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Perspective

Design principles for intrinsically circular polymers with tunable properties

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SUMMARY

This perspective discusses a set of design principles for next-generation kinetically trapped, intrinsically circular polymers (iCPs) that are inherently, selectively, and expediently depolymerizable to their monomer state once their kinetic barriers of deconstruction are overcome, thereby enabling not only the ideal shortest chemical circularity but also tunable performance properties. After describing four elements of the design principles—thermodynamics and kinetics, strategies to overcome trade-offs and unify conflicting properties, predictive modeling, and supply-chain life-cycle assessment and techno-economic analysis, which are illustrated with state-of-the-art examples—it concludes with presenting key challenges and opportunities for sustainable development of iCPs.

INTRODUCTION

Synthetic polymers, especially lightweight, inexpensive, long-lifetime, and high-performance commodity plastics, have fueled modern economies and become indispensable for modern life and the global economy. By 2050, annual production of plastics is predicted to reach ~1.12 billion tons,[1] while plastics manufacturing is predicted to account for 20% of global petroleum consumption,[2] thus contributing significantly to greenhouse gas emissions, fossil-based energy consumption, and carbon pollution.[3] Furthermore, nearly all today's polymers were historically developed for cost, performance, durability, and disposability, rather than for performance and recyclability or degradability. Accordingly, most of today's polymers are developed and manufactured based on a linear economy framework that does not adequately address materials' end-of-life issues, thereby resulting in not only accelerated depletion of finite fossil resources and enormous energy and materials value loss to the economy but also a global plastics pollution crisis.[4–6] Three major approaches have been intensively pursued to address the above-mentioned dire environmental, energy, and societal issues: development of bio-derived renewable polymers,[7–10] chemical recycling and upcycling of today's polymers,[11–18] and redesign of tomorrow's polymers with chemical recyclability[19–21] or biodegradability.[22] To address the *root* of the plastics problem, the design of next-generation sustainable polymers must consider not only their sustainable sources but also their end-of-life options to establish closed-loop life cycles toward a circular materials economy.[23–25]

Preventing plastics pollution is just like preventing any other type of pollution: the best solution is to prevent pollution at the source. In the long run, addressing plastics *waste* is far more costly and energy intensive than developing plastics that will not end up as waste in the first place. The typical arguments that today's plastics are

The bigger picture

Challenges and opportunities:

- Innovative monomer/polymer and catalyst design strategies that can render orthogonality of polymerization and depolymerization to overcome trade-offs, as well as unify conflicting properties and maximize selectivity.
- Predictive thermodynamic and kinetic modeling that can guide monomer design for intrinsically circular polymers (iCPs) and predict iCP's time-dependent properties.
- Metrics for sustainability of the circular plastics economy through life-cycle assessment and techno-economic analysis that can identify key gaps for further research and development to overcome.

much cheaper and new bio-based, recyclable, or biodegradable plastics contaminate recycling streams neglect environmental, financial, and social triple-bottom-line accountability.[26] Here, we posit the concept of ''intrinsically circular polymers'' (iCPs)—circular polymers with intrinsic chemical recyclability—can be exploited to address the root of the plastics problem as iCPs can be designed *de novo* for not only complete, shortest chemical circularity but also tunable performance properties and lower carbon intensity. More specifically, iCPs are *kinetically trapped polymers* that are inherently, selectively, and expediently depolymerizable to their monomer state once the kinetic barrier of deconstruction is overcome by thermal energy, catalysis, or other on-demand external stimuli, while keeping monomer structures and, thus, reconstructed polymer properties intact. We further postulate that the design of iCPs can start at the molecular level—structures of molecular building blocks or monomers—and further extend to include synthetic methodologies and predict higher order structures and complex macroscopic properties of the resulting macromolecules pertaining to their practical performances.

