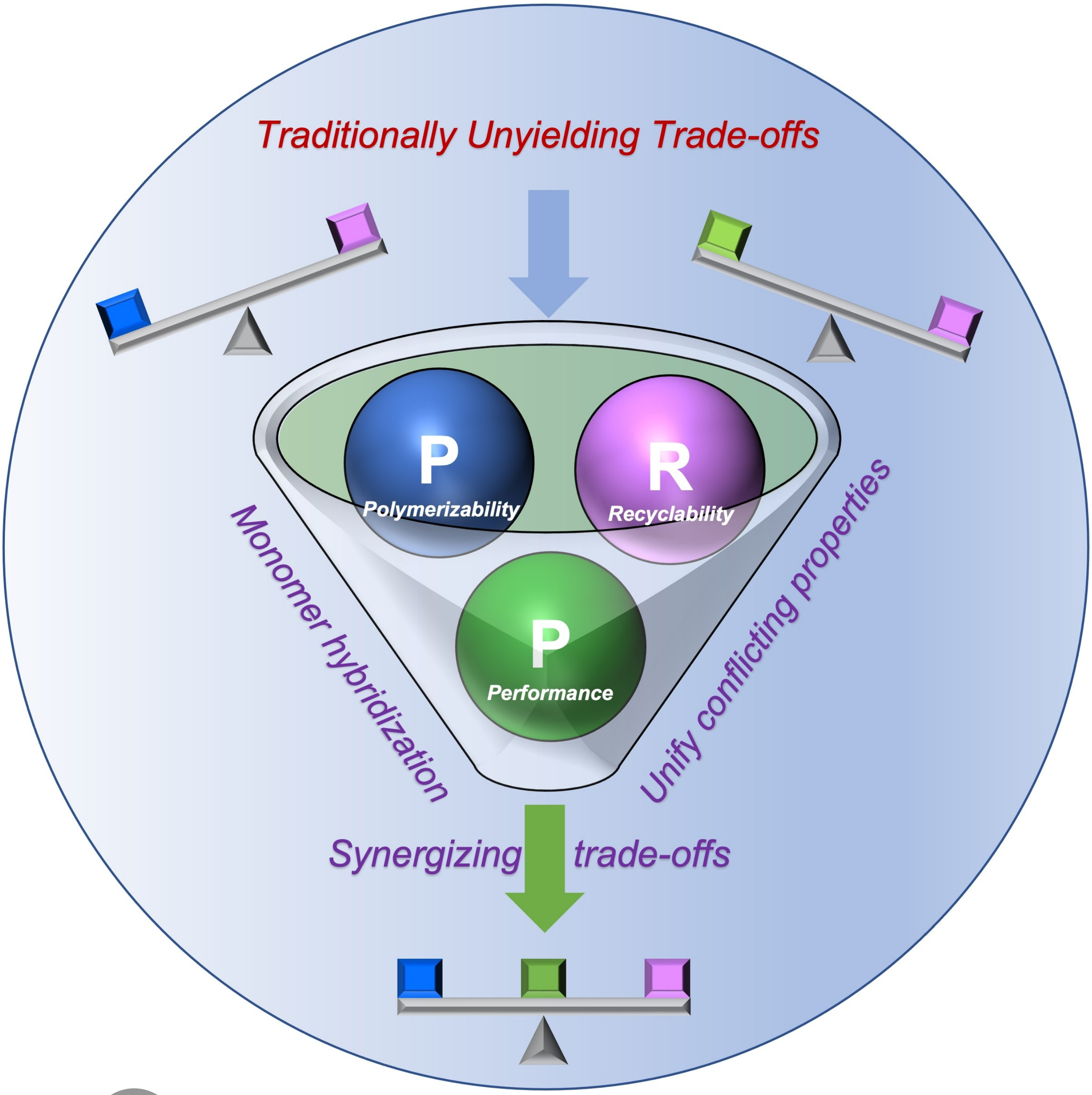
Angewandte Chemie International Edition
www.angewandte.org

How to cite: *Angew. Chem. Int. Ed.* **2023**, *62*, e202301850
doi.org/10.1002/anie.202301850

Recyclable Polymers

Hybrid Monomer Design Synergizing Property Trade-offs in Developing Polymers for Circularity and Performance

*Changxia Shi, Liam T. Reilly, and Eugene Y.-X. Chen**



Abstract: Current search for more sustainable plastics seeks to redesign polymers possessing both chemical recyclability to monomer for a circular plastics economy and desirable performance that can rival or even exceed today's non-recyclable or hard-to-recycle petroleum-based incumbents. However, within a traditional monomer framework it is challenging to optimize, *concurrently*, contrasting polymerizability/depolymerizability and recyclability/performance properties. Here, we highlight the emerging hybrid monomer design strategy to develop intrinsically circular polymers with tunable performance properties, aiming to unify desired, but otherwise conflicting, properties in a single monomer. Conceptually, this design hybridizes parent monomer pairs of contrasting, mismatching, or matching properties into offspring monomers that not only unify the above-described conflicting properties but also radically alter the resultant polymer properties far beyond the limits of what either parent homopolymers or their copolymers can achieve.

1. Introduction

The world we are living in today is largely dependent on polymeric materials including, predominately, plastics. Having risen to prominence in the late 20th century due to their unique combinations of low cost, high strength to weight ratio, durability, processability, and tailorable material performance, these soft yet strong and durable materials have enabled technological, medicinal, and infrastructural breakthroughs at rates previously thought impossible. However, the exponential growth in plastics production and implementation over the past half-century, especially as single-use items, has resulted in enormous finite fossil resource consumption and environmental pollution compounded by short-sighted end-of-life (EoL) design and management. It was estimated that around 8.3 billion tonnnes (bt) of plastic had been produced by 2015, while only ≈9% of which had been recycled and catastrophically ≈80% of which had been leaked into the environment.[1–3] Following the current production and waste management trends, plastic production is predicted to account for 20% of global petroleum consumption and roughly 12 bt of plastic waste will be landfilled or disposed in the natural environment by 2050.[1,4,5] Growing alongside the enormous amount of global production and consumption of plastics are the diverse concerns on their impacts on the ecosystem and human health as well as finite fossil resources.[6–10] In response, multilevel mitigation strategies are being adopted from plastic waste reduction and management to environmental remediation and recovery.[11–27] Concerning the root of the problems, the current commodity plastics are historically designed for a produce-use-dispose linear plastic economy. Such a lifecycle fails to consider numerous EoL issues and therefore directly perpetuates the negative environmental potential of plastic use and waste. As such, the design of next-generation performance polymers that are sustainably sourced and possess inherently sustainable EoL options to establish closed-loop lifecycles toward a circular materials economy is the cornerstone of the current sustainable plastics thrust.

While several notable strategies have been developed with the aim to tackle this global challenge, each unfortunately possesses specific pitfalls which limit their practicality. Taking mechanical recycling for example, there currently exist only few polymers which are both practically capable of and economically worth mechanically reprocessing at scale. Additionally, mechanical recycling leads to inevitable deterioration of material properties following serial reprocessing cycles, known as "downcycling". As a result, most mechanically recycled polymers are only recycled once for practical use and then end up as plastic waste.[28–30] An alternative strategy, which initially gained substantial attention, is the development of biodegradable polymers. Although considered to be environmentally friendly, as these polymers are destined to degrade into CO_2, H_2O, and biomass once they end up in the environment,[26] this approach fails to recover material or energy and thus represents a value loss to the economy.[1] Releasing excess CO_2 to environment is also a concern. Of the strategies to address the environmental and resource crisis resulting from plastic use and production, emerging recycling methods, particularly depolymerization, are becoming more significant in the global move towards a circular economy. At the front of this effort is the design of new monomers and thus polymers with chemical recyclability, as this strategy offers the potential to establish "polymer-monomer-polymer" closed-loop circularity with virgin polymer properties obtained in each cycle.[31–35] In fact, IUPAC has recently acknowledged such closed-loop (de)polymerization processes as one of the top 10 emerging technologies in chemistry.[36]

To successfully design polymers capable of chemical recycling to monomer (CRM),[37] that is, the "polymer-monomer-polymer" closed-loop circularity, both thermodynamics and kinetics of polymerization should be carefully considered. We published a perspective to discuss such thermodynamic and kinetic considerations for the design of intrinsically circular polymers (ICPs), confining chemically recyclable polymer into kinetically trapped polymers that are inherently, selectively, and expediently depolymerizable to their monomer state once the kinetic barriers of deconstruction are overcome.[27] Briefly, any polymerization process, in principal, can be made reversible under specific conditions, however, to realize this potential, there are

---

[*] Dr. C. Shi, L. T. Reilly, Prof. Dr. E. Y.-X. Chen
Department of Chemistry, Colorado State University
Fort Collins, CO 80523-1872 (USA)
E-mail: eugene.chen@colostate.edu

several criteria one must satisfy. First, the difference in relative energy levels of monomer versus polymer states under given conditions must be practical, as determined by the thermodynamics of polymerization. The most relevant thermodynamic parameter is the ceiling temperature (T_c) of polymerization, defined as the temperature at which the (de)polymerization reactions reach an equilibrium state. Exceeding this temperature is necessary for efficient depolymerization and therefor this value must not exceed infrastructural limitations or approach the decomposition temperature (T_d) of the material, otherwise, severe side reactions and high energy input preclude practical depolymerization. Unfortunately, this is the case for many high-performance commodity polymer classes used today such as polyolefins. As such, a second requirement typically arises, which is that the depolymerization must be susceptible to some modes of catalysis which not only lowers the energy input required but offers the additional benefit of facilitating product selectivity which is critical if virgin quality monomer is desired in high yield and purity for repolymerization. Considering these criteria, it becomes apparent why the judicious design of monomers at the molecular level is central to the development of new circular polymers with intrinsic chemical recyclability (i.e., ICPs). Worth noting here is that ICPs differ from the broader concept of chemically recyclable polymers (CRPs), which includes any polymer that can be chemically deconstructed into useful chemicals, including monomer, but does not explicitly consider the depolymerization selectivity, energy input of de/reconstruction and so on. Hence, we surmise and justify the criterion that distinguish ICPs, which are inherently capable of expedient depolymerization to their monomer state with minimized energy input and essentially quantitative selectivity, from the broadly defined CRPs. Central to the intelligent design of ICPs is the unification of traditionally unyielding trade-offs such as conflicting polymerizability/depolymerizability and recyclability/performance properties, which has proven challenging to accomplish in a conventional monomer framework.

It is paramount that in an effort to design ICPs one does not lose sight of the importance of the resultant material's performance properties, as the reality persists that, unless novel circular polymers can rival the material properties of their unsustainable incumbents, the widespread adoption of these materials remains unlikely. Therefore, developing polymers with a closed-loop EoL is necessary, but not sufficient, unless the trade-offs between recyclability and material performance are properly balanced. In this minireview, we will primarily discuss a collection of monomer designs which were constructed based on a hybrid monomer strategy with the aim to unify several desired but conflicting properties into a single monomer. For a traditional monomer framework, it is very challenging to optimize contrasting properties, *concurrently*. To best illustrate this concept, we will highlight three general methods that have been successfully implemented: low ceiling temperature (LCT)/high ceiling temperature (HCT) hybrid, LCT/LCT, and HCT/HCT hybrid systems, with a focus on the general design philosophy in the construction of ICPs with performance properties comparable or superior to unsustainable incumbent plastics. Additionally, the primary challenges associated with this emerging concept are outlined and discussed throughout.

Changxia Shi received his Ph.D. in 2020 under the supervision of Prof. Zi-Chen Li from Peking University. During his Ph.D. study, he joined the group of Prof. Eugene Chen at Colorado State university as a visiting student (2018–2020), where he continued his research as a postdoctoral fellow (2021). His research interests focus on development of high-performance circular plastics and vitrimers that overcome traditional trade-offs and unify conflicting properties.

