

Enabling Closed-Loop Circularity of “Non-Polymerizable” α , β -Conjugated Lactone Towards High-Performance Polyester with the Assistance of Cyclopentadiene

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Abstract: Chemical recycling of polymers to monomers presents a promising solution to the escalating crisis associated with plastic waste. Despite considerable progress made in this field, the primary efforts have been focused on redesigning new monomers to produce readily recyclable polymers. In contrast, limited research into the potential of seemingly “non-polymerizable” monomers has been conducted. Herein, we propose a paradigm that leverages a “chaperone”-assisted strategy to establish closed-loop circularity for a “non-polymerizable” α , β -conjugated lactone, 5,6-dihydro-2H-pyran-2-one (DPO). The resulting PDPO, a structural analogue of poly(δ -valerolactone) (PVL), exhibits enhanced thermal properties with a melting point (T_m) of 114 °C and a decomposition temperature ($T_{d,5\%}$) of 305 °C. Notably, owing to the structural similarity between DPO and δ -VL, the copolymerization generates semi-crystalline P(DPO-*co*-VL)s irrespective of the DPO incorporation ratio. Intriguingly, the inherent C=C bonds in P(DPO-*co*-VL)s enable their convenient post-functionalization via Michael-addition reaction. Lastly, PDPO was demonstrated to be chemically recyclable via ring-closing metathesis (RCM), representing a significant step towards the pursuit of enabling the closed-loop circularity of “non-polymerizable” lactones without altering the ultimate polymer structure.

Over the past half-century, the exponential growth in plastic production and consumption has been driven by its unique features such as low cost, high strength to weight ratio, durability, processability, as well as the ability to customize material performance. However, this growth has been accompanied by a short-sighted end-of-life (EoL) design and management, leading to severe environmental consequences, and accelerating the consumption of finite

fossil resources.^[1] The widespread usage of unsustainable plastics, particularly for single-use items, has precipitated an urgent situation necessitating immediate action to transition from the current linear plastic economy towards a more sustainable circular plastic economy.^[2]

Among several approaches being explored to tackle such issues, chemical recycling of polymers into monomers is gaining recognition as a promising solution,^[2,3] owing to its potential to regenerate polymers with virgin-quality and reduce the demand for raw feedstock. However, striking a balance between polymerizability of the monomer and recyclability of the polymer poses a significant challenge in the pursuit of circular polymers that can produce practical materials and be efficiently recycled into their constituent monomers.^[2f,4] Over the past decade, several families of chemically recyclable polymers have been developed, including polyesters,^[5] polythioesters,^[6] polyamides,^[7] poly(ester amide),^[8] polycarbonates,^[9] polyacetals,^[10] poly(phthalaldehyde)s,^[3a,c] and poly(cyclic olefin)s,^[11] etc. A remarkable demonstration of this effort is the successful ring-opening polymerization (ROP) of γ -butyrolactone,^[12] a monomer once deemed “non-polymerizable”,^[13] achieved through meticulous manipulation of thermodynamic and kinetic conditions, thus establishing the “monomer-polymer-monomer” closed-loop circularity. Despite this accomplishment, the polymerization still requires extremely low temperatures (−40 °C), rendering it impractical for large-scale plastic production. As a result, the same research group later employed a *trans*-ring fused approach to the parent monomer γ -BL to enhance both polymerizability and material properties.^[14] Although similar strategies have been widely adopted to adjust the polymerizability and depolymerizability of “non-polymerizable” monomers or “non-recyclable” polymers,^[15] these approaches typically lead to new polymers, rather than maintaining the inherent polymer structures originated from the parent monomers, which not only impedes the utilization of readily available raw materials but also limits the exploration of the full potential of intriguing polymer structures. Therefore, a pertinent question arises: *Is there a feasible approach to facilitate the polymerization of previously deemed “non-polymerizable” monomers while preserving the target polymer structures?*

In molecular biology, chaperones are proteins that play a crucial role in assisting the conformational folding or unfolding of large proteins or macromolecular protein complexes, without becoming a permanent component of the final structures.^[16] Inspired by this fascinating behavior

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of chaperones, we propose a novel paradigm that utilizes reversible Diels–Alder reaction to facilitate the construction of intrinsically circular polymers from deemed “non-polymerizable” monomers. To investigate the feasibility of this concept, we selected the ROP “non-polymerizable” α , β -conjugated valerolactone,^[17] 5,6-dihydro-2H-pyran-2-one (DPO), which constitutes a crucial structural component of various natural products and can also be synthesized from renewable bioresources,^[18] as a demonstrative example, to construct the intrinsically circular plastics on the basis of DPO via the assistance of reversible Diels–Alder reaction (Scheme 1).

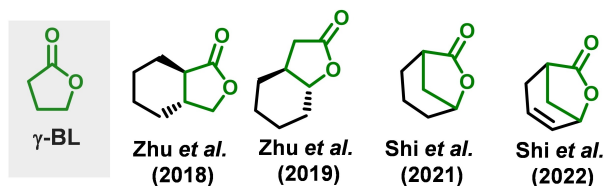
Initially, we endeavored to homopolymerize DPO to obtain PDPO, a poly(δ -valerolactone) (PVL) analogue with C=C bonds being installed in the polyester backbone. Despite our rigorous attempts, both the ROP and ring-opening metathesis polymerization (ROMP) approaches failed to yield the targeted PDPO. Detailed attempts and outcomes are summarized in Table S1. This result can be attributed to the high stability of the six-membered α,β -conjugated lactone structure of DPO, thermodynamically unfavorable for the ROP as compared to δ -VL, known for its relatively high polymerizability.^[4a,19] We then pursued a monomer redesign based on DPO while adhering to the redesign guiding principle of preserving the PDPO polymer structure. Specifically, to mitigate the impact of conjugated

double bonds on the polymerization process, we employed cyclopentadiene as the conjugated diene to react with dienophile DPO in the well-established Diels–Alder reaction, generating a cyclic compound, 3,4,4,5,8,8-hexahydro-5,8-methano-1H-2-benzopyran-1-one (HPO) in 72 % yield with an *endo/exo* ratio of 9/1.^[20] To simplify the polymerization process, only the *endo* product is isolated and used for the following ROP, and the structure of HPO has been unambiguously confirmed by ¹H NMR, ¹³C NMR, HSQC and FT-MS spectrum (Figure S1–S4).