In principle, any polymer could be rendered reversible by manipulating the thermodynamic equilibrium of polymerization and depolymerization processes through adjusting reaction conditions, such as temperature, pressure, concentration, state, etc. However, in reality, whether a polymer can be practically and efficiently deconstructed to its monomer and then reconstructed back to complete the polymer-monomer-polymer life cycle, thereby meeting the criteria of being an iCP, depends on (de)polymerizability (i.e., relative energy levels of monomer versus polymer states under given conditions, as determined by ''thermodynamics'') and energy barrier that determines the *kinetics* of the forward and backward reactions in terms of rate, energy input, and selectivity. A thermodynamic measure of polymerizability (from the monomer's perspective) or depolymerizability (from the polymer's perspective) can be quantified by ceiling temperature (T_c),[27] defined as the temperature at which the de/polymerization reactions reach an equilibrium state. In other words, T_c determines the relative stability of monomer-polymer states at different working temperature (T) regimes.

In this perspective article, we discuss a set of design principles for iCPs with tunable properties from four perspectives that merit consideration: thermodynamics and kinetics, strategies to overcome trade-offs and unify conflicting properties, predictive modeling, as well as supply-chain life-cycle assessment (LCA) and techno-economic analysis (TEA). Note that in this article, by focusing on iCPs, which typically have a low T_c of <200°C (in bulk), we will not discuss polymer systems that do not exhibit intrinsic chemical circularity, such as permanently or dynamically cross-linked thermosets and ''thermodynamically trapped,'' highly exergonic polyolefins composed of robust main-chain C–C bonds, which typically have a high T_c of >400°C. Polymers with a medium T_c of 200°C–400°C, typically for C–X (heteroatom) backboned polymers, can be redesigned to be iCPs or chemically re/up-cycled through engineering reaction/processing conditions and/or catalytic processes.[18] Here, it is important to note that polymers without the stated intrinsic chemical recyclability (e.g., thermoplastics with medium to high T_c values and thermosets) can be rendered chemically circular, although often requiring multiple transformations or catalytic reactions. We conclude this article by presenting several key challenges and opportunities in designing iCPs.

THERMODYNAMIC AND KINETIC CONSIDERATIONS

To satisfy the criteria of iCPs, the thermodynamics and kinetics of the de/polymerization system must be well understood and addressed.[28–30] Specifically, the

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de/polymerization reactions in the face of a monomer-polymer equilibrium are central to the design of an iCP and are to be considered accordingly. This crucial equilibrium can be experimentally observed and quantified as a measure of monomer concentration at equilibrium ($[\mathrm{M}]_{\mathrm{eq}}$). Several external variables, such as temperature, pressure, concentration, state, etc., can be employed to perturb this monomer-polymer equilibrium toward polymer or monomer formation, depending on the favor of the thermodynamic equilibrium. The thermodynamics of a given monomer's polymerizability are related to the Gibbs free energy of polymerization (ΔG_{p}): if $\Delta G_{\mathrm{p}} < 0$, the polymer state is favored and monomer will convert to polymer; whereas if $\Delta G_{\mathrm{p}} > 0$, the reverse is true and depolymerization will occur. It is important to note that both cases are not the equilibrium state; the de/polymerization reactions will occur in thermodynamic competition until an equilibrium is reached (where $\Delta \mathrm{G}_{\mathrm{p}} = 0$). Thus, the extent of de/polymerization reactions—the thermodynamic limit on percent monomer conversion in the forward reaction or percent monomer recovery in the backward reaction—will depend on how far the free energy of the system under given conditions is away from the equilibrium, unless this equilibrium is continuously perturbed by methods, such as precipitation/crystallization of polymer in the polymerization or constant removal of monomer (e.g., by distillation, sublimation, etc.) in the depolymerization. Under these scenarios, the de/polymerization reactions can go to completion or to an extent far exceeding the thermodynamic limit.