Liam Reilly, born in Cambridge, Massachusetts, obtained his BSc in Chemistry from Rochester Institute of Technology (2016–2020) with a focus on organic, polymer, and physical chemistry. He is currently a doctoral candidate at Colorado State University (2020-present) under the supervision of Prof. Eugene Y.-X. Chen. His research interests include polymerization methodology development, organocatalysis, and mechanism elucidation.

Eugene Chen received his Ph.D. in 1995 from the University of Massachusetts, Amherst. After a postdoctoral stint at Northwestern University, he joined Dow Chemical, where he was promoted to Project Leader. He moved to Colorado State University in 2000, where currently he is a University Distinguished Professor, the John K. Stille Endowed Chair in Chemistry, and the Millennial Professor of Polymer Science and Sustainability.

2. General Considerations for Monomer Design

To efficiently design monomers and resultant polymeric systems which can meet the typical challenges associated with combining the conflicting features of chemical recyclability and robust material performance, the thermodynamics of polymerization must be thoroughly understood. The Gibbs free energy of polymerization (ΔG_p) serves as the single master variable representing the magnitude and direction of the polymer-monomer equilibrium. More specifically, forward polymerization can occur only if $\Delta G_p < 0$. For typical polymerization scenarios, although with the exception of entropically driven polymerizations, polymerization thermodynamics feature a favorable enthalpy change ($\Delta H_p < 0$) due to the release of ring strain [for ring-opening polymerization, (ROP)] or the transformation of high-energy bonds to more stable bonds (such as the breaking of a π-bond to form two strong σ bonds in the polymerization of vinyl monomers). Taking a ROP scenario for instance, the driving force for the polymerization of many heterocyclic monomers is the release of their ring strain, which reflects deviations from non-distorted bond angle values, bond stretching and/or compression, repulsion between eclipsed hydrogen atoms, and nonbonding interactions between substituents associated with ring size (angular strain) and geometry (conformational and transannular strain).[38]

Despite the abundant, enthalpically favorable, forward reactions, most addition polymerizations are entropically disfavored ($\Delta S_p < 0$), in large part due to the loss of translational entropy (ΔS_t) that results from the uniaxial alignment of covalently linking discrete monomers into a polymer chain. In reality, there are two major modes of entropy represented within the overall ΔS_p: translational entropy (ΔS_t), which refers to the translational freedom of the entire molecule in three dimensions, and conformational entropy (ΔS_c), which includes rotational entropy (ΔS_r) referring to the rotational freedom of the entire molecule to rotate about any axis and vibrational entropy (ΔS_v) referring to vibrational freedom of the atoms within the molecule to move in space relative to each other. As mentioned above, a typical polymerization leads to a loss of translational entropy relative to the free monomer state ($\Delta S_t < 0$). Conversely, the conformational entropy increases in the typical ROP scenario ($\Delta S_c > 0$), as the bonds in a linear polymer usually have greater rotational and vibrational freedom than those in the cyclic monomer state. Gains in conformational entropy can lead to positive changes in ΔS_p but are rarely large enough to fully offset the large decrease in translational entropy ($|\Delta S_t| \gg |\Delta S_c|$), thus the entropy of polymerization remains negative in most cases ($\Delta S_p < 0$).[39] While it remains quite difficult to quantify the individual contributions of the changes in ΔS_t and ΔS_c to the overall change in ΔS_p, several reports have underlined that the substitution effect,[40–42] such as gem-disubstitution effect,[43] can be employed to manipulate the magnitude of ΔS_p and thereby decrease T_c.[44] One representative example of lowering T_c by manipulating ΔS_p is the recent contribution of Li et al., in which the authors synergistically address not only the poor chemical recyclability but also the low melting temperature (T_m) and mechanical performance of the parent poly(δ-valerolactone) via gem-α,α-disubstitution of the parent δ-valerolactone ring. The observed greatly reduced T_c (from 298 to 67 °C) upon disubstitution is mainly attributed to the pronounced increase in the entropic loss (penalty) of polymerization, which overrides the more negative enthalpic change due to the increased ring strain which results from the substitution.[45]

ΔG_p is further related to standard polymerization enthalpy ($\Delta H_\mathrm{p}^\mathrm{o}$) and entropy ($\Delta S_\mathrm{p}^\mathrm{o}$) and mathematically expressed as $\Delta G_\mathrm{p} = \Delta H_\mathrm{p}^\mathrm{o}\text{-}T\{\Delta S_\mathrm{p}^\mathrm{o} + R\ln[\mathrm{M}]\}$ on the basis of Flory's assumption.[38] Therefore, for any given monomer under standard polymerization conditions, elevated temperatures increase the contribution of the entropic component ($\text{-}T\Delta S_\mathrm{p}^\mathrm{o}$) to offset the contribution of the change in enthalpy ($\Delta H_\mathrm{p}^\mathrm{o}$), which in most cases results in a greater free energy of polymerization (ΔG_p) and a tendency towards depolymerization. Furthermore, there exists a specific temperature, $T_\mathrm{c} = \Delta H_\mathrm{p}^\mathrm{o}/\{\Delta S_\mathrm{p}^\mathrm{o} + R\ln[\mathrm{M}]_0\}$, at which $\Delta G_p = 0$, resulting in the net equilibrium state of the forward and reverse (de)polymerization reactions.

Unlike the polymers produced through the common ROP pathways, which contain cleavable carbon-heteroatom bonds (lactones, lactams, etc.), those produced by vinyl polymerization (α-olefins, styrenics, acrylics) feature chemically resistant and thermally stable carbon-carbon backbones which presents a much greater challenge for accomplishing CRM. While there are several reports focused on copolymerization strategies to improve the degradability of vinyl polymers via incorporation of certain cleavable sites,[46–48] there remains abundant opportunities to enable the ideal CRM closed-loop circularity through manipulations of thermodynamic parameters, which may be accomplished by the judicious tuning of (de)polymerization conditions (concentration, temperature, pressure, and state), in addition to monomeric structure redesign. While limited, several recent reports have served as an exciting proof of concept for chemically recyclable vinyl polymers.[49–52] As is the case for ROP systems, redesign of monomeric structure is a promising strategy for the development of chemically recyclable vinyl polymers. Typically, the polymerization of 1,1-disubstituted vinyl monomers (e.g., methacrylates) is less exothermic than mono-substituted acrylic and styrenic monomers.[49] One strategy to promote closed-loop recyclability of such vinyl monomers is the tuning of the electronics of the pi system. For example, ethyl cyanoacrylate, which features strong 1,1-di-substituted electron-withdrawing groups (CN and COOR), exhibits exceptional monomer recovery.[53,54] Additionally, a bulkier polymer side chain has been shown to reduce T_c due to conformational/steric effects that alter the difference in relative energy states between the monomer and polymer states. Critically, the increased side chain steric bulk also further increases the loss of entropy of polymerization (i.e., making ΔS_p more negative, thus resulting in a lower T_c).[55,56] In addition to the manipulation of monomeric structure and reaction concentration and temperature, strategies invoking kinetic control via labile chain-ends, such as dithiobenzoyl[50,57,58] or halogen chain-end groups[59,60] have also been developed. It is worth noting that while the achievement of the near-quantitative regeneration of the methacrylate monomers under relative mild condition,[50,57,58] the introduction of the labile chain-end does not alter the intrinsic characteristics of the polymerization/depolymerization thermodynamics, but only decreases the kinetic barrier for reactivating the metastable polymer into the monomer-polymer equilibrium via generating the chain-end radicals. The key factor for achieving highly efficient recovery of monomer is the extremely dilute condition of polymer concentration, as aforementioned that any polymer could be rendered reversible by manipulating the thermodynamic equilibrium of (de)polymerization processes through adjusting reaction conditions.

Chemically recyclable polyethylene-like materials have been achieved through the incorporation of a labile or reactively cleavable bond in the polyethylene main chain structure.[61,62] Likewise, the chemical recycling of polycarbonates back to epoxides or cyclic carbonate monomers is an interesting and very active area searching solutions to existing challenges.[63,64] Specifically, the recycled cyclic carbonate monomer is often too thermodynamically stable to repolymerize, which impedes the realization of the closed-loop circularity.[63] On the other hand, the chemical recycling of polycarbonates to epoxide monomers is limited to specific monomer structures, primarily derivatives of cyclopentene epoxide[65–67] and cyclohexene epoxides,[68–71] under optimized catalytic systems, where the entropy penalty associated with the CO_2 release must be capable of offsetting the unfavorable generation of high ring strain epoxide monomers.

3. Hybrid Monomer Design

As previously mentioned, when designing novel ICPs, their material performance must be considered. Polymer scientists have long recognized copolymerization of two or more different monomers as a powerful strategy to produce materials with tailored properties. The manipulation of the chemical nature, composition, and sequence of the comonomers, often delivers improved or unattainable properties in relation to those of the constituent homopolymers.[72–77] However, this strategy also struggles to reconcile intrinsically conflicting properties, as multiple attempts have demonstrated that copolymerization predominately balances one or several properties rather than combining said properties in a truly synergistic fashion.[78,79] In addition, formation of copolymers of different monomers complicates the CRM process and monomer recovery. The examples of hybrid monomer systems, detailed as follows, overcome these challenges.

3.1. HCT/LCT Hybrid Systems

Poly(γ-butyrolactone) (PBL) is a well-known LCT polymer for its facile depolymerizability, thanks to the negligibly low ring strain of its constituent monomer. However, the low energy monomeric state also renders this monomer notorious for energy intensive polymerization conditions (i.e., requirement of very low temperature, $T < T_c$, at a given monomer concentration) and relatively low polymer thermal stability.[80] In contrast, the HCT poly(ε-caprolactone) (PCL) is readily obtained under ambient conditions and exhibits excellent thermal stability due to the relatively high ring strain and polymerizability of its constituent monomer. Conversely, the depolymerization of PCL is thermodynamically disfavored.[81] In addition to the individual polymerization and depolymerization challenges of PBL and PCL, respectively, both polymers suffer from a relatively low melting temperature ($T_m \approx 60\,°C$), which confines their practical material applications. The copolymerization of γ-BL and ε-CL has been explored in an attempt to enhance the polymerizability and thermal stability of the LCT PBL while simultaneously increasing the depolymerizability and recyclability of the HCT PCL. Indeed, the copolymerization of γ-BL and ε-CL proceeds under relatively milder conditions compared to that of γ-BL alone, and the resultant copolymers exhibit enhanced thermal stability relative to PBL. However, over the entire copolymer composition range, the glass-transition temperature (T_g, from −48 °C to −65 °C) and melting-transition temperature (T_m, from 11 °C to 63 °C) of the resulting copolymers are still low and confined within the values of their parent homopolymers (Figure 1).[78]

Considering the observed inability of copolymerization to truly unify the conflicting properties of the respective comonomers, we developed a hybrid monomer design strategy aiming to synergistically reconcile the conflicting properties into a single monomer.[82] Conventional wisdom

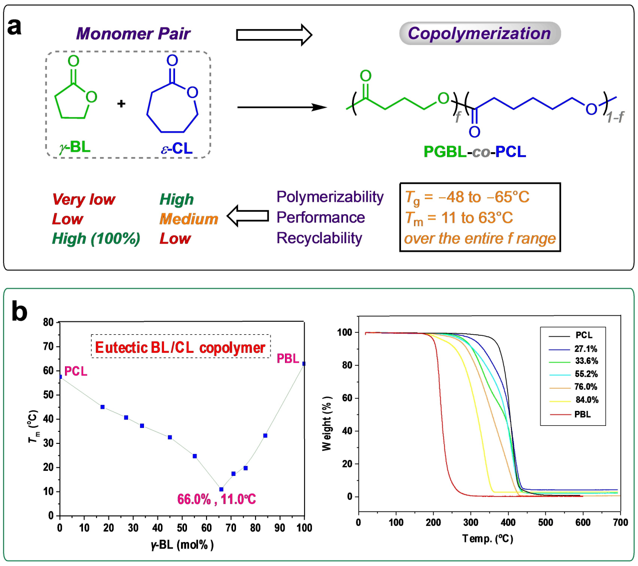


Figure 1. Conventional copolymerization strategy to address property trade-offs. **a**) Copolymerization of LCT γ-BL and HCT ε-CL to give a copolymer with thermal properties lying between the two respective homopolymers. **b**) Plot of T_m values of PBL-*co*-PCL as a function of γ-BL incorporation and thermogravimetric analysis (TGA) curves of PBL-*co*-PCL vs homopolymers PBL and PCL.

