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Thermally Stable and Chemically Recyclable Poly(ketal-ester)s Regulated by Floor Temperature

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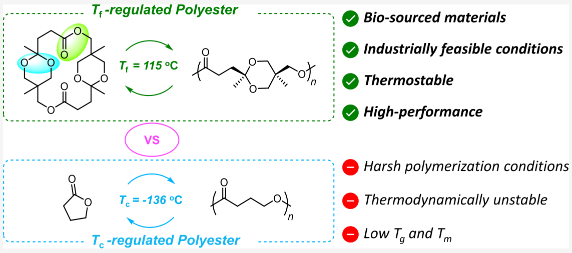

ABSTRACT: Chemical recycling to monomers (CRM) offers a promising closed-loop approach to transition from current linear plastic economy toward a more sustainable circular paradigm. Typically, this approach has focused on modulating the ceiling temperature (T_c) of monomers. Despite considerable advancements, polymers with low T_c often face challenges such as inadequate thermal stability, exemplified by poly(γ-butyrolactone) (PGBL) with a decomposition temperature of ∼200 °C. In contrast, floor temperature (T_f)-regulated polymers, particularly those synthesized via the ring-opening polymerization (ROP) of macrolactones, inherently exhibit enhanced thermodynamic stability as the temperature increases. However, the development of those T_f regulated chemically recyclable polymers remains relatively underexplored. In this context, by judicious design and efficient synthesis of a biobased macrocyclic diester monomer (HOD), we developed a type of T_f -regulated closed-loop chemically recyclable poly(ketal-ester) (PHOD). First, the entropy-driven ROP of HOD generated high-molar mass PHOD with exceptional thermal stability with a $T_{d,5\%}$ reaching up to 353 °C. Notably, it maintains a high $T_{d,5\%}$ of 345 °C even without removing the polymerization catalyst. This contrasts markedly with PGBL, which spontaneously depolymerizes back to the monomer above its T_c in the presence of catalyst. Second, PHOD displays outstanding closed-loop chemical recyclability at room temperature within just 1 min with ^{t}BuOK. Finally, copolymerization of pentadecanolide (PDL) with HOD generated high-performance copolymers (PHOD-*co*-PPDL) with tunable mechanical properties and chemical recyclability of both components.

■ INTRODUCTION

The rapid growth of the plastic industry, coupled with a historical neglect of sustainable and economically viable end-of-life solutions for postconsumer plastics, has led to the current critical situation of plastic waste accumulation.[1−3] Addressing this urgent issue necessitates not only enhancing the recyclability of existing commodity polymers but also innovating new polymers with inherent recyclability, thus contributing to a more sustainable circular plastic economy.[4−8] Chemical recycling to monomers (CRM) has emerged as a prominent and plausible resolution, offering a way to regenerate polymers from recycled monomers without compromising their material performance. This strategy significantly reduces the reliance on petrochemical resources and diminishes the accumulation of plastic waste, fostering a circular economy where the lifecycle of plastics is sustainably managed and their environmental impact is minimized.[9−12]

To facilitate practical chemical recyclability of polymers generated by chain-growth polymerization, it is imperative to judiciously manipulate both thermodynamics and kinetics of the polymerization−depolymerization equilibrium of specific monomers.[9,13,14] Thermodynamically, this involves carefully adjusting the relative energy states of monomers versus those of polymers under specific conditions. Kinetically, it requires management of the energy barrier that influences the rate, energy input, and selectivity of forward and reverse reactions in the (de)polymerization process. For polymers synthesized via ring-opening polymerization (ROP),[11,13,15] the primary driving force of the ROP of monomers of small and medium ring size is a negative change in enthalpy ($\Delta H_p^\circ < 0$), owing to the release of angular and transannular strains,[16,17] coupled with a negative change in polymerization entropy ($\Delta S_p^\circ < 0$), which results from the loss of translational freedom due to covalent linkage of monomer molecules. As such, there exists a critical temperature, termed the ceiling temperature (T_c), defining the maximum temperature at which polymerization can occur at a specific monomer concentration. Above T_c, the entropic penalty overrides the favorable (negative) enthalpy of polymerization, leading to depolymerization ($\Delta G_p > 0$).[18,19]

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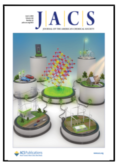

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Accordingly, current design paradigms for CRM primarily focus on strategically manipulating T_c.[20−42] Specifically, polymers with a low T_c, typically below 200 °C in bulk, are classified as intrinsically circular polymers (ICPs).[13] However, those ICPs typically confront challenges such as an extremely low polymerization temperature, insufficient monomer conversion, and inadequate thermal stability. The ROP of γ-butyrolactone (γ-BL) is a case in point, requiring extremely low temperatures (typically −40 °C) that are impractical under industrial conditions.[20] Moreover, to ensure the thermal stability of such kinetically trapped polymers, a stringent purification process to remove any residual catalysts is imperative. Despite these efforts, the resultant polymer, PGBL, manifests only a decomposition temperature of ∼200 °C, which further hinders the practical processing and utility of such recyclable polymers.