Mathematically, ΔG_{p} can be expressed as a sum of the standard Gibbs free energy of polymerization ($\Delta G_{\mathrm{p}}^{\circ}$) and a term relating to the instantaneous monomer concentration to the concentration of growing polymer chains, polymerization temperature (T), and the molar gas constant (R): $\Delta G_{\mathrm{p}} = \Delta G_{\mathrm{p}}^{\circ} + RT \ln\{[\mathrm{P}^{*}_{n}]/[\mathrm{P}^{*}_{n-1}][\mathrm{M}]\}$. Flory's assumption that the reactivity of an active center, located on a sufficiently long macromolecular chain, does not depend on the degree of polymerization, affords an additional approximation: $\Delta G_{\mathrm{p}} = \Delta G_{\mathrm{p}}^{\circ} + RT \ln\{1/[\mathrm{M}]\}$. Considering that $\Delta G_{\mathrm{p}}^{\circ} = \Delta H_{\mathrm{p}}^{\circ} - \mathrm{T}\Delta \mathrm{S}_{\mathrm{p}}^{\circ}$, ΔG_{p} can be further related to standard polymerization enthalpy ($\Delta H_{\mathrm{p}}^{\circ}$) and entropy ($\Delta S_{\mathrm{p}}^{\circ}$) and expressed as $\Delta G_{\mathrm{p}} = \Delta H_{\mathrm{p}}^{\circ} - T\{\Delta S_{\mathrm{p}}^{\circ} + \mathrm{R}\ln[\mathrm{M}]\}$.[28]

At equilibrium ($\Delta G_{\mathrm{p}} = 0$), monomer concentration ([M]) remains constant: $[\mathrm{M}] = [\mathrm{M}]_{\mathrm{eq}}$. The value of $[\mathrm{M}]_{\mathrm{eq}}$ can be determined using standard polymerization parameters ($\Delta H_{\mathrm{p}}^{\circ}$ and $\Delta S_{\mathrm{p}}^{\circ}$) and polymerization temperature, by equation $\ln[\mathrm{M}]_{\mathrm{eq}} = \Delta H_{\mathrm{p}}^{\circ}/RT - \Delta S_{\mathrm{p}}^{\circ}/R$. In the case of a new monomer, the standard polymerization parameters can be obtained from constructing a Van't Hoff plot of $\ln[\mathrm{M}]_{\mathrm{eq}}$ versus $1/T$, using experimentally collected $[\mathrm{M}]_{\mathrm{eq}}$ at varied temperatures.[28–31] Under conditions at which $[\mathrm{M}]_{\mathrm{eq}} = [\mathrm{M}]_0$, no polymerization takes place. In other words, polymerization is possible only when $[\mathrm{M}]_0 > [\mathrm{M}]_{\mathrm{eq}}$.