reasons that polymerizability and depolymerizability mutually inhibit one another, as they are usually opposite directions of the same reaction pathway. This dissonance has consistently hampered the development of ICPs.[27] Thus, we postulated that the development of a hybrid monomer, which incorporates molecular structural motifs of LCT and HCT monomers, may synergistically draw from both the HCT sub-structure for high polymerizability and performance properties and the LCT sub-structure for high depolymerizability and recyclability, as well as synergistically enhance material performance.[82]

3.1.1. Polyester from HCT/LCT Hybrid Lactone

As a proof of concept, LCT γ-BL and HCT ε-CL were selected here as an illustrative example. The offspring monomer, [3.2.1]bicyclic lactone (BiL), was designed based on the structural hybridization between the two monomers, as shown in Figure 2, and can be conveniently synthesized from bio-sourced starting materials at-scale and in a high overall yield.[82] Indeed, BiL can be readily polymerized under ambient conditions to high-molecular weight poly(BiL) (PBiL). The thermodynamics of polymerization were determined to be $\Delta H_p^o = -21.1\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S_p^o = -55.8\ \mathrm{J\,mol^{-1}\,K^{-1}}$. Subsequently, the T_c of BiL was calculated to be 106 °C at $[\mathrm{BiL}]_0 = 1.0$ M. The obtained thermodynamic data showed that BiL exhibits much greater polymerizability than the parent monomer γ-BL, as indicated by a much larger negative change in enthalpy and a substantially elevated T_c: $\Delta H_p^o = -21.1\ \mathrm{kJ\,mol^{-1}}$ vs. $-5.4\ \mathrm{kJ\,mol^{-1}}$ and $T_c =$ 106 °C vs. −136 °C (1.0 M) for the ROP of BiL and γ-BL, respectively.[80,82] The resulting PBiL featured complete chemical recyclability as well via catalysis using a commercial catalyst, either $\mathrm{La(N(SiMe_3)_2)_3}$ or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), under mild conditions (120 °C), mitigating the typically unyielding tradeoff between polymerizability and recyclability.

More intriguingly, compared to its structural analogue of the γ-BL with a *trans*-fused cyclohexene ring at the 3,4-positions of γ-BL (3,4-T6GBL), the ring strain of BiL and 3,4-T6GBL contributes to their thermodynamic polymerizability equally, as indicated by similar ΔH_p^o of $-21.1\ \mathrm{kJ\,mol^{-1}}$ versus $-20\ \mathrm{kJ\,mol^{-1}}$. However, their T_c vary drastically, 106 °C (BiL) versus 0 °C (3,4-T6GBL) at 1.0 M, as a result of the large entropic difference of ΔS_p^o of $-55.8\ \mathrm{J\,mol^{-1}}$ vs. $-72\ \mathrm{J\,mol^{-1}}$ for the ROP of BiL and 3,4-T6GBL, respectively.[83] The decreased entropic penalty for the polymerization of BiL results from the confined atom-bridged monomer structure which acquires more conformational (rotational and vibrational) freedom (ΔS_c) following ring opening. This gain in conformational entropy partially offsets the loss of translational freedom (ΔS_t) and results in a substantial decrease in the total entropic penalty compared to that of the structural analogue 3,4-T6GBL. The additional benefit of such a hybrid monomer structure is the potential for divergent (de)polymerization pathways: the polymerization proceeds via the ring-opening of the HCT sub-structure at ambient temperature, while the depolymerization proceeds through the ring-closing of the LCT sub-structure at elevated temperature, thereby achieving both high polymerizability and depolymerizability and success-

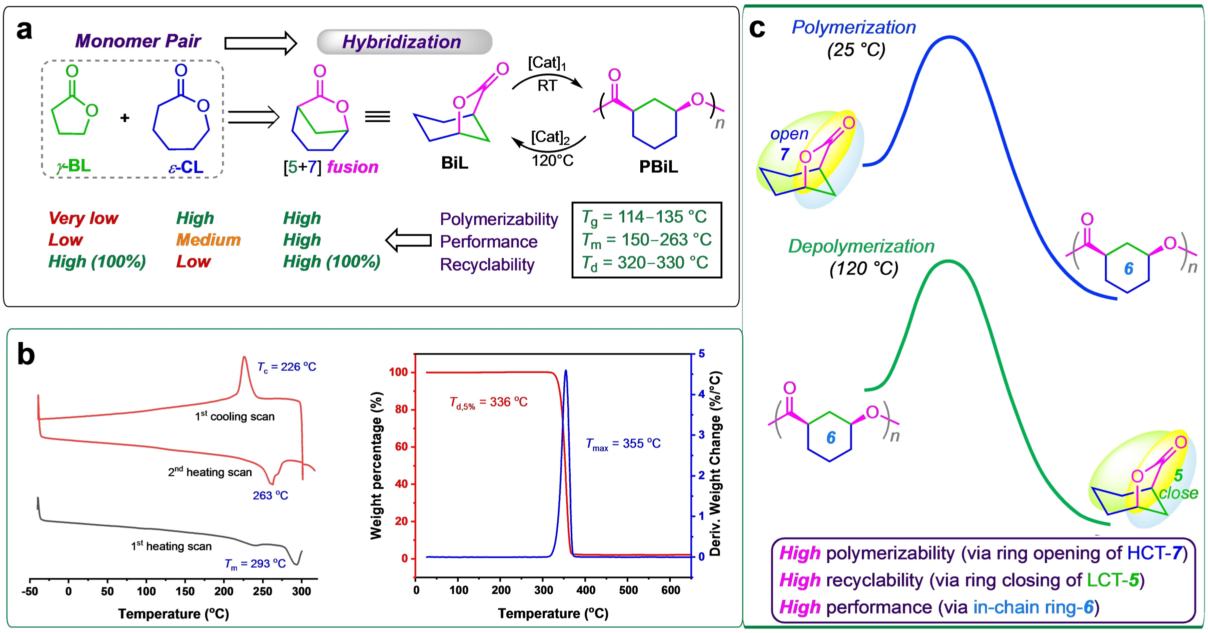


Figure 2. **a**) Schematic illustration of hybridization of the LCT γ-BL with the HCT ε-CL to create a hybrid monomer structure, bicyclic lactone (BiL), which possesses the structural motifs of both the LCT and HCT lactones and leads to the corresponding circular polyester with synergistically enhanced performance and recyclability. **b**) Differential scanning calorimetry (DSC) and TGA curves of PBiL showing high T_m and T_d values. **c**) Schematic illustration of free energy diagrams for (de)polymerization pathways, associated ring-opening and closing events, and summarized role of each ring in the hybrid bicyclic monomer.

fully unifying these otherwise conflicting properties. Moreover, PBiL displays a high T_g up to 135 °C and T_m up to 263 °C, which are ≈200 °C higher than both T_g and T_m values of the parent homopolymers (PBL and PCL) and their copolymers. In addition, mechanical properties of PBiL, particularly Young's modulus, are ≈10× greater than that of the respective parent polymers, demonstrating that the HCT/LCT hybrid monomer strategy is a powerful approach for designing circular polymers with radically different or much enhanced properties over the constituent monomer's parent homopolymers or respective copolymers.

3.1.2. Polyamide from HCT/LCT Hybrid Lactam

With the preliminary success of the HCT/LCT hybrid strategy for intrinsically circular, high-performance polyesters, we expanded this design strategy to hybrid lactams for circular aliphatic polyamides (or nylons). Polyamides have found significant commercial applications, as the inter/intra-chain hydrogen bonds throughout polyamide materials bestow exceptional thermomechanical properties. However, the additional stability these non-covalent interactions provide also renders this important class of polymer exceptionally vulnerable to the traditionally unyielding tradeoff between performance and recyclability. More specifically, nylon 4, produced from the five-membered lactam (5-LM), has attractive textile properties and is considered to be sustainable, as it can be bio-sourced and is also biodegradable and chemically recyclable. However, nylon 4 undergoes concurrent melting and depolymerization during melt processing, due to its relative low T_c of ≈70 °C even in the bulk state.[84] Despite significant mitigation efforts, its thermal instability critically undermines nylon 4′s range of commodity applications. On the contrary, nylon 6, produced via ROP of ε-caprolactam (7-LM) with relatively high ring strain, is thermally robust and its purposed depolymerization requires high temperature (≈300 °C), achieving modest to good yields of 55–86 %.[85] Very recently, Marks et al. achieved CRM of nylon 6 to 7-LM at almost quantitative yield with lanthanide trisamido catalyst $La[N(SiMe_3)_2]_3$, which underlines the ability of catalysis to enable selective and efficient depolymerization, although the catalyzed depolymerization still requires the reaction to be performed at temperatures as high as 240 °C.[86] Hence, the juxtaposition of LCT nylon 4′s intrinsic recyclability and HCT nylon 6′s robust material properties presents an excellent opportunity for applying the synergistic hybrid monomer design strategy to solve the above problems associated with nylons.

Hybridizing 5-LM and 7-LM as LCT and HCT subunits, respectively, afforded an offspring monomer, [3.2.1] bicyclic lactam, 6-azabicyclo[3.2.1]octan-7-one (Figure 3). This hybrid lactam, 5/7-LM, exhibits both high polymerizability and depolymerizability with a calculated T_c of 225 °C at $[M]_0 =$ 1.0 M.[84] As compared to the hybrid lactone analog BiL, the replacement of the ester bond in BiL with an amide bond in 5/7-LM resulted in a concurrent decrease in enthalpy and entropy of polymerization, presumably due to the less distorted bond angle value in 5/7-LM and lower entropic penalty upon ring opening due to the existence of hydrogen bonding interactions. This reasoning was confirmed by the measured values of ΔH_p^o of −21.1 vs. −10.0 kJ mol^{-1}, and ΔS_p^o of −55.8 vs. −20.1 J mol^{-1} K^{-1} for the ROP of BiL and 5/7-LM, respectively. In addition, the resulting nylon 4/6 exhibits a unique set of physical properties: it is semi-crystalline (Figure 3b) yet optically clear, due to the nano-scale nature of its crystalline domains. To further demonstrate the advantageous properties of nylon 4/6, copolymer 4/6-*co*-nylon 4 (50/50 molar ratio) was synthesized and shown to achieve the greatest synergy, offering an amorphous nylon with optical clarity, a high T_g, melt processability, and full chemical recyclability with the aid of Lewis acid catalyst ($ZnCl_2$).