Conversely, in the case of macrolactones (MLs), the enthalpy change (ΔH_p) associated with ring-opening is minimal, and the polymerization process is predominantly driven by entropy (ΔS_p), benefiting from the increased conformational freedom.[43,44] In such scenarios, where $\Delta H_p^o > 0$ and $\Delta S_p^o > 0$, another critical temperature, known as the floor temperature (T_f), becomes relevant.[16,17] T_f denotes the minimum temperature required for polymerization, indicative of an entropy-driven process.[45] Notably, the entropic term ($T\Delta S_p$) in the Gibbs free energy equation ($\Delta G_p = \Delta H_p - T\Delta S_p$) becomes more significant as the temperature increases. Therefore, the ROP of MLs, similar to the polymerization of elemental sulfur and the ROP of octamethylcyclotetrasiloxane (D4) generally requires higher reaction temperatures to attain energetic favorability ($\Delta G_p < 0$).[45−48] Moreover, the entropy change is concentration-dependent, favoring polymerization at high monomer concentrations due to the conformational entropy benefits of the polymers. In contrast, in dilute conditions, translational entropy becomes more dominant, thereby shifting the equilibrium toward the monomers.[49,50]

Given that polymers with an appropriate T_f are anticipated to polymerize at elevated temperatures and depolymerize at lower temperatures or even at room temperature, a stark contrast to the behavior of T_c -regulated recyclable polymers, we assert that transitioning to T_f -regulated polymers could resolve at least three major challenges associated with low-T_c chemically recyclable polymers. (1) T_f-regulated polymers enable the polymerization of monomers at industrially feasible temperatures, avoiding the impractically low temperatures required by low T_c polymers. (2) T_f-regulated polymers are thermodynamically more stable as temperature increases. Therefore, the removal of polymerization catalysts is not as crucial as in the case of kinetically trapped T_c-regulated polymers during heat processing. (3) These T_f-regulated polymers are thermodynamically inclined to depolymerize at ambient temperatures when being treated with appropriate depolymerization catalysts, thus effectively minimizing the energy consumption of chemical recycling. However, instances of chemically recyclable polymers regulated by T_f are relatively rare.

One of the key challenges in developing chemically recyclable polymers with intrinsic high thermodynamic stability lies in the lack of molecular-level design principles for the efficient and selective synthesis and recycling of macrocyclic monomers. On one hand, the synthesis of MLs through depolymerization of polyesters is typically achieved by ring−chain equilibrium under high-dilute solution conditions, a process that consumes significant amounts of solvent and requires long time.[43,51] In addition, ring−chain equilibrium recycling lacks selectivity, often yielding a distribution of macrocyclic homologues instead of a single product.[52−54] Pure MLs have been prepared by catalytic depolymerization of polyesters at high temperatures followed by high vacuum distillation.[55,56] Recently, Odelius et al. developed a high-yield synthetic method for a series of macrocyclic carbonates through the depolymerization of in situ-generated linear polycarbonates at 235−280 °C and 0.05 mbar, and they also demonstrated the rapid anionic ROP of these macrocyclic carbonates and polymer-to-monomer regeneration.[57] Similarly, Zhu et al. reported the preparation of a stable dimer of *trans*-cyclohexyl fused seven-membered carbonates by depolymerization of the polycarbonate under mild conditions. However, these dimers demonstrated reduced reactivity for repolymerization into polycarbonates.[58] This trade-off between synthesis challenges and repolymerizability underscores the need for more effective strategies in the development of T_f-regulated chemical recyclable polymers.

With our ongoing effort to advance the high-performance, chemically recyclable poly(ketal-ester)s,[59,60] herein, we report an efficient synthetic method of a 18-membered macrocyclic diester (HOD) from biosourced material, designed to overcome the aforementioned trade-offs in developing macrocyclic monomer-based circular polymers. HOD displays an ideal T_f of 115 °C (1 M), enabling its rapid polymerization at temperatures that are viable for industrial processes. Furthermore, its corresponding thermodynamically stable polymer (PHOD) can be chemically recycled back to HOD under mild conditions, even at ambient temperature, when catalyzed by ^{t}BuOK (Scheme 1).

RESULTS AND DISCUSSION

HOD Synthesis and Its Ti(O*i*-Pr)$_4$-Catalyzed ROP. To mitigate the dependency on nonrenewable petrochemical resources, we have synthesized an 18-membered macrocyclic

Scheme 1. Synthesis and Schematic Closed-Loop Circularity of T_f -Regulated Thermodynamically Stable Poly(ketal-ester)

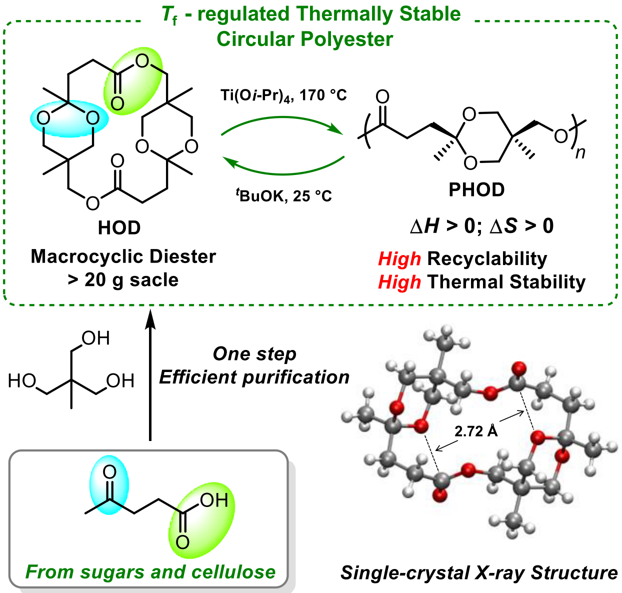

Table 1. Polymerization Results of HOD catalyzed by Ti(O*i*-Pr)$_4$[a]

entry	[M]:[Cat.]	conc.[b](mol/L)	temp. (°C)	time	conv.[c](%)	$M_{n,\,GPC}$[d](kDa)	$Đ$[d]
1	50:1	3	170	1.5 h	91	10.1	1.3
2	100:1	3	170	3 h	90	25.3	1.4
3	200:1	3	170	6 h	90	33.2	1.6
4	300:1	3	170	6 h	86	43.6	1.5
5	400:1	3	170	12 h	88	56.6	1.7
6	200:1	3	200	10 min	94	31.3	1.5

[a] Polymerizations were performed in chlorobenzene with Ti(O*i*-Pr)$_4$ as the catalyst. [b] Concentration was calculated as $n_{HOD}/v_{chlorobenzene.}$ [c] Determined by ^{1}H NMR spectroscopy. [d] Number-average molar mass (M_n), and dispersity indices ($Đ = M_w/M_n$) were determined by SEC in THF relative to polystyrene standards.