Further understanding the influence of these standard parameters is paramount in the design of an iCP. As $\Delta G_{\mathrm{p}} < 0$ is the requirement for polymerization, monomers for which $\Delta H_{\mathrm{p}}^{\circ} < 0$ and $\Delta S_{\mathrm{p}}^{\circ} > 0$ can be spontaneously polymerized at any temperature, whereas those with $\Delta H_{\mathrm{p}}^{\circ} > 0$ and $\Delta S_{\mathrm{p}}^{\circ} < 0$ cannot at all be polymerized. When $\Delta H_{\mathrm{p}}^{\circ} > 0$ and $\Delta S_{\mathrm{p}}^{\circ} > 0$, there is a critical temperature—known as the floor temperature (T_{f}), which is the lowest temperature polymerization can occur and is, thus, entropically driven. At or below T_{f}, which can be calculated by equation $T_{\mathrm{f}} = \Delta H_{\mathrm{p}}^{\circ}/\{\Delta S_{\mathrm{p}}^{\circ} + R\ln[\mathrm{M}]_0\}$, polymerization is thermodynamically forbidden. However, in the most common polymerization cases, such as ring-opening polymerization (ROP) of small to medium-size rings, $\Delta H_{\mathrm{p}}^{\circ} < 0$ (due to release of ring strain) and $\Delta S_{\mathrm{p}}^{\circ} < 0$ (due to loss of translational freedom by covalently linking monomer molecules together), there is a T_{c} phenomenon: when the polymerization temperature is increased to reach at or above T_c, at which $[M]_{eq} = [M]_0$, no polymerization can occur. Based on the thermodynamic parameters obtained from the Van't Hoff plot described earlier, T_c can be calculated by equation $T_c = \Delta H_p^\circ/\{\Delta S_p^\circ + R\ln[M]_0\}$. Above the T_c, the entropic penalty will override the favorable (negative) enthalpy of polymerization, resulting in depolymerization ($\Delta G_p > 0$). Polymers with a high T_c value, such as polyethylene ($T_c \sim 610°C$), are not chemically recyclable because, before the temperature reaches to the T_c, the organic matter will decompose into species or side products other than monomer, not even considering high-energy costs of such depolymerization. Hence, a better option to deconstruct such high T_c polymers is to transform them into other or value-added products (upcycling), rather than to chemically recycle them into monomer. Overall, to successfully meet the requirements of iCPs, a delicate balance between the de/polymerization processes must be achieved. A suitable T_c is necessary for iCPs to satisfy the goal of depolymerization under desired mild conditions wherein the energy requirement for depolymerization is minimized and the selectivity for monomer recovery is maximized. On the other hand, a sufficiently high T_c is necessary to render good polymerizability. From these thermodynamic considerations, for a given monomer-polymer system, the modulation of the polymerization temperature and initial monomer concentration can be exploited to perturb the monomer-polymer equilibrium forward or backward on demand.

The fulfillment of thermodynamic requirements is a necessary—but not sufficient—prerequisite for a de/polymerization reaction to occur. More specifically, polymerizability also has to do with the kinetics of propagation formalism, which is related to the molar Gibbs free energy of activation ($\Delta G_p^\ddagger$, Figure 1), a measure of the energy barrier in the elementary act of propagation. This energy barrier is also dependent on the catalyst used.[10] The use of a highly effective catalyst could significantly lower the energy barrier and, thus, accelerate the polymerization rate, such that the equilibrium is reached within an operable time.

Here, we use an example of our recent work to demonstrate the unification of thermodynamic and kinetic considerations to design an iCP.[31] The ROP of γ-butyrolactone (γ-BL) has unfavorable thermodynamics, which originate from the negligible ring strain of the five-membered lactone ring that brings about too small a negative change of enthalpy ($\Delta H_p^\circ = -5.4$ kJ mol^{-1}) to combat the large negative entropic penalty ($\Delta S_p^\circ = -39.6$ J mol^{-1} K^{-1}) of merging the independent translational motions of individual monomers into a collective trajectory of the interconnected polymer chain. According to the thermodynamic equation, $\Delta G_p = \Delta H_p^\circ - T\{\Delta S_p^\circ + \mathrm{R}\ln[M]\}$, two synergistic strategies were adopted to render an efficient method for ROP of γ-BL. The first strategy is to reduce the entropic penalty of the ROP by performing the polymerization at a low-enough temperature (that is, below the T_c of polymerization, for a given monomer concentration $[M]_0$), whereas the second is to modulate reaction conditions (concentration, solvent, and temperature) such that $[M]_t$ becomes greater than the equilibrium $[M]_{eq}$ and the formed polymer crystallizes or precipitates out of solution system during the polymerization to continuously drive the propagation equilibrium forward. Therefore, through the analysis advocated here, γ-BL, commonly referred to as a "non-polymerizable" monomer, was polymerized successfully at high monomer concentration (10 M) and low polymerization temperature (−40°C), achieving high γ-BL conversions (up to 90%) and affording poly(γ-BL) (PGBL) materials with medium molecular weights (M_n up to 30 kg/mol). With a more effective catalyst and further optimization of reaction conditions, PGBL with M_n = 83 kg/mol has also been achieved.[32]