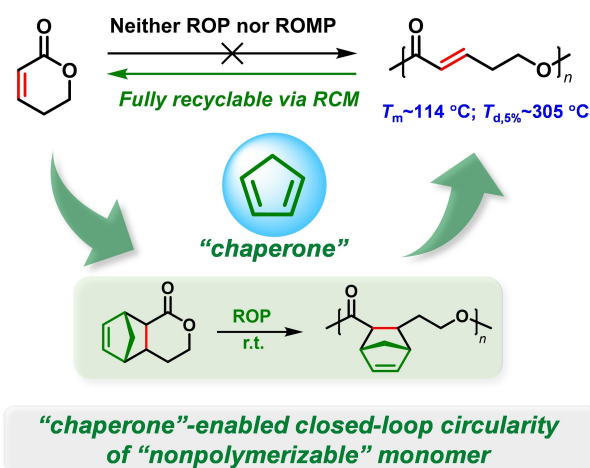
After evaluating several highly active catalysts for the ROP of HPO, including La[N(SiMe₃)₂]₃, 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD), and 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2 λ^5 ,4 λ^5 -catenadi(phosphazene) (^tBu-P₄), the optimized polymerization condition for HPO was determined to be neat ROP at 30 °C using ^tBu-P₄ as the catalyst.^[19c,21] The number-average molecular weight (*M_n*), dispersity (*D*) and monomer conversion information of the resulting PHPO are summarized in Table S2. Specifically, the ^tBu-P₄-catalyzed ROP at [HPO]/[BnOH]/[^tBu-P₄]=500/1/1.5 afforded PHPO with *M_n* up to 24.0 kDa. The structure of the obtained PHPO was characterized by ¹H NMR, ¹³C NMR, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure S5–S7). For example, the ¹H NMR spectrum of PHPO prepared at a [HPO]/[BnOH]/[^tBu-P₄] ratio of 20/1/0.5 represents a linear structure and shows high end-group fidelity, which was also confirmed by MALDI-TOF MS spectrum. The MS spectrum shows only one group of molecular ion peaks with a spacing of 164.1 g/mol, consistent with the exact molar mass of HPO. Besides, the intercept of the plot, 131.0, represents the total mass of BnOH end group and Na⁺, corresponding to the linear PHPO. We then explored the possibility of producing cyclic PHPO by using ^tBu-P₄ alone.²¹ Unlike the controlled ROP with both BnOH and ^tBu-P₄, the ROP of HPO without BnOH afforded PHPO with similar *M_n* of about 24.4 kDa, regardless of variation in [HPO]/[^tBu-P₄] ratio. This observation suggests that possible cyclization occurs at a specific chain length during the ROP of HPO, resulting in cyclic polymers of similar molecular weights.^[22] The purified cyclic PHPO was also characterized by ¹H NMR, ¹³C NMR, and MALDI-TOF MS (Figure S9–S11). To further characterize and confirm the linear and cyclic topology, both linear and cyclic PHPO polymers were subjected to size exclusion chromatography (SEC) featuring triple-detection capabilities—namely light scattering, refractometry, and viscometry. The resultant Mark-Houwink-Sakurada double-logarithmic plot, portraying the correlation between intrinsic viscosity ($[\eta]$) and weight-average molecular weight (*M_w*) for PHPO polymers of both topologies, indicates that the cyclic polymers displayed a lower intrinsic viscosity at the same *M_w*, and the $[\eta]_{\text{cyclic}}/[\eta]_{\text{linear}}$ ratio was found to be 0.7, consistent with the theoretically predicted value (Figure 1A).^[23] In addition, the logarithm plots of *M_w* versus the elution volume reveals that the cyclic PHPO has smaller hydrodynamic volume (Figure 1B).

Both the linear and cyclic PHPOs are amorphous material with glass transition temperatures (*T_g*s) being

Conventional design strategy:



This work:



“chaperone”-enabled closed-loop circularity of “nonpolymerizable” monomer

Scheme 1. (A) Previous efforts of designing new monomers from γ -BL to enhance its polymerizability. (B) The proposed “chaperone”-enabled polymerization strategy in this work, proceeding via the reversible Diels–Alder reaction of cyclopentadiene with “non-polymerizable” DPO and the release of “chaperone” after polymerization. The resulting polymer PDPO can be further recycled back to DPO via RCM strategy.