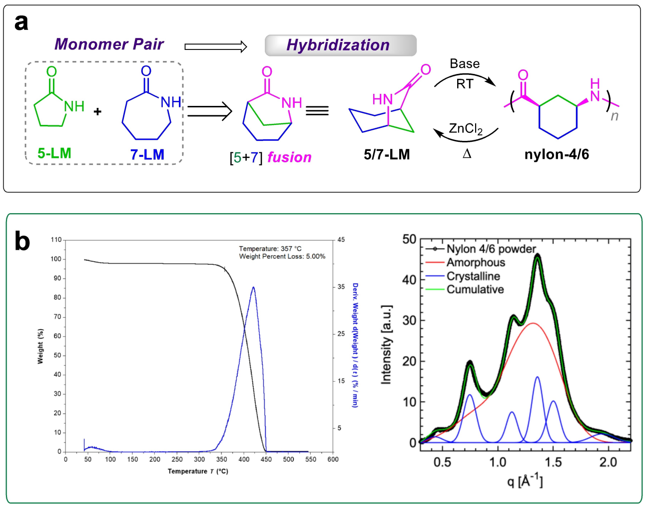


Figure 3. **a**) Design of hybrid lactam monomer 5/7-LM through fusion of sub-structural units of LCT 5-LM with HCT-7-LM for circular hybrid nylon 4/6 with synergistically enhanced (de)polymerization and performance properties. **b**) TGA curve and Wide-angle X-ray scattering (WAXS) profile of nylon-4/6.

3.2. LCT/LCT Hybrid Systems

3.2.1. Polythioester from LCT/LCT Hybrid Thioester

Here we present a case where the hybrid monomer design strategy renders two hardly polymerizable, LCT monomer pairs into an LCT/LCT hybrid monomer that can be readily polymerized into high-molecular-weight, high-performance polymers while retaining intrinsic chemical recyclability. More specifically, γ-butyrothiolactone (γ-BTL), like its lactone analog γ-BL, does not polymerize under many previously explored polymerization conditions due to its negligible ring strain which removes the bulk of the enthalpic driving force for polymerization.[87,88] On the other hand, unlike its lactone congener δ-VL, six-membered δ-valerothiolactone (δ-VTL) is an LCT monomer with a low T_c of −66 °C at 1.0 M, due to its negligibly low ring strain, assessed from the thermodynamic parameters ($\Delta H_p^o =$ −4.9 kJ mol^{-1}, $\Delta S_p^o =$ −23.7 J mol^{-1} K^{-1}).[42] Considering the success of HCT/LCT hybridization in both polyester and polyamide systems, we were curious as to whether the hybridization between two hardly to non-polymerizable LCT monomers might yield a readily polymerizable hybrid monomer. To this end, a bridged bicyclic thiolactone monomer, 2-thiabicyclo[2.2.1]heptan-3-one ($^{[221]}$BTL), was designed and synthesized from a bio-based olefin carboxylic acid, and can be regarded as the hybrid monomer from γ-BTL and δ-VTL (Figure 4a).[89]

Prior to our PBTL work, Lu et al. constructed a similar bicyclic thiolactone—*N*-substituted *cis*-4-thia-L-proline thiolactone, which can be considered the hybridization of γ-BTL with *N*-substituted δ-VTL, from 4-hydroxyproline, a rich bio-sourced material (Figure 4b).[90] The thermodynamic parameters were experimentally determined to be $\Delta H_p^\circ = -15.6\,\text{kJ}\,\text{mol}^{-1}$, $\Delta S_p^\circ = -40.4\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$, with a calculated T_c of 112 °C at standard conditions. The moderate T_c indicated both enhanced polymerizability relative to its parent monomers and feasible recyclability under mild conditions. The site of *N*-substitution offers the opportunity for post-functionalization, offering a broad scope of recyclable polythioesters based on the N^R-BTL platform. However, despite having similar structures to, all the resultant polythioesters were amorphous, presumably due to the *N*-substitution prohibiting efficient chain packing. In addition, Lu et al. also reported *N*-substituted bicyclic lactones (N^R-BTL), the structural analog of N^R-BTL.[91] Different than the polythioesters, the polyesters based on N^R-BL are not depolymerizable to monomer. Likewise, when we replaced the S atom in with the O atom, the resulting bicyclic lactone congener leads to the corresponding polyester that is atactic, amorphous, and also not recyclable—essentially the opposite of the polythioester PBTL. Worth noting here is that both PN^R-BTL and PBTL are fully recyclable in the presence of an organic base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene) (^{t}Bu-P$_4$), and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) etc. These results underscored the dramatically different thermodynamic and kinetic behaviors of lactones and thiolactones, which are in part attributed to the consequences of their different C–X (X = O or S) bond lengths and angles. Overall, these insights continue to promote the advancement of judicious monomer design for ICPs.

We envisioned that possibly several advantages could be manifested by the hybrid bicyclic thioester . First, it should possess greater ring strain than the parent monomers γ-BTL and δ-VTL, which may allow the ROP to proceed at ambient temperature with high monomer conversions and yield high molecular weight polymers. Second, the bridged bicyclic system may provide rigidity to the polymer backbone which in turn stands to enhance resultant thermal and mechanical properties. Third, the depolymerizability and selectivity in chemical recycling of the resulting polymer PBTL should be high since the ring closure of the five-membered thiolactone is kinetically facile and thermodynamically favored. Fourth, the bridged bicyclic monomer exists only in the *cis* configuration, thus eliminating possible isomerization and reinforcing a highly selective depolymerization.

As expected, the offspring monomer indeed exhibited high polymerizability due to the increased ΔH_p° (i.e., more negative value), imparted by the relief of the greater ring strain of the bridged monomer structure. The topology of the resulting polythioester can be controlled by the catalyst structure, affording high molecular weight linear (by superbase + alcohol) or cyclic [by *N*-heterocyclic carbene such as

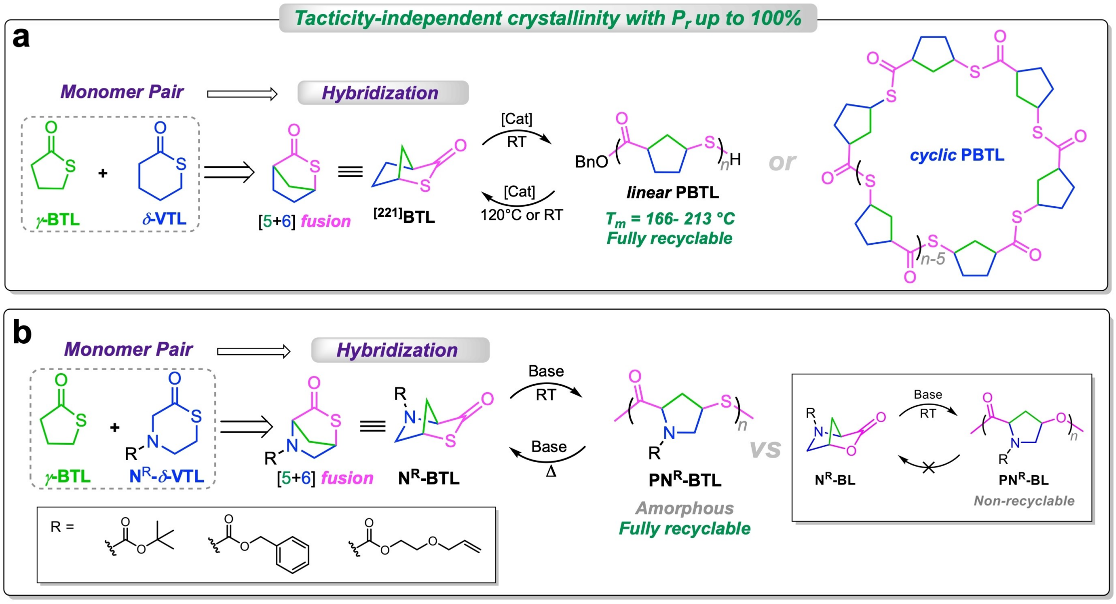


Figure 4. **a**) LCT/LCT hybrid for circular polythioester PBTL with synergistically enhanced performance including tacticity-independent crystallinity with tunable Tm, as well as high thermal stability and full chemical recyclability. **b**) LCT/LCT hybrid for circular amine-functionalized polythioester

1,3-dimesitylimidazol-2-ylidene (IMes)] PBTL, depending on the type of organic catalysts employed.[89] We also demonstrated that the polymerization proceeds through a chain-end controlled mechanism, with the tacticity being controlled through manipulation of polymerization conditions and relative rates of chain propagation vs. epimerization (which yields stereoerrors). Through detailed mechanistic studies, conditions were identified to produce PBTL materials of varying tacticities, ranging from perfectly syndiotactic to essentially atactic PBTL (Figure 5a,b).

Most interestingly, the PBTL materials produced from, which ranged from perfectly stereo-ordered to stereo-disordered tacticities, all exhibited a high degree of crystallinity with T_m values ranging from 166 to 213 °C, with the highest T_m obtained from the perfectly syndiotactic PBTL (Figure 5b). This observation revealed PBTL to be a tacticity-independent crystalline polymer, which is an unusual phenomenon in polymer physics.[92] Of note, while the crystalline nature is tacticity-independent, T_m values can be modulated by the tacticity, as shown in Figure 5c, where the plot of T_m values vs. syndiotacticity (P_r) displays an overall upward trend, and an apparent linear correlation was observed after the syndiotacticity reaches about 50 %. Conventionally, crystallinity is highly dependent on tacticity, as stereo-ordered chains are required to pack effectively into a (semi)crystalline domain. Therefore, a greater degree of stereoregularity leads to a more crystalline polymer with a higher T_m, whereas stereo-disordered or atactic polymers which have a random arrangement of stereocenters are often amorphous, as is the case for even modestly tactic polymers. This longstanding structure–property relationship highlights the importance of achieving a high degree of stereochemical control in polymer synthesis and represents a highly demanding task which has continuously challenged polymer chemists and captivated their attention and efforts. However, there are a few exceptions to this rule. For example, atactic poly(vinylene-cis-1,3-cyclopentylene) [fully hydrogenated polynorbornene (hPN)] is unexpectedly crystalline, which is attributed to the unusual ability to crystallize with good three-dimensional order (a defined unit cell) even in the presence of a high degree of local structural disorder (configurational disorder in the *cis*-cyclopentylene rings).[93–95] Understanding the structure–property relationship within these rare tacticity-independent crystalline polymers is of importance to circumvent the burden of developing exquisite stereoselective syntheses to achieve highly stereoregular, high-performance crystalline polymers. PBTL inspires the interesting opportunity for the development of future tacticity-independent crystalline polymers via the hybrid monomer design strategy.