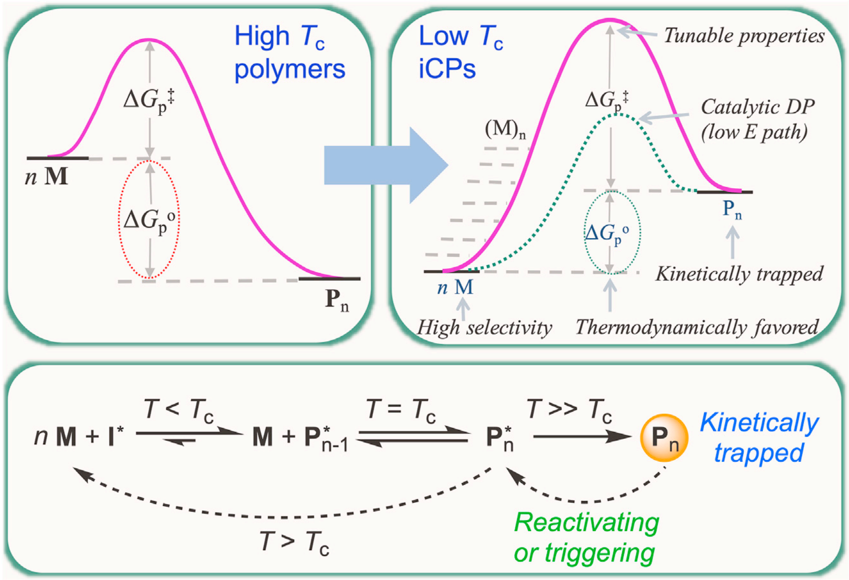

Figure 1. Design of iCPs by reverting thermodynamically trapped polymers to kinetically trapped ones

Such iCPs can be completely and selectively deconstructed back to monomer once the kinetic barrier, which provides kinetic stability and property tuning of iCPs, is overcome by thermolysis (high-energy pathway) or catalysis (low-energy pathway). When $T < T_c$, the forward polymerization takes place, and when $T > T_c$, the backward depolymerization takes place. However, once the polymer chain is deactivated (P_n, devoid of an active site, denoted as *), it is effectively removed from the equilibrium and is thus kinetically trapped, providing kinetic stability even at $T >> T_c$.

At first glance, it is natural to question whether such a low T_c iCP could be stable and retain its structural integrity during daily use or processing where temperatures may be significantly above its T_c. To this end, it is important to note here that, once the active polymerization is quenched and catalyst deactivated or removed, the resulting dead, metastable polymer chain (P_n) is "kinetically trapped" and is no longer in the monomer-polymer equilibrium, thereby providing "kinetic stability" for performance even at T values far above T_c ($T >> T_c$). Reactivation of the trapped state back to the equilibrium state (P_n*) for selective depolymerization to monomer when $T > T_c$ may require a high-energy input to overcome the kinetic barrier ($\Delta G_p^\ddagger$), but catalysts can promote low-energy pathways (Figure 1), thereby minimizing energy input while maximizing selectivity for depolymerization. This thermodynamic and kinetic interplay can be illustrated by PGBL. Specifically, the T_c of PGBL was calculated to be −136°C at 1.0 M or −9°C in the bulk, whereas the T_d (onset degradation temperature, defined by the temperature at 5% weight loss in the thermogravimetric analysis (TGA) curve) of linear PGBL is 201°C, which is 210°C higher than its T_c.[31] Additional strategies, such as topological manipulation and chain-end capping, have been developed to further raise the T_d and enhance the thermal stability of PGBL through the effect of kinetic trapping. For example, the T_d of cyclic PGBL was shown to be 273°C and, after being capped with a silyl ether, a T_d as high as 334°C was measured.[32] Importantly, the kinetically trapped PGBL is depolymerizable by applying sufficient heat (220°C for linear PGBL and 300°C for cyclic PGBL), whereas in the presence of a catalyst, the polymer can be reverted back to monomer at 25°C in minutes.