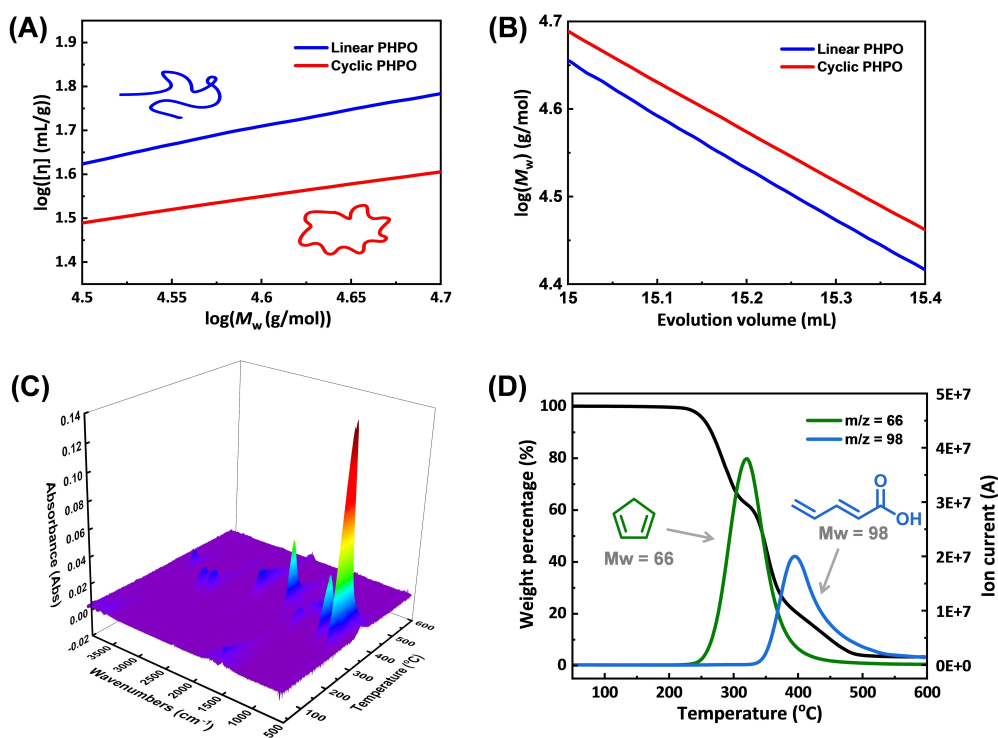


Figure 1. (A) Double logarithm (Mark-Houwink-Sakurada) plots of intrinsic viscosity $[\eta]$ versus absolute M_w of linear PHPO ($M_n = 14.3$ kDa, $\bar{D} = 1.53$) and cyclic PHPO ($M_n = 24.4$ kDa, $\bar{D} = 1.59$). (B) Logarithm plots of M_w versus the elution volume of linear PHPO ($M_n = 14.3$ kDa, $\bar{D} = 1.53$) and cyclic PHPO ($M_n = 24.4$ kDa, $\bar{D} = 1.59$). (C) Three-dimensional FT-IR spectrum. (D) Overlay of single ion curves of selected ions and TGA curves during simultaneous TGA-IR-MS analysis for thermal degradation of PHPO at a heating rate of $20^\circ\text{C}/\text{min}$.

around 33°C , as determined by differential scanning calorimetry (DSC) (Figure S12). This is attributed to the lack of stereoselectivity in the current polymerization system between the enantiomers of *endo*-HPO, resulting in an atactic PHPO. Thermogravimetric analysis (TGA) of PHPO revealed that its thermal decomposition was a two-step process. Intriguingly, the first stage occurred at around 230°C with 39% weight loss, presumably corresponding to the release of cyclopentadiene through retro-DA reaction (Figure 1D). To gain further insight into the mechanisms underlying this thermal degradation, a coupled Thermogravimetric Analysis-Fourier Transform Infrared Spectroscopy-Gas Chromatography-Mass Spectrometry (TGA-FTIR-GC-MS) approach was employed to analyze the decomposition products (Figures 1C and 1D). The overlay of the single-ion curves and TGA profiles obtained during the simultaneous TGA-FTIR-GC-MS analysis revealed that the decomposition products in the first stage predominantly consisted of cyclopentadiene, while the subsequent decomposition process yielded a compound with an m/z value of 98, which could potentially correspond to either DPO or 2,4-pentadienoic acid (Figure 1D). The thermal degradation product of PDPO were then collected and subjected to ^1H NMR analysis, confirming that 2,4-pentadienoic acid was the product (Figure S13).

Encouraged by the decomposition findings, the retro-DA reaction of PHPO ($M_n = 19.2$ kDa) was initially explored in diphenyl ether (b.p.: 258.3°C) at 250°C , achieving complete conversion within 3 hours. However, the molecular

weight of the resultant PDPO was reduced to M_n of 5.9 kDa, deviating significantly from the theoretical value. This reduction in molecular weight is presumably due to the minor chain scission occurred via *cis*-elimination through the six-membered transition state, leading to lower-molar-mass PDPO with alkene and carboxylic acid termini.^[5c,24] To suppress the undesired thermal degradation, the temperature was lowered to 190°C , and an excess of maleic anhydride was added to facilitate the retro-DA reaction. Remarkably, the reaction reached completion after 12 h, yielding PDPO with a high M_n of 12.9 kDa, consistent with theoretical expectations. The retro Diels-Alder reaction could also be realized by using DPO instead of maleic anhydride as the dienophile under similar conditions. The conversion of PHPO was about 95%, and the original monomer HPO (*endo/exo* ratio of 3/2) was regenerated, thus no cyclopentadiene was wasted.