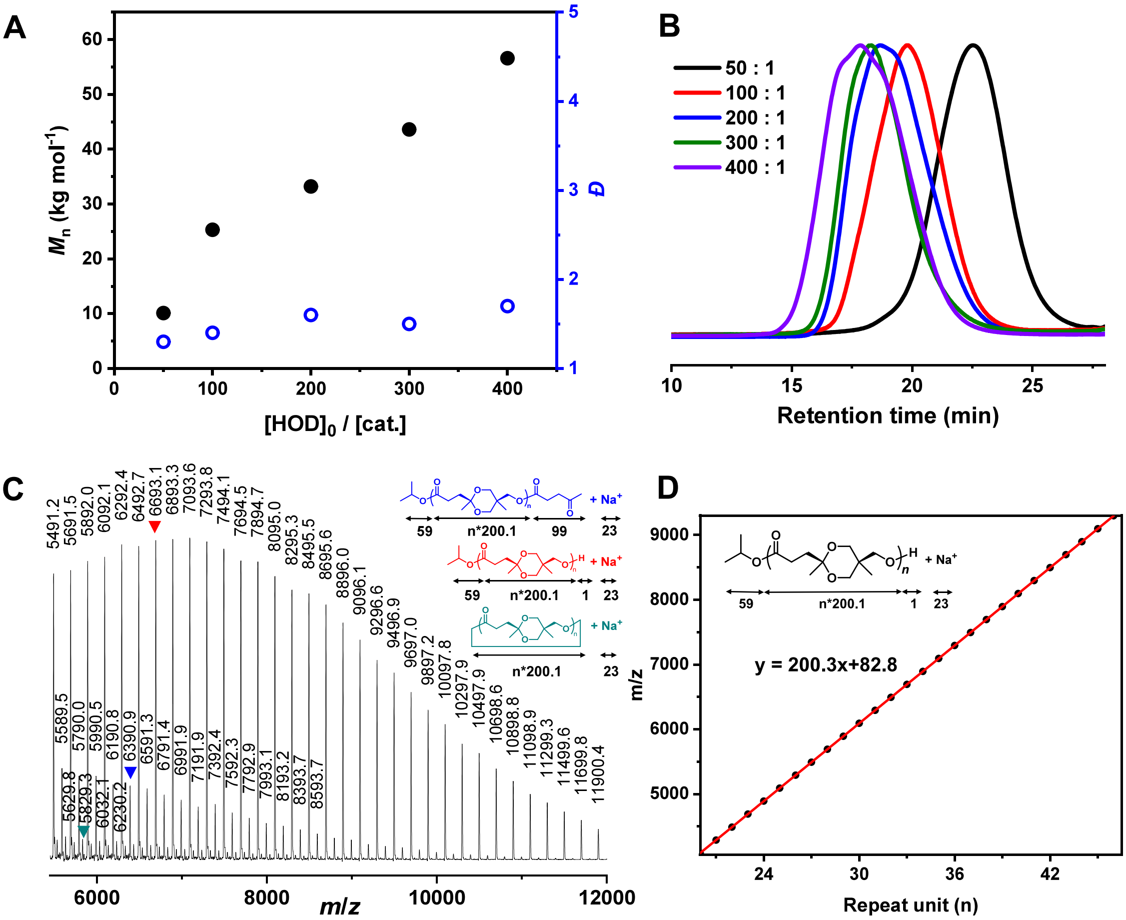

Figure 1. (A) Plots of M_n and $Đ$ as a function of $[M]_0/[cat.]$ ratio. (B) Overlay SEC profiles at different $[M]_0/[cat.]$ ratios at 170 °C. (C) MALDI-TOF-MS of PHOD. (D) Polt of *m*/*z* values (*y*) of the PHOD versus the theoretical number of repeat units (*x*).

ketal diester, named as HOD, through a strategic one-pot dehydration reaction. This synthesis involved levulinic acid, identified by the US Department of Energy as a top value-added compound derived from biomass,[61] and combined it with 1,1,1-tris(hydroxymethyl)ethane (TME), a common precursor in polyester manufacturing. A mixed solvent system of cyclohexane and toluene was optimized to facilitate the efficient precipitation of the generated HOD. This approach avoided the use of dilute solution and achieved over 20 g of high-purity HOD per batch in an 80% overall yield, with purification requiring only simple filtration and washing (Scheme 1). It is a rare case to obtain pure macrocycles at such high concentration.[62] The unique stereostructure of the six-membered ketal ring in the HOD was elucidated using nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectroscopy (Figures S1 and S2). Complementing this, single-crystal X-ray diffraction (XRD) analysis confirmed HOD's stable chair conformation, featuring *cis*-aligned substituents covalently bonded through ester linkages (Scheme 1, Table S1). More specifically, the single-crystal diffraction pattern shows that the distance between the ketal atom O and the carbonyl atom C (2.72 Å) is significantly smaller than the sum of their van der Waals radii (3.22 Å). This demonstrates the existence of n → π^* interactions between the two atoms in HOD, and thus providing additional stabilizing effect on HOD.[63] Furthermore, natural bond orbital (NBO) analysis confirms the existence of interactions in HOD (Figures S4 and S5, Table S2).[64−66] Recent work has demonstrated the existence of n → π^* interactions in or between some polymer