Besides the impressive tunable thermal performance and high thermal stability (Figure 5d), PBTL also exhibits

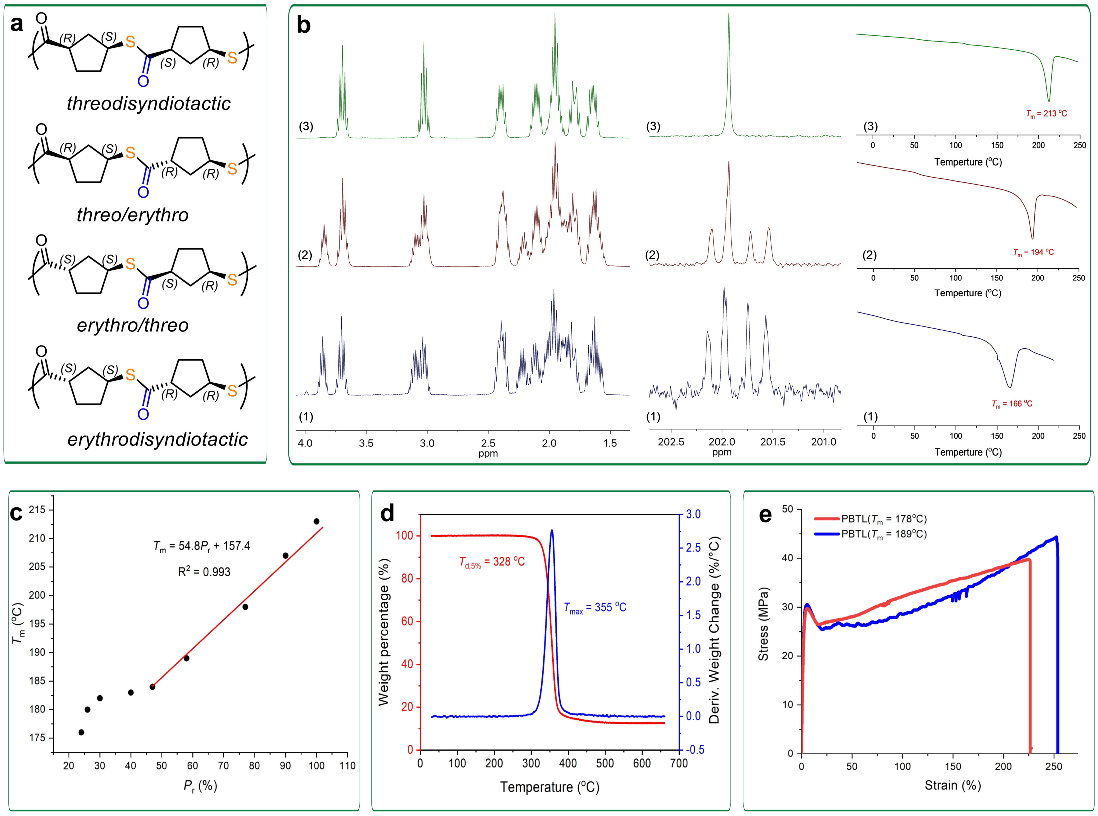


Figure 5. **a**) PBTL structures of representative four stereo-arrangements (tacticities), out of 16 total possible diads. **b**) NMR spectra and DSC curves of PBTL with varied stereoregularity, demonstrating tacticity-independent crystallinity. **c**) T_m values as a function of syndiotacticity (P_r) for the cyclic PBTL materials produced by IMes. **d**) TGA curves of PBTL showing high thermal stability. **e**) Stress-strain tensile profiles of PBTL materials with T_m = 178, 189 °C, displaying high elastic modulus as well as ultimate strength and elongation.

excellent mechanical properties. Typically, high crystallinity imparts high strength, but also undesired brittleness—which is a well-known tradeoff in semicrystalline polymers. However, in this PBTL case, the tacticity-independent crystallinity results in high ultimate strength ($\varepsilon_B = 41.4 \pm 3.0$ MPa) and Young's modulus ($E = 2.00 \pm 0.18$ GPa), and the single chain level chaos preserves the ductility of the PBTL, with an elongation at break reaching 233±22% (Figure 5e) for the PBTL with $T_m = 178$, 189°C.[89] Overall, the hybrid monomer successfully unified three conventionally uncompromising trade-offs that have continued to challenge the rational design for circular polymers with both high chemical recyclability and high-performance material properties: crystallinity/ductility, depolymerizability/performance, and stereo-disorder/crystallinity.

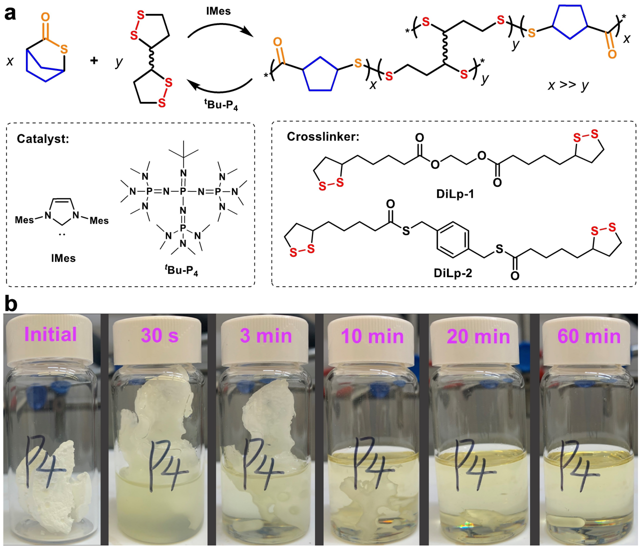


Figure 6. **a**) Copolymerization of LCT/LCT hybrid with α-lipoic acid-derived bis-dithiolane comonomer crosslinker (1–5 mol%) for the construction of an intrinsically circular semicrystalline polythioester vitrimer. **b**) Photographs of in situ depolymerization of crosslinked PBTL catalyzed by 0.2 mol% ^{t}Bu-P$_4$ at ambient temperature, showing dissolution of the network and depolymerization back to the monomer (also confirmed by NMR and isolation).

3.2.2. Intrinsically Circular Polythioester Vitrimer from LCT/LCT Comonomer Pair

The superior material properties of thermosets make them indispensable in the polymer industry, yet the lack of reprocessability and the resistance to chemicals and solvents present tougher challenges to address their EoL problem.[96,97] While many notable achievements have been made towards the development of a more sustainable lifecycle for polymeric materials, those strategies are predominantly based on the features of thermoplastics and are not readily applicable to the chemically crosslinked, non-reprocessable thermosets. The emergence of covalent adaptable networks (CANs) or vitrimers (CANs by an associative exchange mechanism for network reconfiguration) are designed to render crosslinked polymers with mechanical reprocessability.[98–102] However, there are still some fundamental challenges facing vitrimers. Most prominently, the inevitable deterioration of their material properties following serial reprocessing cycles renders their lifecycle finite.[102] To address this key limitation, we created a PBTL-based semicrystalline vitrimer that is both mechanically reprocessable and chemically recyclable, through the compatible copolymerization of thiolactone BTL and α-lipoic acid-derived bis-dithiolane, which also served as the crosslinker (Figure 6).[103] The anionic polymerization of (±)-methyl lipoate shares the same ROP mechanism of thiolactones,[104] which enables the copolymerization compatibility between thiolactones and lipoates. More judiciously, both the BTL and the bis-dithiolane are LCT monomers, thus enabling facile monomer recovery from depolymerization of their derived polymers.[89,103,105] This strategy afforded a vitrimeric system that not only exhibits plasticity and malleability under external stimuli via the installed, dynamically exchangeable disulfide linkages but can also be completely recycled to initial monomer on demand—offering a facile closed-loop EoL option once serial reprocessing deteriorates performance and the material can no longer meet the application requirements. In addition, the resultant semicrystalline PBTL vitrimer exhibited superior creep and solvent resistance, a tunable degree of crystallinity from 0 to 47% and T_m from 91 to 178°C. Traditionally, on one hand, the introduction of dynamic bonds enables the reprocessability of chemically crosslinked thermosets, but on the other hand, the dynamic nature of these crosslinks will allow topological reorganization even below the processing temperature especially as the temperature increases approaching the bond activation temperature. In this PBTL-based semicrystalline vitrimeric system, the tunable T_m derived from the PBTL segments can effectively "lock" the dynamic covalent bonds until processing conditions are met, thus suppressing creep.

Overall, this work serves as a proof of concept for intrinsically circular vitrimers via the introduction of intrinsic chemical recyclability to vitrimeric systems, where the crystallinity within the network structure and the activation barrier for dynamic bond exchange synergistically restrict creep, while reprocessability and recyclability also work synergistically to render such thermoset materials with, in principle, infinite lifecycles.

3.3. HCT/HCT Hybrid Systems

This hybrid monomer design can even be extended to an HCT/HCT monomer for enhanced thermal properties and chemical recyclability. For example, Rieger and co-workers designed a bicyclic lactone structure containing atom-bridged six- and seven-membered rings, which can be regarded as the hybridization of HCT δ-valerolactone (δ-VL) ($T_c = 298$°C at $[M]_0 = 1.0$ M) and HCT ε-CL ($T_c = 1305$°C at $[M]_0 = 1.0$ M),[106] which can be synthesized from commercially available norcamphor via a one-step Baeyer–Villiger oxidation (Figure 7).[107] This hybrid lactone was

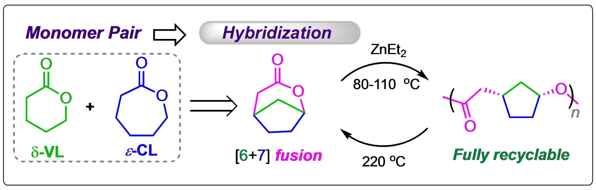


Figure 7. HCT/HCT hybrid of δ-VL and ε-CL, affording polyester with enhanced thermal properties and chemical recyclability.

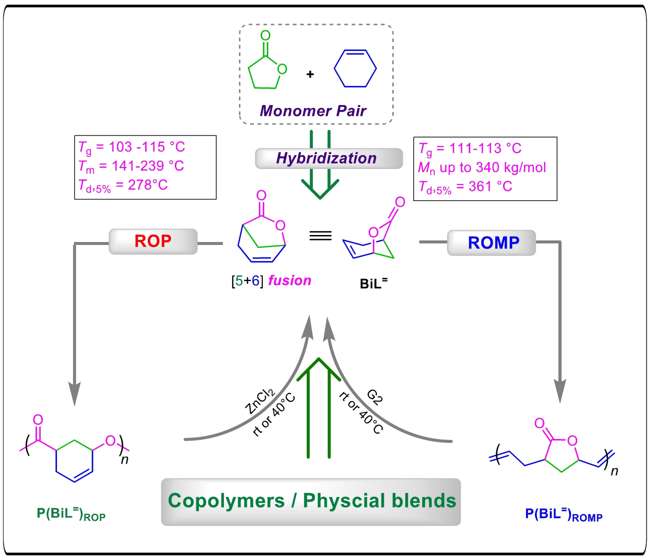


Figure 8. LCT/LCT hybrid of the lactone and cyclic olefin pair for constructing circular polyester or poly(cyclic olefin) with synergistically enhanced (de)polymerization and performance properties. The (de)polymerization processes are orthogonal, depending on the catalyst, and the catalyzed CRM can be performed at near room temperature (25–40 °C) and even on the copolymer or physical blend, all leading to the single hybrid monomer.

efficiently polymerized to the corresponding high molecular weight polymer. The in-chain incorporated cyclopentane enhanced the rigidity of the resulting polyester, which resulted in an increase in T_g by 50 °C in comparison to both parent polymers. More importantly, the resulting polymer exhibits complete and selective depolymerization by La(N(SiMe$_3$)$_2$)$_3$ at 180 °C, whereas the high HCT poly(δ-VL) and poly(ε-CL) lack facile chemical recyclability to recover their monomers selectively.[45,33]

3.4. Bifunctional Hybrid Systems

3.4.1. Polyester and Poly(cyclic olefin) from LCT/LCT Lactone/Olefin Hybrid with Orthogonal (De)polymerization

Following the success of the LCT/LCT hybrid monomer systems, we developed a demonstrative example of the hybrid monomer design strategy to achieve the orthogonal (de)polymerization of a bifunctional monomer, bringing about "one monomer—two polymers—one monomer" closed-loop circularity (Figure 8). As previously described, γ-BL is an LCT monomer for ROP, while cyclohexene is considered a "nonpolymerizable" LCT monomer for ROMP.[108,109] The LCT/LCT hybridization of these two different monomer classes affords bicyclic lactone/olefin bifunctional monomer BiL$^=$ {6-oxabicyclo[3.2.1]oct-3-en-7-one}, which undergoes orthogonal polymerization between ROP and ROMP, depending on the catalyst employed, thereby affording two different classes of polymeric materials from this single monomer: polyester P(BiL$^=$)$_{ROP}$ via ROP and functionalized poly(cyclic olefin) P(BiL$^=$)$_{ROMP}$ via ROMP.[110] Within the ROP manifold, both organic and metal-based catalysts can be used to efficiently catalyze the ROP via the ester bond, while keeping the C=C bond intact. Besides the topological control between cyclic and linear architectures, the microstructure of the resulting P(BiL$^=$)$_{ROP}$ can also be tuned from being atactic to highly syndiotactic, corresponding to amorphous to semicrystalline polyesters. Within the ROMP manifold, Ru-based Grubbs catalysts showed high reactivity and selectivity towards the C=C bond, even with a 25-ppm catalyst loading, while leaving the ester bond untouched. Additionally, both the resulting polymers retain the inherent olefin and lactone functionalities which can lead to more material possibilities by means of post-functionalization.