The resultant polymer PDPO was characterized by ^1H NMR and ^{13}C NMR spectroscopy (Figure S14, S15). Notably, the ^1H NMR spectrum of PDPO exhibited a coupling constant of 15.7 Hz for the C=C bonds (Figure S14), indicating the exclusive presence of *trans* C=C bonds in the polymer. This evidence provides crucial insight into the structural characteristics of PDPO and sheds light on the factors that contribute to its unique properties and potential applications. The thermal properties of PDPO were then investigated. PDPO also displayed enhanced thermal stability, with a high decomposition temperature ($T_{d,5\%}$, defined as the temperature at which 5% weight loss) of 305°C ,

revealed by TGA, approximately 30 °C higher than that of PVL (Figure 2A). Remarkably, PDPO was found to be not only a semi-crystalline polyester, but also displayed a high melting transition temperature (T_m) of 114 °C (Figure 2B). In contrast to its saturated analogue, PVL, which has a relatively low T_m of 56 °C,^[4a,5d] the introduction of *trans* C=C bonds in the polymer backbone increase the T_m of the resulting polymer effectively. The semi-crystalline feature of PDPO was further confirmed by the Wide-Angle X-ray Scattering (WAXS) pattern, which exhibited the main diffraction peak at 2θ of 22.1° (Figure 2C), corresponding to a d spacing of 4.0 Å. Overall, the introduction of the conjugated *trans* C=C bonds in PVL substantially alters the thermal properties of the resulting polyester. These findings underscore the importance of molecular structure on the material properties and suggest that PDPO may have unique

advantages for certain applications due to its distinguished thermal properties.

Given the exceptional thermal properties demonstrated by PDPO, we subsequently conducted a study to investigate the potential enhancement of thermal properties by incorporating DPO into PVL. To this end, we synthesized three P(DPO-*co*-VL) copolymers with varying DPO incorporation ratios of 5 %, 11 %, and 49 %, respectively (Figure 3A). The incorporation of DPO into PVL was confirmed by Diffusion-Ordered NMR Spectroscopy (DOSY) (Figure 3E), and the randomness of the copolymers was confirmed by ¹³C NMR (Figure S30). As expected, P(DPO-*co*-VL) inherited the excellent thermal stability, exhibiting a high $T_{d,5\%}$ of 294 °C (Figure 3B). However, the incorporation of DPO into PVL did not enhance the T_m . Nonetheless, an encouraging observation was that the crystallinity of PVL remained

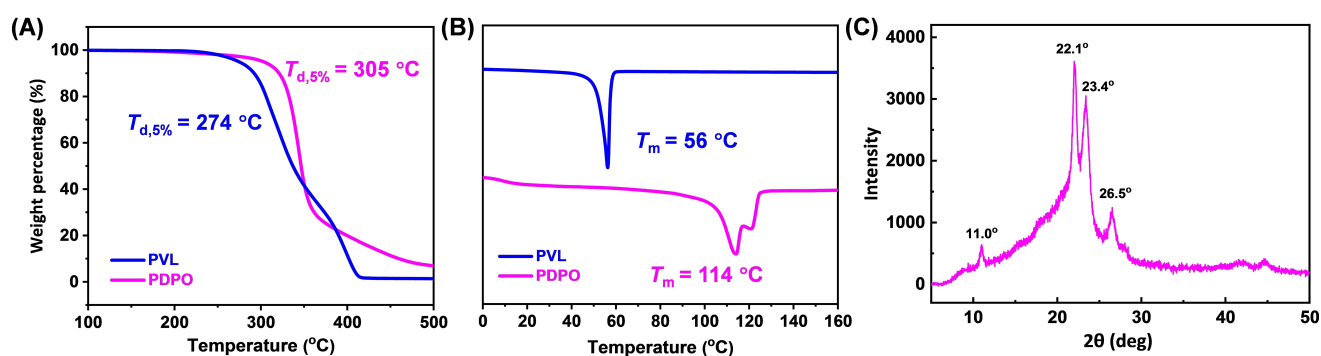


Figure 2. (A) TGA thermograms of PVL ($M_n = 12.3$ kDa, $\mathcal{D} = 1.29$) and PDPO ($M_n = 12.9$ kDa, $\mathcal{D} = 1.45$). (B) The second heating scan DSC thermograms for PVL and PDPO. (C) WAXS pattern of PDPO.