It is important to point out that kinetically trapped iCPs can exhibit tunable performance properties by modulating the intrinsic or catalytic kinetic barrier (Figure 1), whereas the relative thermodynamic stability of monomer versus polymer states (as defined by T_c values) can be controlled by monomer (thus polymer) structure. Therefore, both monomer and catalyst designs are essential components for successful development of iCPs with not only full chemical recyclability but also practically useful and tunable properties. It is worth noting here that kinetically trapped iCPs do not require end capping to render sufficient stability, unlike self-immolative polymers (SIPs).[33,34] SIPs are polymers that can depolymerize head-to-tail upon cleavage of their end caps that are pre-installed to protect or stabilize the chain and serve as a depolymerization trigger.[35,36] This chain-end capping for stability requires stoichiometric (per polymer chain), costly chain-end-capping reagents, a living polymerization process to end cap "every" chain, and reactive reagents (or other stimuli) to cleave the end caps to trigger depolymerization, thus adding more cost and contamination of the reformed monomer. In this context, iCPs can be considered as kinetically stabilized, whereas SIPs are thermodynamically stabilized, thus requiring cleavage of a chemical bond to trigger the depolymerization. Here, it is also noted that some low T_c polymers will spontaneously depolymerize back to monomer at T not far above T_c, even after removing the catalyst, such as polyaldehydes,[37] due to the low energy barrier (low kinetic stability) of depolymerization. However, these low-energy-barrier iCPs can still be further stabilized by controlling for cyclic topology or exploiting aforementioned end-capping strategies—both of which effectively increase the kinetic barrier for depolymerization.

STRATEGIES TO OVERCOME TRADE-OFFS AND UNIFY CONFLICTING PROPERTIES

Undoubtedly, to replace today's commercial polymers, iCPs need to match or even exceed the performance properties of the present unsustainable competitors, which usually exhibit excellent stability and processability, as well as application-specific thermal and mechanical properties. The design principles of iCPs require trade-offs between a monomer's polymerizability and polymer's depolymerizability, as well as between the polymer's recyclability and performance, until a practically useful balance is struck. These stringent thermodynamic, kinetic, and real-world performance requirements present a formidable challenge for developing practically useful iCPs.

Among the strategies developed to overcome trade-offs and unify conflicting properties, monomer design has been gradually accepted as the cornerstone of discovering new iCPs. In addition, a new monomer has new standard thermodynamic parameters, which can be modeled or predicted (*vide infra*). These parameters can guide monomer design, and this design can then be further coupled with tuning the reaction conditions (temperature, concentration, pressure, state, etc.) to rationally regulate the de/polymerization dynamics. For (hetero)cyclic monomers, the de/polymerization behavior and performance properties are inherently linked with monomer's ring size and substituent effects.[30] Thus, considerable focus, with much preliminary success, has been placed on ROP of low strain lactones[19,38–42] and low T_c polyolefins.[43–46]

Taking γ-BL as an instance, the synthesis of PGBL requires energy intensive, industrially undesirable low-temperature conditions (−40°C), and PGBL exhibits limited thermostability and crystallinity, with a low melting transition temperature (T_m) of ~60°C. These properties initially rendered PGBL insufficient for common applications, despite having complete recyclability. The limited stability and mechanical performance properties of PGBL have been recently addressed by *trans*-fusing a