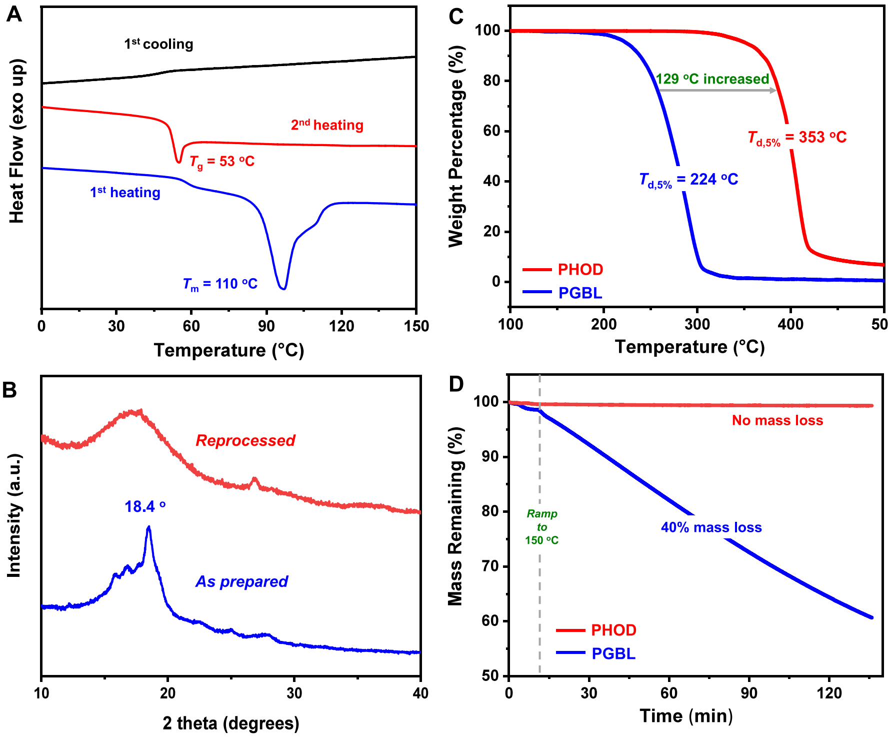

Figure 2. (A) DSC thermograms of the PHOD. (B) Powder XRD profiles of PHOD. (C) TGA thermograms of PHOD (26.9 kDa, $Đ$ = 1.42) and PGBL (14.5 kDa, $Đ$ = 1.22). (D) Isothermal thermograms for PHOD and PGBL performed at 150 °C for 120 min.

chains,[33,67,68] but such interactions have rarely been addressed in monomers.

Initial ROP condition screenings employed commercially available simple organometallic catalysts, such as tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) and titanium isopropoxide ($Ti(O\textit{i}\text{-}Pr)_4$), at varied monomer concentrations and temperatures (Table 1 and Table S3). Specifically, the catalyst $Sn(Oct)_2$ only achieved low HOD conversion, yielding low molar mass PHOD, regardless of the monomer concentration (1.0 or 3.0 M) and reaction temperature (110, 140, or 170 °C) (Table S3). Switching from $Sn(Oct)_2$ to $Ti(O\textit{i}\text{-}Pr)_4$, a nontoxic, inexpensive catalyst known for its high catalytic activity in the ROP of MLs,[69] increased the HOD conversion to 91% in 1.5 h with [HOD]:[$Ti(O\textit{i}\text{-}Pr)_4$] ratio of 50:1 in chlorobenzene (0.5 mL for 600 mg HOD, 3.0 M) at 170 °C, affording PHOD with a molar mass (M_n) of 10.1 kDa and a dispersity ($Đ$) of 1.3 (Table 1, entry 1). Subsequent polymerization runs with $Ti(O\textit{i}\text{-}Pr)_4$ at 170 °C, across a range of [HOD]:[$Ti(O\textit{i}\text{-}Pr)_4$] ratios from 100:1 to 400:1, were conducted (Table 1, entry 2−5). Size exclusion chromatography (SEC) analysis of the resulting polymers revealed a linear and proportional increase in molar mass (M_n = 25.3−56.6 kDa) with increasing the [HOD]:[$Ti(O\textit{i}\text{-}Pr)_4$] ratio, while the dispersity remained relatively low ($Đ$ = 1.3−1.7) (Figure 1A,B), suggesting a relatively controlled polymerization. The polymerization reached 95% monomer conversion within 10 min when further increasing the polymerization temperature to 200 °C (Table 1, entry 6).

Characterization of Poly(ketal-ester) PHOD: Structural Features and Thermal Properties. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analysis of a low-molar-mass PHOD using [HOD]:[$Ti(O\textit{i}\text{-}Pr)_4$] = 100:1 revealed three distinct series of molecular ion peaks (Figure 1C). Each series displayed a consistent peak spacing of 200.1 Da between adjacent molecular ion peaks, equivalent to half of the exact molar mass of HOD (m/z = 200.1), as evidenced by the slope (200.3) in the linear plot correlating m/z values (y-axis) with the number of HOD repeat units (x-axis; Figure 1D). The intercept of the major molecular ion peaks plot, at 82.8, corresponds to the combined mass of the chain ends and Na^+ [60.1 (iPrO/H) + 23.0 (Na^+) g mol^{-1}] (Figure 1D). The existence of a minor series of molecular ion peaks suggests the presence of ketone chain ends (m/z = 179.5), presumably attributed to ketal dissociation induced by trace water and catalyzed by Lewis acid under elevated temperature conditions (Figure S6). Furthermore, another minor series of molecular ion peaks corresponding to cyclic PHOD also existed, and this cyclic PHOD is generated from the intramolecular transesterification during the polymerization. The NMR spectra of PHOD also confirmed its chemical structure (Figures S7−S9). In the ^{1}H NMR spectrum, the existence of a small signal at 2.21 ppm (CH_3−C═O) confirmed the presence of dissociated ketal (Figure S8), accounting for approximately 0.4 mol % of the total ketal content. Moreover, the ^{13}C NMR spectrum of PHOD displayed only one set of signals as in HOD, indicating that PHOD maintains the *cis*-1,4-disubstituted six-membered ketal configuration (Figure S9).