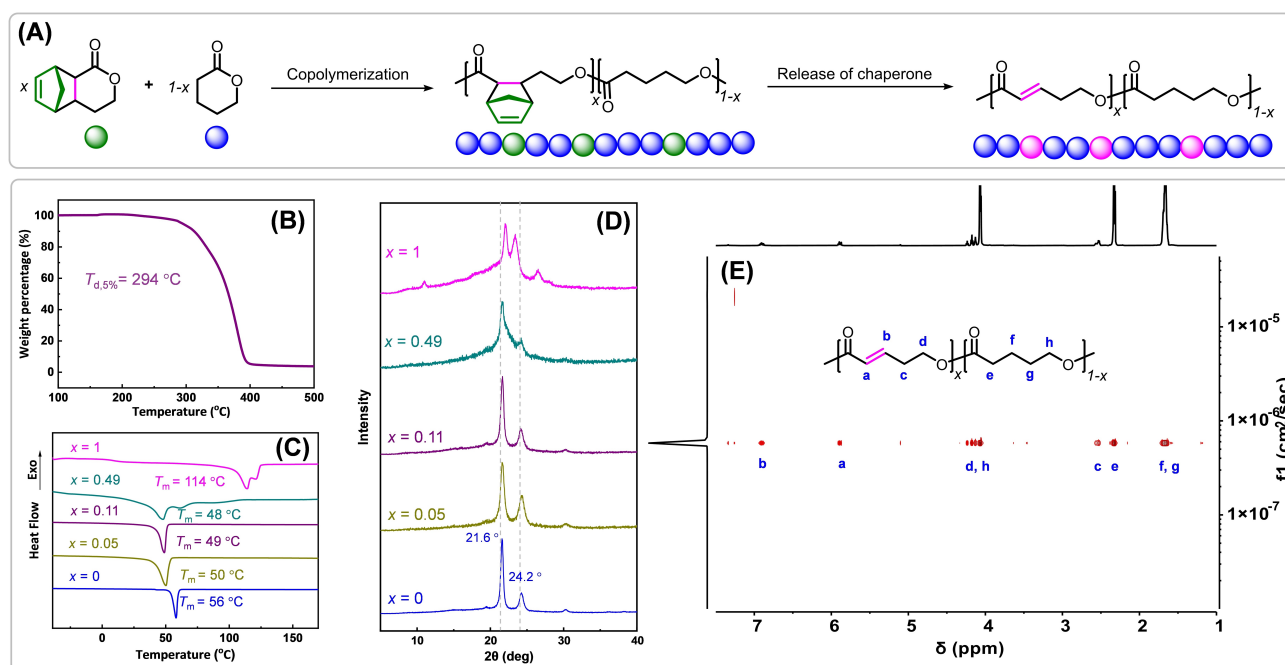


Figure 3. (A) Two-step synthesis of P(DPO-*co*-VL). (B) TGA thermogram of P(DPO-*co*-VL) (11 mol % DPO, $M_n = 17.3$ kDa, $\mathcal{D} = 1.37$). (C) The second heating scan DSC thermograms for PDPO, P(DPO-*co*-VL) (DPO incorporation ratio (x): 49 %, 11 %, 5 %), and PVL. (D) WAXS patterns of PDPO, P(DPO-*co*-VL) and PVL. (E) ¹H NMR DOSY spectrum of P(DPO-*co*-VL) (11 mol % DPO).

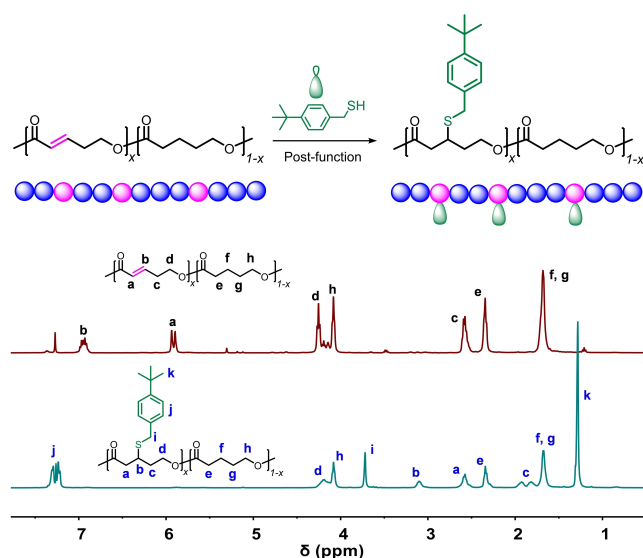


Figure 4. Post-polymerization functionalization of P(DPO-co-VL) via Michael addition of mercaptan: the ^1H NMR (CDCl_3) spectra of P(DPO-co-VL) ($x=0.49$) before and after functionalization.

unaltered, even with a high DPO incorporation ratio of up to 49 % (Figure 3C). The semi-crystalline features of these three copolymers were also confirmed by their WAXS patterns (Figure 3D). Specifically, the WAXS pattern of low DPO incorporation ratio (5 % and 11 %) P(DPO-co-VL) exhibited sharp diffraction peaks at $2\theta=21.6^\circ$ and 24.2° , consistent with the diffraction pattern of PVL. However, the WAXS pattern of high DPO incorporation ratio (49 %) P(DPO-co-VL) showed a broad diffraction peak at $2\theta=21.6^\circ$, presumably due to the overlap of diffraction pattern of PVL and PDPO. Besides, the DSC thermogram of P(DPO-co-VL) with 49 % DPO incorporation showed a broad T_m from 20 to 110°C , indicating the complex crystalline structures in P(DPO-co-VL) (Figure 3C). More importantly, the incorporation of DPO into PVL enables the possibility of post-polymerization functionalization. As a demonstrative example, P(DPO-co-VL) was modified with 4-(*tert*-butyl)benzyl mercaptan via Michael addition to the C=C bonds, affording functionalized PVL materials (Figure 4).

We hypothesized that the low polymerizability of DPO is attributed to the more thermodynamically stability of the monomer state than PDPO, while PDPO exhibited excellent thermal stability, presumably due to it is in a kinetically trapped state. Thus, we initially tested the possibility of chemically recycling of PDPO with TBD as the catalyst via alkoxide back-biting pathway (Table S4, entry 1). However, this strategy was proved to be unfeasible. This result is predictable due to the *trans* C=C bonds in PDPO and the *cis* C=C bond in DPO. We then attempted the TBD-catalyzed depolymerization of PDPO with 30 % repeat units in the *cis*-configuration obtained through photo-isomerization.^[25] However, still no monomer regeneration was observed. Despite observation of DPO generation in a system of in situ photo-isomerization of PDPO and TBD-catalyzed

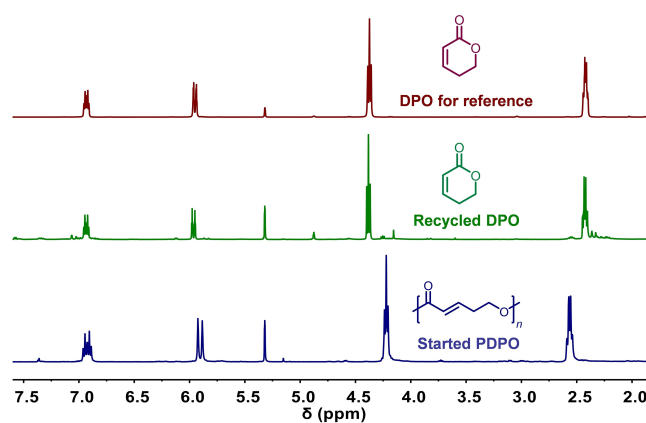


Figure 5. Overlay of the ^1H NMR (CD_2Cl_2) spectra of reference DPO, recycled DPO via RCM strategy, and started PDPO ($M_n=5.9$ kDa, $D=1.14$).