Importantly, both polyester P(BiL$^=$)$_{ROP}$ and polyolefin P(BiL$^=$)$_{ROMP}$ are thermally robust with $T_{d,5\%}$ up to 278 °C and 361 °C, respectively, and also chemically recyclable under mild conditions with a suitable catalyst. In the depolymerization of P(BiL$^=$)$_{ROP}$, screening of a series Lewis acid catalysts revealed that ZnCl$_2$ exhibited unusual activity and enabled depolymerization at even very mild temperatures (25–40 °C). However, under the exact same conditions, the saturated structural analogue without the double bond, PBiL, showed no sign of depolymerization. Even in the mixture of P(BiL$^=$)$_{ROP}$ and PBiL, only P(BiL$^=$)$_{ROP}$ was selectively depolymerized back to the monomer BiL$^=$, while the PBiL remained untouched. The ΔH_p^o of P(BiL$^=$)$_{ROP}$ was determined to be −34.7 kJ mol^{-1}, indicating a considerably higher ring strain in the lactone ring of BiL$^=$ compared to that of BiL ($\Delta H_p^o = -21.1$ kJ mol^{-1}).[82] This difference can be attributed to the more distorted monomer structure of BiL$^=$. Despite such a strong enthalpic driving force towards polymerization, the relatively high entropic penalty ($\Delta S_p^o =$ −88.7 J mol^{-1}K^{-1} for BiL$^=$ vs. −55.8 J mol^{-1}K^{-1} for PBiL) lowers the total free energy of polymerization enough to result in the relatively low T_c of P(BiL$^=$)$_{ROP}$. This unusual observation that the higher T_c monomer BiL$^=$ ($T_c = 118$ °C) exhibits greater depolymerizability than the relatively lower T_c monomer BiL ($T_c = 106$ °C) again highlights the importance of catalyst innovation and catalyst-substrate match for efficient and selective depolymerization. In regard to the depolymerization of P(BiL$^=$)$_{ROMP}$, the cyclohexene core structure of BiL$^=$ is slightly distorted which results in a moderate ring strain netting a $\Delta H_p^o = -19.8$ kJ mol^{-1}. This increase in ring strain, compared to the parent cyclohexene, provides the enthalpic driving force for the ROMP of the cyclohexene substructure, which is otherwise a "nonpolymerizable" monomer. In a similar fashion to the ROP product, the relatively high entropic penalty ($\Delta S^{o}_{p} = -58.3\ \mathrm{J\,mol^{-1}\,K^{-1}}$) produces a low T_c at 66 °C (1.0 M) for the ROMP, which confers closed-loop circularity to the ROMP pathway as well. Overall, LCT/LCT lactone/cyclic olefin hybrid monomer BiL⁼ renders orthogonality in both polymerization and depolymerization processes, allowing to close the entire one monomer—two polymers (polyester and polyolefin)—one monomer circular loop.

3.4.2. Vinyl Polymer and Polyester from HCT/LCT Polar Olefin/Lactone Hybrid with Orthogonal (De)polymerization

The concept that a bifunctional monomer can undergo orthogonal (de)polymerization to produce two different classes of circular polymers is rather appealing. To expand the utility of the hybrid monomer design to achieve orthogonally polymerized circular materials, here we critically analyze bifunctional α-methylene-γ-butyrolactone (MBL), which is a naturally occurring and biomass-sourced bifunctional monomer containing both a highly reactive exocyclic C═C bond and a highly stable five-membered γ-BL. This bifunctional monomer can be viewed as the structural hybridization of HCT methyl methacrylate (MMA) and LCT γ-BL and is active towards vinyl-addition polymerization (VAP) affording vinyl polymer $\mathrm{P(MBL)_{VAP}}$ and ROP forming unsaturated polyester $\mathrm{P(MBL)_{ROP}}$ (Figure 9a). MBL has received growing attention as a promising alternative to the petroleum-based MMA monomer, due to not only its renewability, but also its superior material performance and polymerizability. Atactic PMMA exhibits a T_g around 105 °C and is soluble in most common organic solvents, whereas PMBL boosts the T_g of the resultant $\mathrm{P(MBL)_{VAP}}$ to 195 °C and possesses enhanced solvent, heat, and scratch resistance.[111] More intriguingly, we have shown that the tethering effect of the incorporated lactone units (γ-BL) within PMBL enhances depolymerization selectivity by mitigating side reactions encountered with the primary radical species produced by random chain scission processes via reversible primary radical "fragmentation" and reformation.[51] On this basis, Hong et al. achieved the efficient depolymerization of $\mathrm{P(MBL)_{VAP}}$ derivatives with monomer recovery up to 99.8 % with heating, thus successfully constructing sustainable acrylic polymers with closed-loop chemical recyclability.[52]

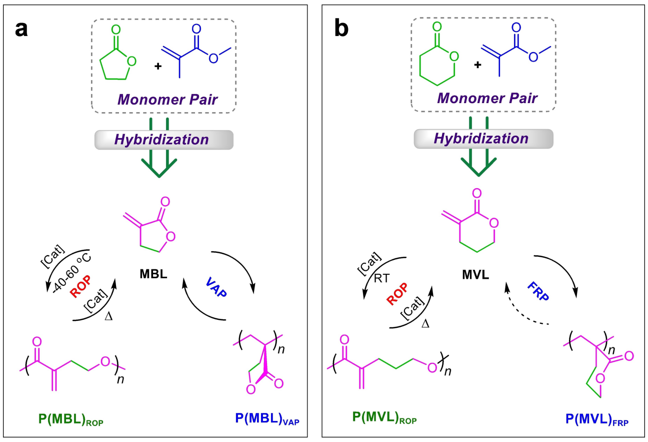


Figure 9. **a**) HCT/LCT polar olefin/lactone hybrid MBL and **b**) HCT/HCT polar olefin/lactone hybrid MVL for circular functionalized vinyl polymers (acrylics) and unsaturated polyesters with synergistically enhanced performance and orthogonal (de)depolymerization.

The ROP of the bifunctional MBL bearing the highly reactive exocyclic double bond and the minimally strained γ-BL ring was thought to be even more challenging than the ROP of γ-BL due to the two competing polymerization process, known to favor VAP and resist ROP. The development of chemoselective ROP of MBL was enabled by critical analysis of the thermodynamics of polymerization, catalyst selectivity, and polymerization conditions.[112] The study showed that the VAP reaction is thermodynamically favored, while the ROP reaction is kinetically favored.[113] In the end, the orthogonality in both polymerization and depolymerization processes has been achieved, offering another example of closed one monomer—two polymers (vinyl polymer and polyester)—one monomer loop.[110]

3.4.3. Vinyl Polymer and Polyester from HCT/HCT Polar Olefin/Lactone Hybrid with Orthogonal (De)polymerization

Likewise, bifunctional α-methylene-δ-valerolactone (MVL) can be considered as the hybrid monomer of HCT MMA and HCT δ-VL, which also exhibits orthogonal polymerization of exocyclic C═C bond and six-membered lactone subunit, as well as full chemical recyclability of both the resultant polymers (Figure 9b). The thermally initiated free radical polymerization (FRP) of MVL was investigated, yielding a T_c of 83 °C at 1.0 M, based on $\Delta H^{o}_{p} = -38.8\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{o}_{p} = -108.8\ \mathrm{J\,mol^{-1}\,K^{-1}}$. These thermodynamic parameters indicated the potential for depolymerization under mild conditions, although there was no mentioning of the recycling of $\mathrm{P(MVL)_{FRP}}$.[114] Noteworthy here is that the sterically hindered nonplanar lactone ring situated perpendicular to the plane of the backbone is mainly responsible for the reduced polymerizability (thus enhanced recyclability), in comparison with the planar exocyclic C═C and five-membered lactone hybrid, namely MBL,[115] where the planarity of MBL favors the delocalization of the growing radical into the carbonyl group, thus, resulting in a more favorable forward reaction.

The chemoselective δ-VL ROP manifold has been achieved recently by both groups of Xu[116] and Li.[117] In comparison to the ROP of MBL, the replacement of the more stable five-membered lactone, γ-BL with the more strained six-membered lactone, δ-VL, results in greater polymerizability for the ROP of the hybrid monomer, MVL, as supported by thermodynamic parameters ($\Delta H^{o}_{p} = -16.5\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{o}_{p} = -46.1\ \mathrm{J\,mol^{-1}\,K^{-1}}$).[117] The calculated $T_c = 93$ °C at 1.0 M is greatly enhanced compared to that of $\mathrm{P(MBL)_{ROP}}$ (−126 °C at 1.0 M, $\Delta H^{o}_{p} = -5.9\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{o}_{p} = -40.1\ \mathrm{J\,mol^{-1}\,K^{-1}}$).[112] Hence, MVL strikes a much more practical balance between polymerizability and recyclability. In addition, in contrast to the amorphous nature of

$P(MBL)_{ROP}$, $P(MVL)_{ROP}$ is a semicrystalline polymer ($T_m = 79\,°C$) with a degree of crystallinity degree of 52 %.[118] The enhanced crystallization characteristic of $P(MVL)_{ROP}$ is presumably due to the additional methylene linkage in the repeating unit. Furthermore, the $P(MVL)_{ROP}$ with high molar masses exhibits good mechanical properties with a tensile strength of 20.0 MPa and an elongation at break of 291 %, comparable with several commodity plastics. These examples further underline the critical importance of the judicious design of monomers at the molecular level for the construct of next-generation high-performance sustainable polymers.

3.4.4. Poly(ester-amide) and Poly(ester-thioester) from HCT/LCT Dilactone/Dilactam and Dilactone/Dithiolactone Hybrids

Poly(glycolic acid) (PGA) and its derivatives are sustainably sourced and biodegradable but lack the chemical recyclability required for a closed-loop life cycle. The high ring strain of the dilactone monomer such as glycolide poses a significant challenge to efficient depolymerization. To combat this problem, a monomer design strategy has been employed whereby one glycolic acid unit is replaced with either an amino acid[119,120] or an α-mercapto acid in the dilactone monomer structure,[121] resulting in the creation of hybrid monomers that incorporate two different functional groups to facilitate the recycling of the resulting monomers (Figure 10).

Specifically, six-membered dilactam is an LCT monomer, as evidenced by the facile cyclization under basic conditions.[122] Accordingly, Li et al. developed chemically recyclable poly(ester-amide)s via the ROP of morpholino-2,5-dione derivatives, which can be regarded as the lactone/lactam hybrid monomer of HCT dilactone and LCT dilactam[119] (Figure 10a). The resulting polymers possess excellent mechanical properties, achievable via tuning side chain substituents. The hybrid monomer was obtained in high purity and efficiency through either solution depolymerization catalyzed by solid acid Amberlyst 15 ion-exchange resin at 120 °C, or bulk depolymerization catalyzed by $Sn(Oct)_2$ at 140 °C under vacuum.[119,120] Likewise, dithiolactone (or thiolactide) is an LCT monomer with a T_c of only −67 °C at 1.0 M, based on the thermodynamic parameters $\Delta H_p^o = -4.9\,kJ\,mol^{-1}$ and $\Delta S_p^o = -23.9\,J\,mol^{-1}\,K^{-1}$.[123] Substitution of the glycolic acid in glycolide with α-mercapto acid affords dilactone/dithiolactone hybrid with a suitable T_c of 165 °C ($\Delta H_p^o = -22.2\,kJ\,mol^{-1}$ and $\Delta S_p^o = -50.7\,J\,mol^{-1}\,K^{-1}$). The hybrid lactone/thiolactone monomer can be recycled at 120 °C under vacuum with PhSNa as the catalyst, highlighting the dilactone/dithiolactone hybrid as an effective strategy for converting "non-recyclable" polyester into a chemically recyclable polymer.[121] Notably, in both hybrid lactone/lactam and lactone/thiolactone monomers, the contrast in bond stability (amide, ester, and thioester bonds) gives rise to perfect ROP regioselectivity.