The thermal properties of PHOD (M_n = 55.6 kDa and $Đ$ = 1.7) were initially characterized by using differential scanning calorimetry (DSC). The first heating scan revealed that PHOD is a semicrystalline polymer, exhibiting a T_m of 110 °C, which can be attributed to its well-defined *stereo*-configuration structure (Figure 2A). The semicrystalline nature of PHOD was further corroborated by powder X-ray diffraction (pXRD) analysis. The pXRD pattern displayed sharp diffraction peaks at 2θ values of 18.4°, corresponding to a d-spacing of 0.48 nm (Figure 2B). Interestingly, during the second heating scan of

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DSC, only a glass transition temperature (T_g) of 53 °C was observed, suggesting a relatively slow crystallization of PHOD (Figure 2A).

Thermal Stability of T_f-Regulated PHOD versus T_c-Regulated PGBL. The thermal stability of PHOD was measured by thermogravimetry analysis (TGA). PHOD exhibited exceptional thermostability, as evidenced by a $T_{d,5\%}$ (temperature at 5% weight loss) of 353 °C and a maximum rate of decomposition temperature (T_{max}) reaching 407 °C (Figure 2C). To highlight the advantages of T_f-regulated polymers over T_c-regulated counterparts, poly(γ-butyrolactone) (PGBL), known for its low T_c and suitability for chemical recycling to monomer, was chosen for comparison.[20] While PGBL, a kinetically trapped polymer, can be used at temperatures well above its T_c of −9 °C in bulk, it exhibited a considerably lower $T_{d,5\%}$ of only 224 °C, about 129 °C lower than that of PHOD under an identical heating rate of 20 °C/min (Figure 2C). In a more practical scenario, an isothermal experiment was conducted on PGBL at 150 °C under a N_2 atmosphere. A significant 40% mass loss was observed within 120 min. In stark contrast, the T_f -regulated PHOD, which gains increasing thermodynamic stability at elevated temperatures, exhibited no mass loss under similar conditions, underscoring its superior thermal stability (Figure 2D).

To gain deeper insight into the contrasting thermostability performances of PHOD and PGBL, TGA-FTIR-GC-MS coupling analysis was employed to compare the decomposition mechanisms of PHOD and PGBL (Figures S11−S15). Specifically, IR-temperature 3D plots confirmed that both polymers undergo a single thermal decomposition process, as indicated by a single mass-loss step in their respective TGA thermograms. The consistency of absorption peaks throughout the decomposition process underscores a uniform composition of the decomposition products. Therefore, the product generated at the maximum rate of mass loss can be considered representative of the entire thermal decomposition process (Figures S16−S19). GC analysis revealed that only two products, the monomer and initiator, were present in the thermal decomposition of PGBL. This indicates that at elevated temperatures, the monomer state becomes more thermodynamically stable than the polymer state in PGBL, leading to rapid generation of γ-butyrolactone (GBL) once the kinetic barrier for depolymerization is overcome (Figures S20−S23).[20] In contrast, the thermal decomposition of PHOD yielded multiple products, as identified by MS analysis. These products were fragments resulting from the random scission of the polymer chain (Figures S20 and S24−S35), indicating a different decomposition pathway from PGBL. Therefore, T_f-regulated polymers such as PHOD represent an effective design strategy to tackle the long-standing challenge of achieving thermostability in intrinsically circular polymers. Distinct from T_c-regulated polymers, the T_f-regulated polymer PHOD exhibits enhanced thermodynamic stability as the temperature increases until it reaches the threshold of random thermal decomposition. More importantly, the resultant PHOD, even without undergoing a postpolymerization catalyst removal process, has been shown to possess sufficient thermal stability for direct utilization, as evidenced by a $T_{d,5\%}$ of 345 °C and a T_{max} of 403 °C (Figure 3A), aligning well with the practical requirements of industrial production and applications.

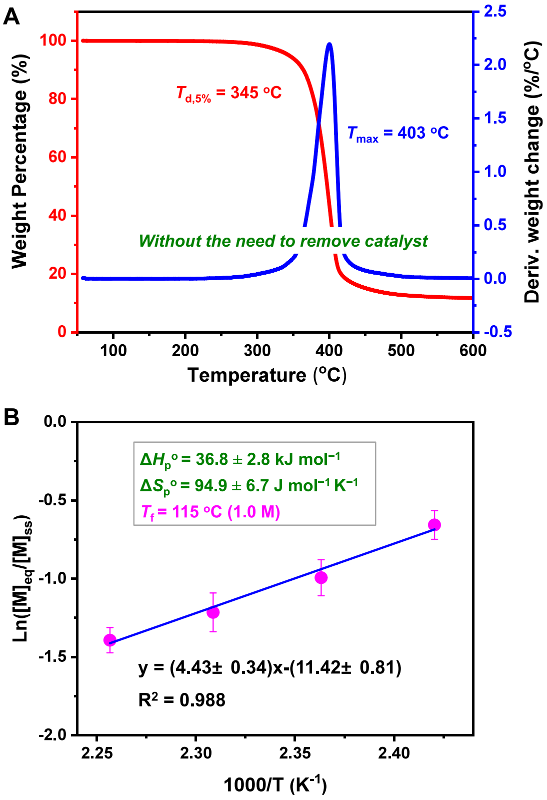

Figure 3. (A) TGA and DTG thermograms of crude PHOD containing 0.5 mol % Ti(O*i*-Pr)$_4$. (B) Van't Hoff analysis of the polymerization of HOD in chlorobenzene (1 M).