depolymerization, the conversion remained disappointingly low at 10 %, even with a long depolymerization time of 60 h. Subsequently, we redirected our efforts towards ring-closing metathesis (RCM) as a strategy for establishing the closed-loop circularity of PDPO. To our delight, the depolymerization of PDPO catalyzed by Hoveyda-Grubbs II catalyst (4 mol %) in CD_2Cl_2 (10 mg/mL) at reflux achieved clean and selective recovery of DPO with >96 % yield and >99 % selectivity in 6 days (Figure 5).^[26] The slow depolymerization rate is presumably due to the electron-deficient nature of the conjugated *trans* C=C bond or the “release-return” mechanism of Hoveyda-Grubbs II catalysts.^[27] Further optimizations of the depolymerization conditions are on-going in our laboratory through catalyst system innovation.

In summary, this work demonstrates the successful implementation of a “chaperone”-facilitated ROP of a “non-polymerizable” α , β -conjugated lactone DPO, yielding its constituent polyester PDPO that cannot be produced either through direct ROP or ROMP. The resulting PDPO not only exhibited fully chemical recyclability but also displayed superior thermal properties compared to its structural analogue, PVL. This approach also enabled the synthesis of semi-crystalline P(DPO-co-VL)s, irrespective of the DPO incorporation ratio, with intrinsic functionality derived from DPO. Thus, by elucidating the role of “chaperone” chemistry in assisting the polymerization of “non-polymerizable” monomers, we have established a pathway towards closed-loop circularity of target polymer without compromising its inherent structure. Analogously, this conceptual strategy holds potential for tackling challenges associated with the recycling of “non-recyclable” polymers by leveraging “chaperone” assistance in their recovery process.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: α , β -Conjugated lactones · Polyesters · Closed-loop Circularity · Diels–Alder reaction · Ring-closing metathesis