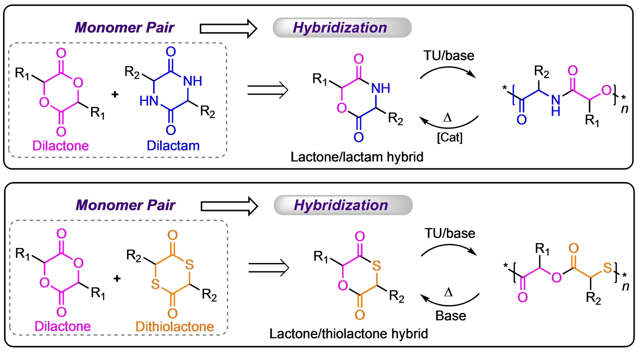


Figure 10. **a**) HCT/LCT six-membered dilactone/dilactam hybridization gives lactone/lactam hybrid and **b**) HCT/LCT six-membered dilactone/dithiolactone hybridization gives lactone/thiolactone hybrid. TU = thiourea.

4. Summary and Outlook

In this minireview, we highlighted notable examples which demonstrate the effectiveness of the hybrid monomer design as a strategy towards the synergistic unification of conflicting (de)polymerizability and recyclability/performance properties. While analyzing those examples, we carefully examined and rationalized this strategy's ability to endow polymeric systems with full chemical recyclability by altering the thermodynamics and kinetics of polymerization through the judicious redesign of monomer structure. Specifically, we discussed examples of this design philosophy for the redesign of a high-performance polyester, polyamide, and polythioester for achieving complete closed-loop monomer-polymer-monomer life cycles. We also provided an example for the preparation of a bifunctional and orthogonally (de)polymerizable hybrid monomer which not only confirms the possibility of a one-monomer–two-polymer–one-monomer lifecycle but also points to other potential orthogonal systems which could offer unprecedented custom application control and full chemical recyclability. Lastly, we included several examples of alternative bifunctional hybrid monomers and discussed their monomer structure as it relates to their polymerization behavior and polymeric properties. Overall, we presented the strategy and rationale for the development of hybrid monomers as they have demonstrated the ability to solve challenges related to intrinsic chemical recyclability and conflicting property unification, dissected key examples which highlight the frontier of this design philosophy's implementation, and offered fundamental explanations and insights regarding the successes achieved so far.

However, there are still several unmet challenges relating to this emerging strategy. First, the further development of the structure–property relationship within these hybrid systems is needed. A traditionally challenging area of study, the relationship between the monomer structure and the resultant polymeric properties is especially relevant to this sub-field. This is exemplified by the discussed examples which highlight how small changes in hybrid monomer structure result in drastically different polymerization behavior and material performance, especially, for example the exploration of the origin of unique material performance, such as the tacticity-independent crystallinity, is pivotal to hone the expertise in hybrid monomer design. Theoretical and computational studies should significantly accelerate discoveries of hybrid monomer structures and the advanced polymer properties as well as the establishment of the structure–property relationships within this class. Second, catalyst innovation for the depolymerization of polymer blends and mixtures is needed. We put forward the "one-monomer—two-polymers—one-monomer" closed-loop as a representative example to address the trade-offs between the material polymerizability and the recyclability, while the depolymerization requires two different catalysts in two sequential stages. Innovation in depolymerization catalysis towards catalyzing multiple depolymerization pathways at once which thereby enables the simultaneous depolymerization of polymer blends and mixtures will be critical to the wider adoption of this technology—both for the chemical recycling of mixed waste streams and the reprocessing of such "one-monomer–two-polymers–one-monomer" hybrid systems. Currently, the development of multifunctional depolymerization catalysts or compatible catalytic systems is a necessary yet under explored area of research. Third, the source and scalability of the designed hybrid monomers and the corresponding polymers need to be demonstrated beyond the fundamental study and discovery stage. At the initial design and exploratory study phase, the source and scalability of the monomer are typically not of primary concern. However, for new ICPs to be competitive and sustainable in the marketplace, besides their demonstrated circularity and materials performance, they should be derived from bio-renewable resources or waste plastics, scalable, and cost-competitive. In this context, we note that we have successfully synthesized bio-derived hybrid monomers such as BiL$^{=}$ at scales up to hundreds of grams while maintaining high overall yield (>90%). The scalability and economics of new, more sustainable polymers are often the major obstacle that must be overcome before they can enter the marketplace. Early engagement with techno-economic analysis and life cycle assessment will accelerate the advancement of their technology readiness level. However, in the longer terms, sustainable materials alternatives such as ICPs overviewed herein will prevail in the inevitable future circular materials economy.

Acknowledgements

Funding was provided by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office (AMO) and Bioenergy Technologies Office (BETO). This work was performed as part of the Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE) Consortium and was supported by AMO and BETO under Contract DE-AC36-08GO28308 with the National Renewable Energy Laboratory (NREL), operated by Alliance for Sustainable Energy, LLC.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Chemical Recycling to Monomer · Circular Economy · Hybrid Monomer Design · Intrinsically Circular Polymer · Property Trade-Offs

[1] R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782.

[2] P. Stegmann, V. Daioglou, M. Londo, D. P. van Vuuren, M. Junginger, *Nature* **2022**, *612*, 272–276.

[3] L. Cabernard, S. Pfister, C. Oberschelp, S. Hellweg, *Nat. Sustainability* **2022**, *5*, 139–148.

[4] J. Zheng, S. Suh, *Nat. Clim. Change* **2019**, *9*, 374–378.

[5] World Economic Forum; Ellen MacArthur Foundation, and McKinsey & Company. (**2016**). The new plastics economy: rethinking the future of plastics. https://ellenmacarthurfoundation.org/the-new-plastics-economy-rethinking-thefuture- of-plastics.

[6] K. L. Law, *Annu. Rev. Mar. Sci.* **2017**, *9*, 205–229.

[7] K. L. Law, R. C. Thompson, *Science* **2014**, *345*, 144–145.

[8] C. M. Rochman, M. A. Browne, B. S. Halpern, B. T. Hentschel, E. Hoh, H. K. Karapanagioti, L. M. Rios-Mendoza, H. Takada, S. Teh, R. C. Thompson, *Nature* **2013**, *494*, 169–171.

[9] D. Lithner, Å. Larsson, G. Dave, *Sci. Total Environ.* **2011**, *409*, 3309–3324.

[10] 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.

[11] Y. Zhu, C. Romain, C. K. Williams, *Nature* **2016**, *540*, 354–362.

[12] M. A. Hillmyer, *Science* **2017**, *358*, 868–870.

[13] D. K. Schneiderman, M. A. Hillmyer, *Macromolecules* **2017**, *50*, 3733–3749.

[14] X. Zhang, M. Fevre, G. O. Jones, R. M. Waymouth, *Chem. Rev.* **2018**, *118*, 839–885.

[15] A. Rahimi, J. M. García, *Nat. Chem. Rev.* **2017**, *1*, 0046.

[16] J. C. Worch, A. P. Dove, *ACS Macro Lett.* **2020**, *9*, 1494–1506.

[17] F. Zhang, M. Zeng, R. D. Yappert, J. Sun, Y. H. Lee, A. M. LaPointe, B. Peters, M. M. Abu-Omar, S. L. Scott, *Science* **2020**, *370*, 437–441.

[18] A. Tennakoon, X. Wu, A. L. Paterson, S. Patnaik, Y. Pei, A. M. LaPointe, S. C. Ammal, R. A. Hackler, A. Heyden, I. I. Slowing, G. W. Coates, M. Delferro, B. Peters, W. Huang, A. D. Sadow, F. A. Perras, *Nat. Catal.* **2020**, *3*, 893–901.

[19] 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.

[20] K. P. Sullivan, A. Z. Werner, K. J. Ramirez, L. D. Ellis, J. R. Bussard, B. A. Black, D. G. Brandner, F. Bratti, B. L. Buss, X. Dong, S. J. Haugen, M. A. Ingraham, M. O. Konev, W. E. Michener, J. Miscall, I. Pardo, S. P. Woodworth, A. M. Guss, Y. Román-Leshkov, S. S. Stahl, G. T. Beckham, *Science* **2022**, *378*, 207–211.

[21] 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.

[22] A. H. Westlie, E. Y.-X Chen, C. M. Holland, S. S. Stahl, M. Doyle, S. R. Trenor, K. M. Knauer, *Macromol. Rapid Commun.* **2022**, *43*, 2200492.