Chemical Recyclability of PHOD. Typically, there exists a persistent trade-off between thermostability and chemical recyclability in polymers that can be chemically recycled back to monomers. Unlike the depolymerization of T_c-regulated circular polymers, which necessitates high temperatures to render the monomer state thermodynamically favorable, the T_f-regulated system presents a different paradigm. In this case, the monomer state (HOD) is more thermodynamically favorable than the polymer state (PHOD) at lower temperatures. This allows for low-energy-input depolymerization, potentially feasible even at room temperature. The crucial aspect lies in ensuring that the depolymerization occurs within an operable time scale, which can be achieved by employing highly efficient depolymerization catalysts.

To quantitatively assess the recyclability of thermodynamically stable PHOD at different temperatures, the T_f for HOD polymerization was determined by measuring the equilibrium monomer concentration $[\mathrm{HOD}]_{eq}$ at various temperatures (140, 150, 160, and 170 °C), using a ratio of [HOD]:[Ti(O*i*-Pr)$_4$] of 20:1 in chlorobenzene with an initial monomer concentration $[\mathrm{HOD}]_0$ of 1.0 M. The Van't Hoff plot of $\ln[\mathrm{HOD}]_{eq}$ versus $1/T$ from this experiment yielded a linear relationship, from which the standard state thermodynamic parameters were calculated (Figure 3B): enthalpy change of polymerization (ΔH_p°) = 36.8 ± 2.8 kJ mol^{-1}, and entropy change (ΔS_p°) = 94.9 ± 6.7 J mol^{-1} K^{-1}. Based on the equation $T_f = \Delta H_p^\circ / \{\Delta S_p^\circ + R\ln[\mathrm{HOD}]_0\}$, T_f was calculated to be 115 °C at $[\mathrm{HOD}]_0 = 1.0$ M. This implies that, under standard state conditions, the ROP of HOD is thermodynamically favored above 115 °C, whereas depolymerization becomes more favorable below this temperature.

The calculated thermodynamic parameters indicated that the ROP of HOD is entropy-driven, and chemical recycling of PHOD by depolymerization into HOD under mild conditions, even at room temperature, is possible. However, the primary challenge lies in identifying a highly effective depolymerization catalyst that can sufficiently lower the energy barrier to ensure a complete and selective depolymerization within a practical time scale. To be noted, the polymerization catalyst Ti(O*i*-Pr)$_4$ exhibits very low catalytic activity for transesterification at ambient temperatures;[69−71] it cannot catalyze the depolymerization of PHOD at low temperatures. Therefore, we turned to organobase catalysts for the depolymerization of PHOD. Our initial attempts with triethylamine (NEt$_3$) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalysts yielded no depolymerization within 48 h, at either 25 or 80 °C (Table S4). Increasing the catalyst's basicity by using 2 wt % 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) at 80 °C, 95% of PHOD was converted into its constituent monomer HOD in 48 h (Table 2, entry 1). However, reducing the temperature to 25 °C, only 78% conversion was achieved even after 240 h (Table 2, entry 2), likely due to the insufficiency of TBD in lowering the energy barrier at this low temperature. We then tried 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino) phosphoranylideneamino]-2λ^5,4λ^5-catenadi(phosphazene) (^{t}Bu-P$_4$), one of the strongest known neutral bases with a pK_a of 30.2 in dimethyl sulfoxide (DMSO).[72] Excitingly, this catalyst enabled almost quantitative conversion (>99%) of PHOD into HOD in just 1 min at 25 °C (Table 2, entry 3), indicating that enhancing the basicity of the catalyst can efficiently minimize the energy barrier for depolymerization of PHOD. Similarly, potassium *tert*-butoxide (^{t}BuOK), a simpler and more cost-effective catalyst but with a similar basicity (pK_a of 32.5 in DMSO),[73] demonstrated a comparable ability to quantitatively depolymerize PHOD within merely 1 min, even at a lower catalyst loading (Table 2, entry 6). During depolymerization, the formed HOD precipitated from the solution, and after simple filtration and washing, pure HOD was obtained in nearly quantitative yield, as revealed by its ^{1}H NMR spectrum (Figure 4). The exceptional recyclability of PHOD into HOD can be attributed to two key factors: First, the favorable thermodynamics, wherein the monomer state possesses a lower relative energy level compared to the polymer state at temperatures below its T_f; second, the precipitation of the generated HOD, which plays an essential role in driving the depolymerization to completion, even at a relatively high concentration of 200 g/L (1 mol L^{-1} of repeating unit), by continuously perturbing the PHOD-HOD equilibrium, thereby overcoming the thermodynamic constraints.

Table 2. Depolymerization Results of PHOD Catalyzed by Various Base Catalysts at Varied Temperatures[a]

entry	cat.	temp. (°C)	time	conv.[b] (%)
1	TBD (2 wt %)	80	48 h	95
2	TBD (2 wt %)	25	240 h	78
3	^{t}Bu-P$_4$ (2 mol %)	25	<1 min	>99
4	^{t}Bu-P$_4$ (1 mol %)	25	10 min	79
5	^{t}BuOK (2 wt %)	25	<1 min	>99
6	^{t}BuOK (1 wt %)	25	<1 min	>99

[a] All depolymerization reactions were conducted in a 200 mg/mL solution of toluene. [b] Determined by ^{1}H NMR spectroscopy using trimethoxybenzene as internal standard.