- [1] a) J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. Perryman, A. Andrady, R. Narayan, K. L. Law, *Science* **2015**, *347*, 768–771; b) R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782; c) M. Ellen, *Science* **2017**, *358*, 843; d) S. B. Borrelle, J. Ringma, K. L. Law, C. C. Monnahan, L. Lebreton, A. McGivern, E. Murphy, J. Jambeck, G. H. Leonard, M. A. Hilleary, M. Eriksen, H. P. Possingham, H. De Frond, L. R. Gerber, B. Polidoro, A. Tahir, M. Bernard, N. Mallos, M. Barnes, C. M. Rochman, *Science* **2020**, *369*, 1515–1518.
- [2] a) M. Hong, E. Y.-X. Chen, *Green Chem.* **2017**, *19*, 3692–3706; b) A. Rahimi, J. M. García, *Nat. Chem. Rev.* **2017**, *1*, 0046; c) D. K. Schneiderman, M. A. Hillmyer, *Macromolecules* **2017**, *50*, 3733–3749; d) X. Zhang, M. Fevre, G. O. Jones, R. M. Waymouth, *Chem. Rev.* **2018**, *118*, 839–885; e) M. Hong, E. Y. X. Chen, *Trends Chem.* **2019**, *1*, 148–151; f) L. D. Ellis, N. A. Rorrer, K. P. Sullivan, M. Otto, J. E. McGeehan, Y. Román-Leshkov, N. Wierckx, G. T. Beckham, *Nat. Catal.* **2021**, *4*, 539–556; g) C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y. X. Chen, F. A. Leibfarth, H. Sardon, *Nature* **2022**, *603*, 803–814; h) A.-C. Albertsson, M. Hakkarainen, *Science* **2017**, *358*, 872–873; i) D. E. Fagnani, J. L. Tami, G. Copley, M. N. Clemons, Y. D. Y. L. Getzler, A. J. McNeil, *ACS Macro Lett.* **2021**, *10*, 41–53; j) X. Tang, E. Y. X. Chen, *Chem* **2019**, *5*, 284–312; k) Y. Liu, X.-B. Lu, *Chem. Eur. J.* **2023**, *29*, e202203635.
- [3] a) C. E. Diesendruck, G. I. Peterson, H. J. Kulik, J. A. Kaitz, B. D. Mar, P. A. May, S. R. White, T. J. Martínez, A. J. Boydston, J. S. Moore, *Nat. Chem.* **2014**, *6*, 623–628; b) C. Jehanno, M. M. Perez-Madrigal, J. Demarteau, H. Sardon, A. P. Dove, *Polym. Chem.* **2019**, *10*, 172–186; c) J. A. Kaitz, O. P. Lee, J. S. Moore, *MRS Commun.* **2015**, *5*, 191–204; d) J. Zhou, T.-G. Hsu, J. Wang, *Angew. Chem. Int. Ed.* **2023**, *n/a*, e202300768; e) G. W. Coates, Y. D. Y. L. Getzler, *Nat. Rev. Mater.* **2020**, *5*, 501–516.
- [4] a) D. K. Schneiderman, M. A. Hillmyer, *Macromolecules* **2016**, *49*, 2419–2428; b) L. T. J. Korley, T. H. Epps, B. A. Helms, A. J. Ryan, *Science* **2021**, *373*, 66–69; c) C. Shi, L. T. Reilly, E. Y.-X. Chen, *Angew. Chem. Int. Ed.* **2023**, *62*, e202301850; d) J.-G. Rosenboom, R. Langer, G. Traverso, *Nat. Rev. Mater.* **2022**, *7*, 117–137.
- [5] a) M. Häubler, M. Eck, D. Rothauer, S. Mecking, *Nature* **2021**, *590*, 423–427; b) C. Shi, Z.-C. Li, L. Caporaso, L. Cavallo, L. Falivene, E. Y. X. Chen, *Chem* **2021**, *7*, 670–685; c) L. Zhou, Z. Zhang, C. Shi, M. Scoti, D. K. Barange, R. R. Gowda, E. Y.-X. Chen, *Science* **2023**, *380*, 64–69; d) X.-L. Li, R. W. Clarke, J.-Y. Jiang, T.-Q. Xu, E. Y. X. Chen, *Nat. Chem.* **2023**, *15*, 278–285; e) Z. Zhou, A. M. LaPointe, T. D. Shaffer, G. W. Coates, *Nat. Chem.* **2023**, *15*, 856–861; f) A. L. Kocen, S. Cui, T. W. Lin, A. M. LaPointe, G. W. Coates, *J. Am. Chem. Soc.* **2022**, *144*, 12613–12618; g) A. Arroyave, S. Cui, J. C. Lopez, A. L. Kocen, A. M. LaPointe, M. Delferro, G. W. Coates, *J. Am. Chem. Soc.* **2022**, *144*, 23280–23285; h) S. M. Parke, J. C. Lopez, S. Cui, A. M. LaPointe, G. W. Coates, *Angew. Chem. Int. Ed.* **2023**, *62*, e202301927; i) L. Cederholm, J. Wohler, P. Olsén, M. Hakkarainen, K. Odelius, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204531; j) P. Zhang, V. Ladel, N. Hadjichristidis, *J. Am. Chem. Soc.* **2023**, *145*, 14756–14765; k) T. M. McGuire, A. Buchard, C. Williams, *J. Am. Chem. Soc.* **2023**, *145*, 19840–19848; l) Y. M. Tu, X. M. Wang, X. Yang, H. Z. Fan, F. L. Gong, Z. Cai, J. B. Zhu, *J. Am. Chem. Soc.* **2021**, *143*, 20591–20597; m) Y. M. Tu, F. L. Gong, Y. C. Wu, Z. Cai, J. B. Zhu, *Nat. Commun.* **2023**, *14*, 3198–3206; n) J. Li, F. Liu, Y. Liu, Y. Shen, Z. Li, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207105; o) Z. Li, D. Zhao, Y. Shen, Z. Li, *Angew. Chem. Int. Ed.* **2023**, *62*, e202302101.
- [6] a) J. Yuan, W. Xiong, X. Zhou, Y. Zhang, D. Shi, Z. Li, H. Lu, *J. Am. Chem. Soc.* **2019**, *141*, 4928–4935; b) C. Shi, Z. Zhang, M. Scoti, X.-Y. Yan, E. Y. X. Chen, *ChemSusChem* **2023**, *16*, e202300008; c) W. Xiong, W. Chang, D. Shi, L. Yang, Z. Tian, H. Wang, Z. Zhang, X. Zhou, E.-Q. Chen, H. Lu, *Chem* **2020**, *6*, 1831–1843; d) C. Shi, M. L. McGraw, Z.-C. Li, L. Cavallo, L. Falivene, E. Y. X. Chen, *Sci. Adv.* **2020**, *6*, eabc0495; e) Y. Zhu, M. Li, Y. Wang, X. Wang, Y. Tao, *Angew. Chem. Int. Ed.* **2023**, *62*, e202302898; f) Y. Wang, Y. Zhu, W. Lv, X. Wang, Y. Tao, *J. Am. Chem. Soc.* **2023**, *145*, 1877–1885; g) Y. Wang, M. Li, J. Chen, Y. Tao, X. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 22547–22553; h) P. Yuan, Y. Sun, X. Xu, Y. Luo, M. Hong, *Nat. Chem.* **2022**, *14*, 294–303; i) K. A. Stellmach, M. K. Paul, M. Xu, Y.-L. Su, L. Fu, A. R. Toland, H. Tran, L. Chen, R. Ramprasad, W. R. Gutekunst, *ACS Macro Lett.* **2022**, *11*, 895–901.
- [7] a) R. M. Cywar, N. A. Rorrer, H. B. Mayes, A. K. Maurya, C. J. Tassone, G. T. Beckham, E. Y. X. Chen, *J. Am. Chem. Soc.* **2022**, *144*, 5366–5376; b) L. Wursthorn, K. Beckett, J. O. Rothbaum, R. M. Cywar, C. Lincoln, Y. Kratish, T. J. Marks, *Angew. Chem. Int. Ed.* **2023**, *62*, e202212543.
- [8] a) C. X. Shi, Y. T. Guo, Y. H. Wu, Z. Y. Li, Y. Z. Wang, F. S. Du, Z. C. Li, *Macromolecules* **2019**, *52*, 4260–4269; b) Y.-T. Guo, C. Shi, T.-Y. Du, X.-Y. Cheng, F.-S. Du, Z.-C. Li, *Macromolecules* **2022**, *55*, 4000–4010.
- [9] a) Y. Liu, H. Zhou, J.-Z. Guo, W.-M. Ren, X.-B. Lu, *Angew. Chem. Int. Ed.* **2017**, *56*, 4862–4866; b) Y. Liu, X.-B. Lu, *Macromolecules* **2023**, *56*, 1759–1777; c) F. N. Singer, A. C. Deacy, T. M. McGuire, C. K. Williams, A. Buchard, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201785; d) Y. Yu, B. Gao, Y. Liu, X.-B. Lu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204492; e) T. M. McGuire, A. C. Deacy, A. Buchard, C. K. Williams, *J. Am. Chem. Soc.* **2022**, *144*, 18444–18449; f) W. Zhang, J. Dai, Y.-C. Wu, J.-X. Chen, S.-Y. Shan, Z. Cai, J.-B. Zhu, *ACS Macro Lett.* **2022**, *11*, 173–178.
- [10] a) B. A. Abel, R. L. Snyder, G. W. Coates, *Science* **2021**, *373*, 783–789; b) H. G. Hester, B. A. Abel, G. W. Coates, *J. Am. Chem. Soc.* **2023**, *145*, 8800–8804.
- [11] a) C. Shi, R. W. Clarke, M. L. McGraw, E. Y. X. Chen, *J. Am. Chem. Soc.* **2022**, *144*, 2264–2275; b) J. D. Feist, Y. Xia, *J. Am. Chem. Soc.* **2020**, *142*, 1186–1189; c) H. Chen, Z. Shi, T.-G. Hsu, J. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 25493–25498; d) J. Zhou, D. Sathe, J. Wang, *J. Am. Chem. Soc.* **2022**, *144*, 928–934.
- [12] M. Hong, E. Y. X. Chen, *Nat. Chem.* **2016**, *8*, 42–49.
- [13] K. N. Houk, A. Jabbari, H. K. Hall, C. Alemán, *J. Org. Chem.* **2008**, *73*, 2674–2678.