[23] R. J. Conk, S. Hanna, J. X. Shi, J. Yang, N. R. Ciccia, L. Qi, B. J. Bloomer, S. Heuvel, T. Wills, J. Su, A. T. Bell, J. F. Hartwig, *Science* **2022**, *377*, 1561–1566.
[24] N. M. Wang, G. Strong, V. DaSilva, L. Gao, R. Huacuja, I. A. Konstantinov, M. S. Rosen, A. J. Nett, S. Ewart, R. Geyer, S. L. Scott, D. Guironnet, *J. Am. Chem. Soc.* **2022**, *144*, 18526–18531.
[25] 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.
[26] T. P. Haider, C. Volker, J. Kramm, K. Landfester, F. R. Wurm, *Angew. Chem. Int. Ed.* **2019**, *58*, 50–62.
[27] 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.
[28] Z. O. G. Schyns, M. P. Shaver, *Macromol. Rapid Commun.* **2021**, *42*, 2000415.
[29] K. Ragaert, L. Delva, K. Van Geem, *Waste Manage.* **2017**, *69*, 24–58.
[30] I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2020**, *59*, 15402–15423.
[31] M. Hong, E. Y.- X. Chen, *Green Chem.* **2017**, *19*, 3692–3706.
[32] M. Hong, E. Y.- X. Chen, *Trends Chem.* **2019**, *1*, 148–151.
[33] X. Tang, E. Y.- X. Chen, *Chem* **2019**, *5*, 284–312.
[34] X.- B. Lu, Y. Liu, H. Zhou, *Chem. Eur. J.* **2018**, *24*, 11255–11266.
[35] Y. Liu, X.-B. Lu, *Chem. Eur. J.* **2023**, *29*, e202203635.
[36] IUPAC Top Ten Emerging Technologies in Chemistry. https://iupac.org/what-we-do/top-ten/. Accessed 2021-11-01.
[37] G. W. Coates, Y. D. Y. L. Getzler, *Nat. Rev. Mater.* **2020**, *5*, 501–516.
[38] A. Duda, A. Kowalski, in *Handbook of Ring-Opening Polymerization*, Wiley-VCh, Weinheim, **2009**, pp. 1–51.
[39] D. K. Schneiderman, M. A. Hillmyer, *Macromolecules* **2016**, *49*, 2419–2428.
[40] J. Zhou, D. Sathe, J. Wang, *J. Am. Chem. Soc.* **2022**, *144*, 928–934.
[41] D. Sathe, H. Chen, J. Wang, *Macromol. Rapid Commun.* **2022**, e2200304.
[42] 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.
[43] M. E. Jung, G. Piizzi, *Chem. Rev.* **2005**, *105*, 1735–1766.
[44] 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.
[45] X. L. Li, R. W. Clarke, J. Y. Jiang, T. Q. Xu, E. Y.-X. Chen, *Nat. Chem.* **2023**, *15*, 278–285.
[46] P. Shieh, W. Zhang, K. E. L. Husted, S. L. Kristufek, B. Xiong, D. J. Lundberg, J. Lem, D. Veysset, Y. Sun, K. A. Nelson, D. L. Plata, J. A. Johnson, *Nature* **2020**, *583*, 542–547.
[47] P. Shieh, H. V. T. Nguyen, J. A. Johnson, *Nat. Chem.* **2019**, *11*, 1124–1132.
[48] J. D. Feist, D. C. Lee, Y. Xia, *Nat. Chem.* **2022**, *14*, 53–58.
[49] M. R. Martinez, K. Matyjaszewski, *CCS Chem.* **2022**, *4*, 2176–2211.
[50] H. S. Wang, N. P. Truong, Z. Pei, M. L. Coote, A. Anastasaki, *J. Am. Chem. Soc.* **2022**, *144*, 4678–4684.
[51] R. A. Gilsdorf, M. A. Nicki, E. Y.- X. Chen, *Polym. Chem.* **2020**, *11*, 4942–4950.
[52] Z.-H. Zhang, X. Wang, B. Weng, Y. Zhang, G. Zhang, M. Hong, *ACS Polym. Au* **2022**, *2*, 266–274.
[53] A. J. Christy, S. T. Phillips, *Sci. Adv.* **2023**, *9*, eadg2295.
[54] M. G. Han, S. Kim, S. X. Liu, *Polym. Degrad. Stab.* **2008**, *93*, 1243–1251.
[55] M. R. Martinez, Y. Cong, S. S. Sheiko, K. Matyjaszewski, *ACS Macro Lett.* **2020**, *9*, 1303–1309.
[56] M. R. Martinez, S. Dadashi-Silab, F. Lorandi, Y. Zhao, K. Matyjaszewski, *Macromolecules* **2021**, *54*, 5526–5538.
[57] J. B. Young, J. I. Bowman, C. B. Eades, A. J. Wong, B. S. Sumerlin, *ACS Macro Lett.* **2022**, *11*, 1390–1395.
[58] H. S. Wang, N. P. Truong, G. R. Jones, A. Anastasaki, *ACS Macro Lett.* **2022**, *11*, 1212–1216.
[59] M. R. Martinez, D. Schild, F. De Luca Bossa, K. Matyjaszewski, *Macromolecules* **2022**, *55*, 10590–10599.
[60] Y. Sano, T. Konishi, M. Sawamoto, M. Ouchi, *Eur. Polym. J.* **2019**, *120*, 109181.
[61] M. Häußler, M. Eck, D. Rothauer, S. Mecking, *Nature* **2021**, *590*, 423–427.
[62] M. Eck, S. T. Schwab, T. F. Nelson, K. Wurst, S. Iberl, D. Schleheck, C. Link, G. Battagliarin, S. Mecking, *Angew. Chem. Int. Ed.* **2023**, *62*, e202213438.
[63] D. J. Darensbourg, *Polym. Degrad. Stab.* **2018**, *149*, 45–51.
[64] Y. Liu, X.-B. Lu, *Macromolecules* **2023**, *56*, 1759–1777.
[65] Y. Liu, H. Zhou, J. Z. Guo, W. M. Ren, X.- B. Lu, *Angew. Chem. Int. Ed.* **2017**, *56*, 4862–4866.
[66] Y. Yu, L.-M. Fang, Y. Liu, X.-B. Lu, *ACS Catal.* **2021**, *11*, 8349–8357.
[67] G. W. Yang, Y. Wang, H. Qi, Y. Y. Zhang, X. F. Zhu, C. Lu, L. Yang, G.- P. Wu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202210243.
[68] A. J. Plajer, C. K. Williams, *Angew. Chem. Int. Ed.* **2022**, *61*, e202104495.
[69] X. Liao, F. C. Cui, J. H. He, W. M. Ren, X.- B. Lu, Y.- T. Zhang, *Chem. Sci.* **2022**, *13*, 6283–6290.
[70] Y. Yu, B. Gao, Y. Liu, X.- B. Lu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204492.
[71] T. M. McGuire, A. C. Deacy, A. Buchard, C. K. Williams, *J. Am. Chem. Soc.* **2022**, *144*, 18444–18449.
[72] F. R. Mayo, C. Walling, *Chem. Rev.* **1950**, *46*, 191–287.
[73] X. Tang, A. H. Westlie, E. M. Watson, E. Y.-X. Chen, *Science* **2019**, *366*, 754–758.
[74] X. Tang, A. H. Westlie, L. Caporaso, L. Cavallo, L. Falivene, E. Y.-X. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 7881–7890.
[75] M. Hakkarainen, A. Höglund, K. Odelius, A.-C. Albertsson, *J. Am. Chem. Soc.* **2007**, *129*, 6308–6312.
[76] J. A. Wilson, S. A. Hopkins, P. M. Wright, A. P. Dove, *ACS Macro Lett.* **2016**, *5*, 346–350.
[77] J. A. Wilson, S. A. Hopkins, P. M. Wright, A. P. Dove, *Biomacromolecules* **2015**, *16*, 3191–3200.
[78] M. Hong, X. Tang, B. S. Newell, E. Y.- X. Chen, *Macromolecules* **2017**, *50*, 8469–8479.
[79] X. Tang, C. Shi, Z. Zhang, E. Y.- X. Chen, *Macromolecules* **2021**, *54*, 9401–9409.
[80] M. Hong, E. Y.- X. Chen, *Nat. Chem.* **2016**, *8*, 42–49.
[81] H. Abe, N. Takahashi, K. J. Kim, M. Mochizuki, Y. Doi, *Biomacromolecules* **2004**, *5*, 1480–1488.
[82] C. Shi, Z.-C. Li, L. Caporaso, L. Cavallo, L. Falivene, E. Y.- X. Chen, *Chem* **2021**, *7*, 670–685.
[83] J. B. Zhu, E. M. Watson, J. Tang, E. Y.-X. Chen, *Science* **2018**, *360*, 398–403.
[84] 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.
[85] A. Kamimura, S. Yamamoto, *Org. Lett.* **2007**, *9*, 2533–2535.
[86] L. Wursthorn, K. Beckett, j. O. Rothbaum, R. M. Cywar, C. Lincoln, Y. Kratish, T. J. Marks, *Angew. Chem. Int. Ed.* **2022**, *61*, e202212543.
[87] C. G. Overberger, J. K. Weise, *J. Am. Chem. Soc.* **1968**, *90*, 3533–3537.
[88] H. Kikuchi, N. Tsubokawa, T. Endo, *Chem. Lett.* **2005**, *34*, 376–377.

[89] C. Shi, M. L. McGraw, Z.- C. Li, L. Cavallo, L. Falivene, E. Y.-X. Chen, *Sci. Adv.* **2020**, *6*, eabc0495.

[90] J. Yuan, W. Xiong, X. Zhou, Y. Zhang, D. Shi, Z. Li, H. Lu, *J. Am. Chem. Soc.* **2019**, *141*, 4928–4935.

[91] J. Yuan, D. Shi, Y. Zhang, J. Lu, L. Wang, E.-Q. Chen, H. Lu, *CCS Chem.* **2020**, *2*, 236–244.

[92] P. Corradini, F. Auriemma, C. De Rosa, *Acc. Chem. Res.* **2006**, *39*, 314–323.

[93] L.-B. W. Lee, R. A. Register, *Macromolecules* **2005**, *38*, 1216–1222.

[94] N. Kafle, Y. Makita, Y. Zheng, D. Schwarz, H. Kurosu, P. Pan, J. M. Eagan, Y. Nakama, S. Hayano, T. Miyoshi, *Macromolecules* **2021**, *54*, 5705–5718.

[95] Y. Nakama, S. Hayano, K. Tashiro, *Macromolecules* **2021**, *54*, 8122–8134.

[96] M. R. Vengatesan, A. M. Varghese, V. Mittal, in *Thermosets*, Second Edition, (Ed.: Q. Guo), Elsevier, Amsterdam, **2018**, pp. 69–114.

[97] Y. Liu, Z. Yu, B. Wang, P. Li, J. Zhu, S. Ma, *Green Chem.* **2022**, *24*, 5691–5708.

[98] G. M. Scheutz, J. J. Lessard, M. B. Sims, B. S. Sumerlin, *J. Am. Chem. Soc.* **2019**, *141*, 16181–16196.

[99] W. Zou, J. Dong, Y. Luo, Q. Zhao, T. Xie, *Adv. Mater.* **2017**, *29*, 1606100.

[100] A. Martinez, A. Dobson, N. J. Bongiardina, C. N. Bowman, *Adv. Mater.* **2020**, *32*, e1906876.

[101] Y. Jin, Z. Lei, P. Taynton, S. Huang, W. Zhang, *Matter* **2019**, *1*, 1456–1493.

[102] N. Zheng, Y. Xu, Q. Zhao, T. Xie, *Chem. Rev.* **2021**, *121*, 1716–1745.

[103] C. Shi, Z. Zhang, M. Scoti, X. Y. Yan, E. Y.-X. Chen, *ChemSusChem* **2023**, *16*, e202300008.

[104] Y. Liu, Y. Jia, Q. Wu, J. S. Moore, *J. Am. Chem. Soc.* **2019**, *141*, 17075–17080.

[105] Q. Zhang, D.- H. Qu, B. L. Feringa, H. Tian, *J. Am. Chem. Soc.* **2022**, *144*, 2022–2033.

[106] J. Su, G. Xu, B. Dong, R. Yang, H. Sun, Q. Wang, *Polym. Chem.* **2022**, *13*, 5897–5904.

[107] J. Bruckmoser, S. Remke, B. Rieger, *ACS Macro Lett.* **2022**, *11*, 1162–1166.

[108] P. v. R. Schleyer, J. E. Williams, K. R. Blanchard, *J. Am. Chem. Soc.* **1970**, *92*, 2377–2386.

[109] P. A. Patton, C. P. Lillya, T. J. McCarthy, *Macromolecules* **1986**, *19*, 1266–1268.

[110] C. Shi, R. W. Clarke, M. L. McGraw, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2022**, *144*, 2264–2275.

[111] R. R. Gowda, E. Y.-X. Chen, *Encyclopedia of Polymer Science and Technology, Vol. 8*, 4th ed., (Ed.: H. F., Mark), Wiley, Hoboken, **2014**, pp. 235–271.

[112] X. Tang, M. Hong, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 14326–14337.

[113] Y. Shen, W. Xiong, Y. Li, Z. Zhao, H. Lu, Z. Li, *CCS Chem.* **2021**, *3*, 620–630.

[114] M. Ueda, M. Takahashi, Y. Imai, C. U. Pittman, *Macromolecules* **1983**, *16*, 1300–1305.

[115] M. Ueda, M. Takahashi, Y. Imai, C. U. Pittman, *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 2819–2828.

[116] T. Q. Xu, Z. Q. Yu, X. M. Zhang, *Macromol. Chem. Phys.* **2019**, *220*, 1900150.

[117] J. Li, F. Liu, Y. Liu, Y. Shen, Z. Li, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207105.

[118] F. J. Camarena-Maese, F. Martínez-Hergueta, J. P. Fernández-Blázquez, R. W. Kok, J. Reid, A. Callanan, *Polymer* **2020**, *203*, 122775.

[119] 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.

[120] Y.-T. Guo, C. Shi, T.-Y. Du, X.-Y. Cheng, F.-S. Du, Z.-C. Li, *Macromolecules* **2022**, *55*, 4000–4010.

[121] Y. Wang, Y. Zhu, W. Lv, X. Wang, Y. Tao, *J. Am. Chem. Soc.* **2023**, *145*, 1877–1885.

[122] T. R. Blake, W. C. Ho, C. R. Turlington, X. Zang, M. A. Huttner, P. A. Wender, R. M. Waymouth, *Chem. Sci.* **2020**, *11*, 2951–2966.

[123] Y. Wang, M. Li, J. Chen, Y. Tao, X. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 22547–22553.

Manuscript received: February 6, 2023
Accepted manuscript online: April 18, 2023
Version of record online: May 10, 2023