76% conv.) containing a large amount of acetone (98%) and a small amount of TMG (2%) was obtained at 180 °C after 4 h (Table 1 run 5, Figure S15). Further increasing the Lewis acidity of the catalyst, lanthanum compounds were used for PTMG depolymerization. $LaCl_3$ showed no activity for depolymerization of PTMG (M_n = 26.6 kg mol^{-1}), but $[La(OBn)_3]_x$ showed good activity and excellent selectivity for depolymerization of PTMG to TMG (Table 1 runs 6 and 7, Figure S16). The depolymerization with 5 mol % $[La(OBn)_3]_x$ affords the pure monomer in near quantitative yield (97%) at 200 °C after 2 h, highlighting the thermal recyclability of the PTMG (Table 1 run 7, Figure S16). Further, we scanned a series of basic catalysts to lower the depolymerization temperature of PTMG. When 5 mol % Na_2CO_3 or ^{t}BuOK was used for the depolymerization of PTMG at 200 °C under

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reduced pressure, no depolymerization occurred after 4 h (Table 1 runs 8 and 9). DBU (5 mol %) can depolymerize PTMG but produced a mixture (5% conv.) containing methacrylic acid and unknown impurity (Table 1 run 10, Figure S17). When TBD was used as the catalyst, a liquid mixture containing methacrylic acid, TMG, and unknown impurity was obtained (56%) at 180 °C after 4h (Table 1 run 11, Figure S18). NaOH, which is a strong base, was subsequently tested. At 2 wt % NaOH, the depolymerization of PTMG (M_n = 26.6 kg mol^{-1}) at a relative low temperature of 150 °C was completed (98%) (Table 1 run 12). When PTMG with a higher molecular weight (123 kg mol^{-1}) was mixed with 2.0 wt % NaOH, pure TMG was obtained (80% conversion) at 170 °C. Increasing the NaOH loading from 2 to 5 wt % enhanced the PTMG conv. to 89%.

An effective method for depolymerizing high-molecular-weight PTMG involves an initial reduction in molecular weight through alkaline hydrolysis using MeOH/NaOH (5 wt %) followed by catalytic depolymerization of the resulting low-molecular-weight PTMG at 150 °C. Refluxing PTMG (M_n = 1139 kg mol^{-1}, $Đ$ = 1.10) in MeOH with 5 wt % NaOH at 50 °C resulted in a product with decreased molecular weight (M_n = 12.7 kg mol^{-1}, $Đ$ = 1.82) (Figure S19). Subsequent removal of MeOH allowed depolymerization at 150 °C under reduced pressure (0.08 Torr), leading to the production of pure TMG (97% conv.) (Figure 8). The recovered monomer was then repolymerized with [^{t}Bu-P$_4$]/[TMG] = 1/6500, yielding PTMG with a comparable molecular weight (M_n = 1205 kg mol^{-1}, $Đ$ = 1.11) (Figure S21).

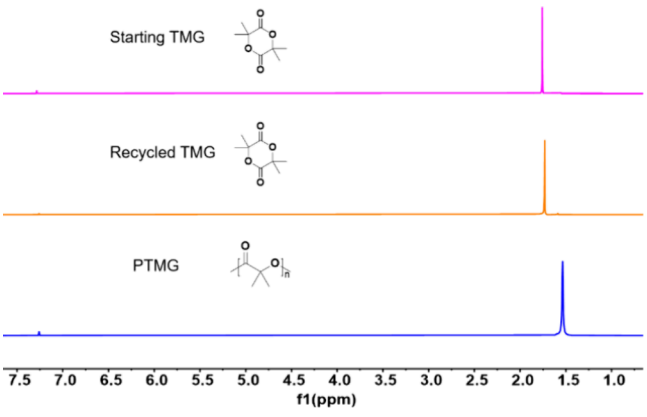

Figure 8. Chemical recyclability of PTMG as shown by overlaying ^{1}H NMR spectra ($CDCl_3$). PTMG (M_n = 1139 kg mol^{-1}) prepared from the ROP with ^{t}Bu-P$_4$ in toluene at 20 °C, [TMG]/[^{t}Bu-P$_4$]/[BnOH] = 6500/1/1, bottom; the solid product recovered after thermal depolymerization after basic hydrolysis and depolymerization at 150 °C, middle; starting TMG, top.

CONCLUSIONS

The potential of the biobased aliphatic polyester PTMG derived from TMG has been previously underestimated due to issues related to uncontrolled synthesis and limited chemical recyclability to the monomer. We have pioneered an effective living organopolymerization of TMG, achieving the ultrahigh-molecular-weight (1139 kg mol^{-1}) and metal-free polyester PTMG. The ultrahigh-molecular-weight PTMG demonstrates outstanding mechanical properties, including a high tensile strength of ∼80.0 MPa and a high modulus of ∼4.94 GPa. Consequently, PTMG had significantly greater strength compared to commercialized PLLA (M_n = 58.6 kg mol^{-1}). Their excellent mechanical properties are complemented by superior barrier characteristics, with gas barrier performance significantly surpassing that of PLLA and even exceeding PET. The transparency of PTMG is the same as that of the PLLA and is better than common optical materials PMMA and PS. Investigating the catalytic depolymerization of PTMG using various Brønsted acids, inorganic acids, and bases led to the discovery of NaOH as an effective catalyst. This catalyst facilitates the selective depolymerization of PTMG into high-purity TMG with quantitative yield under mild conditions at 150 °C. Catalytic depolymerization of PTMG at lower temperatures is more energy-efficient and selective than high-temperature thermolysis, which can result in competing decomposition and elimination reactions. The recovered monomer can be repolymerized to regenerate the original polymer, effectively completing the monomer−polymer−monomer cycle. This study underscores the importance of discovering effective catalysts for polymerization and depolymerization to synthesize ultrahigh-molecular-weight polymers with strong mechanical properties and to achieve high-purity, high-yield monomers under mild conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c00841.

Experimental methods, materials, and polymer characterization (PDF)

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Notes

The authors declare no competing financial interest.

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