- [14] J. B. Zhu, E. M. Watson, J. Tang, E. Y. X. Chen, *Science* **2018**, 360, 398–403.
- [15] C. Shi, L. T. Reilly, V. S. Phani Kumar, M. W. Coile, S. R. Nicholson, L. J. Broadbelt, G. T. Beckham, E. Y. X. Chen, *Chem* **2021**, 7, 2896–2912.
- [16] a) D. Balchin, M. Hayer-Hartl, F. U. Hartl, *Science* **2016**, 353, aac4354; b) H. Saibil, *Nat. Rev. Mol. Cell Biol.* **2013**, 14, 630–642; c) F. U. Hartl, A. Bracher, M. Hayer-Hartl, *Nature* **2011**, 475, 324–332.
- [17] X.-J. Wang, M. Hong, *Angew. Chem. Int. Ed.* **2020**, 59, 2664–2668.
- [18] a) M. T. Davies-Coleman, D. E. A. Rivett, *Fortschritte der Chemie organischer Naturstoffe / Progress in the Chemistry of Organic Natural Products* (Eds.: M. T. Davies-Coleman, J. Galambos, L. Hough, C. E. James, R. Khan, K. Krohn, M. Lounasmaa, D. E. A. Rivett, W. Herz, H. Grisebach, G. W. Kirby, C. Tamm), Springer Vienna, Vienna, **1989**, pp. 1–35; b) M. Chen, G. Dong, *J. Am. Chem. Soc.* **2019**, 141, 14889–14897.
- [19] a) P. Olsén, K. Odelius, A. C. Albertsson, *Biomacromolecules* **2016**, 17, 699–709; b) X. L. Li, R. W. Clarke, H. Y. An, R. R. Gowda, J. Y. Jiang, T. Q. Xu, E. Y. Chen, *Angew. Chem. Int. Ed. Engl.* **2023**, e202303791; c) Y. Lou, L. Xu, N. Gan, Y. Sun, B.-L. Lin, *Innovation* **2022**, 3, 100216; d) R. M. Rapagnani, R. J. Dunscomb, A. A. Fresh, I. A. Tonks, *Nat. Chem.* **2022**, 14, 877–883.
- [20] a) H. Yanai, A. Takahashi, T. Taguchi, *Tetrahedron Lett.* **2007**, 48, 2993–2997; b) H. Yanai, A. Takahashi, T. Taguchi, *Tetrahedron* **2007**, 63, 12149–12159.
- [21] a) M. Hong, E. Y. X. Chen, *Angew. Chem. Int. Ed.* **2016**, 55, 4188–4193; b) C.-J. Zhang, L.-F. Hu, H.-L. Wu, X.-H. Cao, X.-H. Zhang, *Macromolecules* **2018**, 51, 8705–8711.
- [22] a) J. Ochs, C. A. Pagnacco, F. Barroso-Bujans, *Prog. Polym. Sci.* **2022**, 134, 101606; b) H. A. Brown, R. M. Waymouth, *Acc. Chem. Res.* **2013**, 46, 2585–2596; c) Y. A. Chang, R. M. Waymouth, *J. Polym. Sci. Part A* **2017**, 55, 2892–2902.
- [23] J. Roovers, *In cyclic polymers 2nd edn* (ed. Semlyen, J.A.) **2000**, pp. 347–384.
- [24] G. W. Fahnhorst, T. R. Hoye, *ACS Macro Lett.* **2018**, 7, 143–147.
- [25] Z.-Q. Wan, W.-M. Ren, S. Yang, M.-R. Li, G.-G. Gu, X.-B. Lu, *Angew. Chem. Int. Ed.* **2019**, 58, 17636–17640.
- [26] G. Si, C. Tan, M. Chen, C. Chen, *Angew. Chem. Int. Ed.* **2022**, 61, e202203796.
- [27] a) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, 122, 8168–8179; b) W. J. Neary, T. A. Isais, J. G. Kennemur, *J. Am. Chem. Soc.* **2019**, 141, 14220–14229; c) J. M. Bates, J. A. M. Lummiss, G. A. Bailey, D. E. Fogg, *ACS Catal.* **2014**, 4, 2387–2394.

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