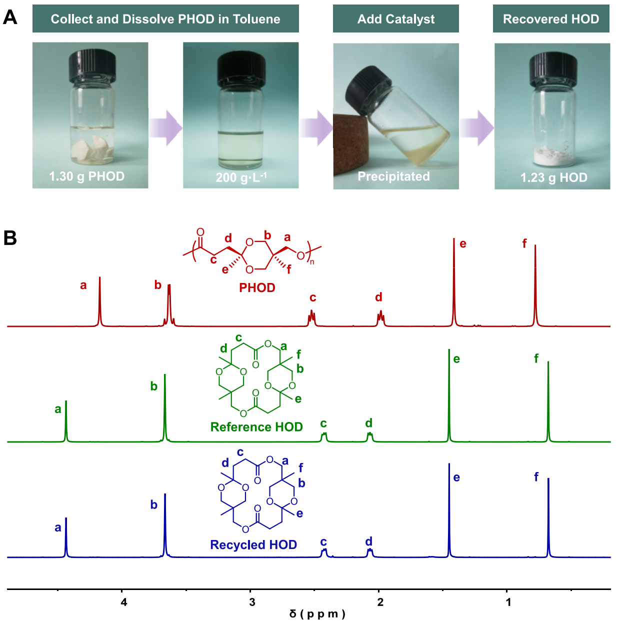

Figure 4. (A) Images of closed-loop recycling process of PHOD. (B) Overlay of ^{1}H NMR spectra measured in CDCl$_3$ of PHOD (top); the reference HOD for comparison (middle); and recycled HOD by filtration (bottom).

Tunable Mechanical Properties and Chemical Recyclability of HOD-Based Copolymers. PHOD is a hard but brittle material, characterized by a high Young's modulus (E) of 1.03 GPa, an ultimate tensile strength at break (σ_B) of 41.4 MPa, an elongation at break (ε_B) of approximately 7%, and a toughness (U_T) of 1.8 MJ m^{-3} (Figure 5A). To tailor these mechanical properties, copolymerization is an effective approach. In this context, pentadecanolide (PDL), a commercially available natural macrolide,[74] was chosen as the copolymerization monomer, due to its entropy-driven polymerization characteristics that align with those of HOD. Copolymerization of PDL and HOD was conducted under identical conditions to those used for HOD polymerization.[75] Kinetic studies revealed that PDL exhibits higher reactivity than HOD. For instance, in a copolymerization run with a ratio of [HOD]$_0$/[PDL]$_0$/[Ti(O*i*-Pr)$_4$] = 300/100/1.5, PDL achieved nearly quantitative (>99%) conversion within 45 min, while the conversion of HOD reached only 40%. By further extending the reaction time, more HOD was incorporated into the formed polymer chains through transesterification (Figure S36).[76] Subsequently, a series of copolymers, PHOD-*co*-PPDL, were synthesized by varying the feed ratio of PDL to HOD (Table S5, Figures S37 and S38). Due to transesterification during polymerization, these copolymers are obtained as random copolymers, as supported by their ^{13}C NMR spectra (Figure S39). The T_g of these copolymers decreased as the PDL content increased, located between 22 and 35 °C (Figure S40). Notably, the thermal decomposition temperature of the copolymers did not significantly decrease; for instance, the $T_{d,5\%}$ of PHOD$_{81}$-*co*-PPDL$_{19}$ remained at 351 °C (Figure S41).

Indeed, the incorporation of even a small amount of PDL significantly enhances the toughness of the otherwise brittle PHOD (Figures S42 and S43, Table S6). Specifically, the U_T