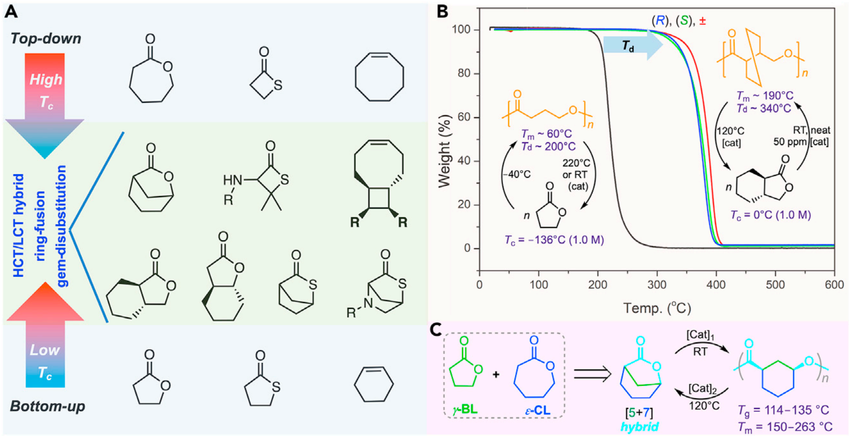

Figure 2. Examples of monomers designed for iCPs by different strategies

(A) Examples of constructing iCP monomers via bottom-up, top-down, and hybrid monomer design strategies.

(B) Demonstration of *trans*-ring-fusing effects on monomer T_c and polymer thermal properties (T_m, T_g, and T_d shown by the TGA curve) while maintaining full chemical recyclability.

(C) Demonstration of HCT/LCT monomer hybridization leading to a new hybrid monomer that can overcome trade-offs and, thus, unify conflicting HCT/LCT polymer properties.

cyclohexyl ring to the γ-BL core, affording a fused bicyclic lactone monomer ($\Delta H_p° = -20$ kJ mol^{-1}, $\Delta S_p° = -72$ J mol^{-1} K^{-1}, $T_c = 0°C$ at 1.0 M or 88°C in bulk),[47] which led to much-enhanced monomer polymerizability at ambient temperature and high molecular weight polymers ($M_n > 1{,}000$ kg/mol), as well as better polymer thermal stability (T_d ~340°C) and crystallinity (T_m ~190°C), while still maintaining the full chemical recyclability as an iCP (Figure 2). However, the resulting highly crystalline polymer was a brittle material; to increase its ductility as a packaging material, synthesizing a copolymer with a sufficient amount of the flexible PGBL incorporated was required.[48]

Although copolymerization of two or more different monomers can be an effective strategy to mitigate property trade-offs, increasing speciation can complicate the chemical recycling and the copolymer properties are often still confined within those of constituent homopolymers.[49] To this end, a "hybrid monomer design" strategy was introduced to synergistically couple a high ceiling temperature (HCT) sub-structure (ε-caprolactone) for high polymerizability and performance properties with a low ceiling temperature (LCT) sub-structure (γ-BL) for high depolymerizability and recyclability within the same monomer structure ($\Delta H_p° = -21.1$ kJ mol^{-1}, $\Delta S_p° = -55.8$ J mol^{-1} K^{-1}, $T_c = 106°C$ at 1.0 M).[50] The bridged bicyclic framework of the resulting hybrid monomer locks the monomer structure in the *cis*-configuration, resulting in an additional degree of chemical recyclability and depolymerization selectivity (Figure 2). The in-chain cyclohexane renders the resulting polymer a high-performance material with a tensile modulus 10× greater and thermal transitions ~200°C higher than its constituent parent polymers. Thus, hybrid monomer design provides a powerful approach to not only unify conflicting (de)polymerizability and performance properties but also radically alter properties of the resulting iCPs.

Similarly, γ-thiobutyrolactone (γ-TBL), like its lactone analog γ-BL, does not polymerize under many previously explored polymerization conditions due to negligible ring strain.[51,52] Poly(thioester)s (PTEs) are supposed to have better (de) polymerizability due to the intrinsically labile thioester bond, as compared with their polyester analogs. A significant development to that end is that the ROP of chiral *N*-substituted *cis*-4-thia-L-proline thiolactones (ΔH_p° = −15.6 kJ mol^{-1}, ΔS_p° = −55.7 J mol^{-1} K^{-1}, T_c = 112°C at 1.0 M), which leads to polythioesters that are readily functionalizable and show full chemical recyclability.[53] However, the resulting PTEs exhibit relatively low thermal stability with a T_d of ~200°C and no observable T_m, despite their chiral structure. In addition, dilute conditions (1.0 g polymer/ 100 mL solvent) were needed to achieve their full chemical recyclability. To render such promising PTEs with high crystallinity for high-performance properties and better chemical recyclability, a bridged bicyclic thiolactone was designed (ΔH_p° = −14.1 kJ mol^{-1}, ΔS_p° = −40.4 J mol^{-1} K^{-1}, T_c = −20°C at 1.0 M).[54] This monomer, upon efficient polymerization with a suitable catalyst/initiator system, led to stereo-disordered to perfectly stereo-ordered PTEs, all exhibiting high crystallinity and full chemical recyclability. Significantly, such PTEs defy aforementioned trade-offs by possessing an unusual set of desired properties, including intrinsic tacticity-independent crystallinity and chemical recyclability, tunable tacticities from stereorandom to perfect stereoregularity, and combined high-performance properties, such as high thermal stability (T_d >320°C), crystallinity (T_m = 166 to 213°C), high mechanical strength (~41 MPa), modulus (~2.0 GPa), and ductility (~220% elongation at break).