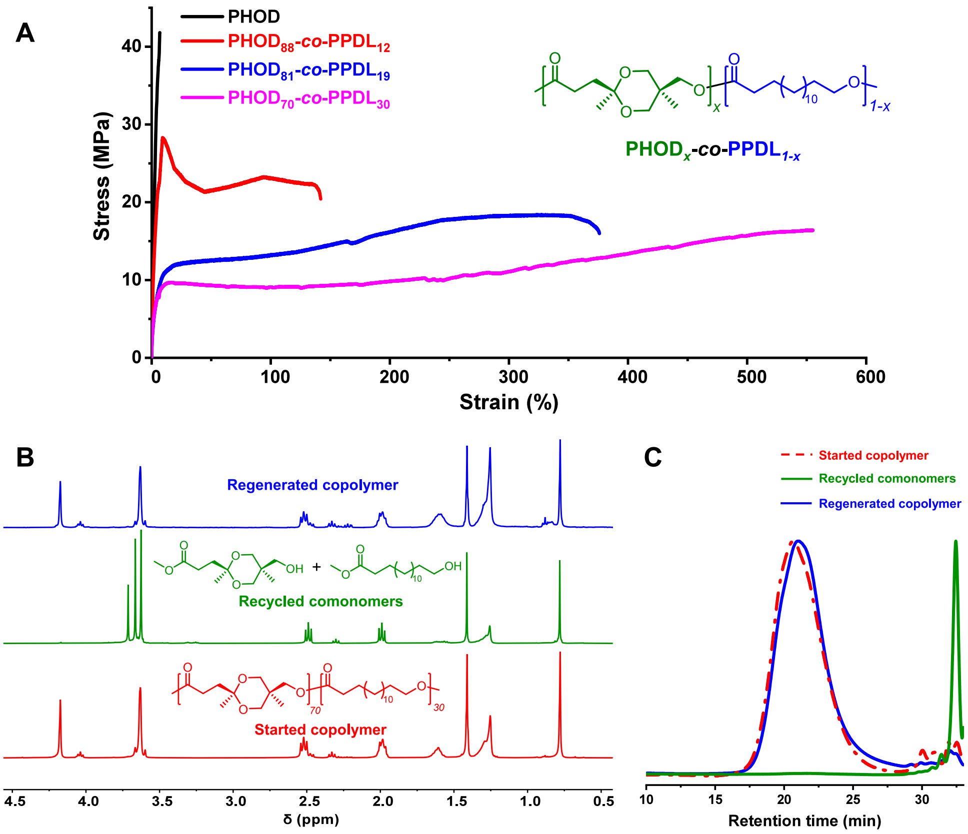

Figure 5. (A) Overlay plots of stress/strain curves of PHOD and PHOD-*co*-PPDL. (B) Overlay of ^{1}H NMR spectra measured in $CDCl_3$ of started PHOD-*co*-PPDL (bottom); recycled comonomers (middle); and regenerated PHOD-*co*-PPDL (top). (C) Overlay SEC profiles of started copolymer (red), recycled comonomers (green), and regenerated copolymer (blue).

of PHOD$_{88}$-*co*-PPDL$_{12}$ was measured to be 33.1 MJ m^{-3}, which is an increase of more than 18 times compared to that of pure PHOD (U_T = 1.8 MJ m^{-3}). This improvement was realized despite a decrease in E from 1.03 to 0.85 GPa, and σ_B from 41.4 to 21.6 MPa. Further increasing the PPDL incorporation ratio to 19 and 30% resulted in even more ductile copolymers, with U_T values rising to 52.2 MJ m^{-3} for PHOD$_{81}$-*co*-PPDL$_{19}$ and 64.6 MJ m^{-3} for PHOD$_{70}$-*co*-PPDL$_{30}$, respectively. These copolymers maintained relatively high Young's moduli (E = 376 MPa for PHOD$_{81}$-*co*-PPDL$_{19}$ and 329 MPa for PHOD$_{70}$-*co*-PPDL$_{30}$) and ultimate tensile strengths at break (σ_B = 16.7 MPa for PHOD$_{81}$-*co*-PPDL$_{19}$ and 16.4 MPa for PHOD$_{70}$-*co*-PPDL$_{30}$), along with significant elongations at break (ε_B = 329% for PHOD$_{81}$-*co*-PPDL$_{19}$ and 555% for PHOD$_{70}$-*co*-PPDL$_{30}$), as illustrated in Figure 5A. The overall performances of these PHOD-*co*-PPDL copolymers surpass those of commodity plastics like low-density polyethylene (LDPE), which typically exhibit $E \approx 280$ MPa, $\sigma_B \approx$ 10 MPa, and $\varepsilon_B \approx 200\%$.[77] Furthermore, the high-toughness thin film of PHOD$_{81}$-*co*-PPDL$_{19}$ also exhibits high transparency, showcasing its potential as a biobased, recyclable packaging material.

Unlike other selective recycling methods for copolymers, which often require specific block sequences or controlled temperatures,[22,29,78] the unique precipitation equilibrium in our system enables straightforward, selective recycling of HOD from random copolymers. HOD can be recycled with over 80% isolated yield, irrespective of the copolymer composition (Table S7 and Figure S44). To fully establish the closed-loop circularity of PHOD-*co*-PPDL, methanolysis was employed for depolymerization. Specifically, the depolymerization of PHOD$_{70}$-*co*-PPDL$_{30}$ (M_n = 38.0 kDa, $Đ$ = 1.9) was catalyzed by 2 wt % TBD in methanol (200 mg/mL) at 80 °C, leading to the quantitative conversion of the copolymer into its methanolysis products within 1 h (Figure 5B). These methanolysis products are readily repolymerizable into PHOD-*co*-PPDL through step-growth polymerization, catalyzed by 1 wt % Ti(O*n*-Bu)$_4$. The regenerated PHOD-*co*-PPDL exhibited a similar M_n of 35.5 kDa with a slightly lower $Đ$ of 1.7 (Figure 5C), indicating the feasibility of establishing closed-loop circularity of PHOD-*co*-PPDL through a methanolysis approach.

■ CONCLUSIONS

In summary, this work presents a rare example of T_f -regulated closed-loop circularity in poly(ketal-ester). This polymer was prepared by the entropy-driven ROP of a macrocyclic diester HOD, and it exhibits exceptional thermostability with a $T_{d,5\%}$ of up to 353 °C. Remarkably, this polymer can be quantitatively converted back into its constituent monomer HOD at 25 °C, catalyzed by a simple base ^{t}BuOK. In essence, such T_f -regulated systems offer at least two advantages over T_c-regulated ones: (1) Enhanced thermodynamic stability: the resultant polymer is more thermodynamically stable as the temperature increases, allowing for a significantly high processing temperatures compared to kinetically trapped T_c-regulated polymers. (2) Cost-effective recycling: the feasibility of depolymerization under mild conditions presents a more cost-effective recycling pathway, circumventing the high energy costs typically associated with standard recycling processes.

Additionally, a transformation from hard to ductile mechanical properties was achieved through the copolymerization of HOD with PDL, a commercially available natural macrolide. Both components can be recycled via methanolysis, effectively regenerating PHOD-*co*-PPDL with comparable molecular weight and dispersity by step-growth polymerization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c03523.

Experimental details, additional figures, and tables (PDF)

Accession Codes

CCDC 2216476 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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Notes

The authors declare the following competing financial interest(s): X.-B. Meng, T. Zhou, F.-S. Du and Z.-C. Li have filed a provisional patent application (Chinese patent application No. 2024100670384). All other authors declare no competing interest.

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