Collectively, the above-mentioned cases are all based on monomer redesign to increase the ring strain of extremely low T_c monomer, namely, a "bottom-up" approach (Figure 2), to strike a balance between the (de)polymerizability and performance properties. An alternative strategy is to decrease the ring strain from high T_c monomers via monomer redesign, a "top-down" approach. One such example of the top-down approach is the demonstration of the reversibility of ROP of a gem-dimethyl-substituted four-membered thiolactone (ΔH_p° = −9.4 kJ mol^{-1}, ΔS_p° = −28.1 J mol^{-1} K^{-1}, T_c = 61°C at 1.0 M).[55] A combination of the Thorpe-Ingold effect and the long bond length of C–S (1.76–1.83 Å, which is about 0.3 Å longer than the C–O bond, 1.36–1.44 Å)[56] considerably lowers the ring strain of otherwise highly strained, four-membered heterocyclic monomers, thereby enabling the recyclability of PTEs based on such four-membered thiolactones. Most recently, reducing the ring strain of cyclooctene by *trans*-fusing cyclobutane at the 5 and 6 positions resulted in a redesigned monomer with ΔH_p° = −7.1 kJ mol^{-1}, ΔS_p° = −15.1 J mol^{-1} K^{-1}, and T_c = 197°C at 1.0 M), successfully rendering de/polymerization reversibility of this system.[57]

The above-mentioned examples highlight the daunting task of designing iCPs that exhibit combined desirable, but often conflicting, properties due to challenges of often seemingly unyielding trade-offs between the monomer-polymer equilibrium and performance properties. The hybrid monomer design, which can also be considered a natural marriage between the bottom-up and top-down approaches (Figure 2), can take advantage of complementary and synergistic effects of sub-monomer structures to strike a balance between the (de)polymerizability and performance properties, as well as unify conflicting properties that are conventionally difficulty to optimize concurrently in a single monomer structure.

PREDICTIVE MODELING OF (DE)POLYMERIZABILITY AND PROPERTIES

The potential design space for iCPs suggests that a computational approach to relate structure, thermodynamics, and kinetics is a valuable complement to experimental design and synthesis. Density functional theory (DFT) is a powerful computational approach based on first principles to simulate structural, thermodynamic, and kinetic properties of materials at the atomic level. In the context of iCPs, DFT offers the potential to evaluate ΔH_p, ΔS_p, ΔG_p and associated T_c values for novel monomers, which have little to no experimental data available, thereby helping to guide experimental efforts to explore the chemical recyclability of novel polymers. For de/polymerization of a given polymer, DFT, in conjunction with transition-state theory, can be used to estimate kinetic properties, i.e., activation energy (E_a) and pre-exponential frequency factor (A), using statistical mechanics. An important consideration in applying DFT to calculate T_c values is that the thermodynamic properties depend on the exchange and correlational functionals and basis sets selected; therefore, T_c predictions vary as well. In addition, the application of DFT is most commonly applied in the gas phase, but polymerization is more typically carried out in condensed phases, such as in solutions (commonly in academic labs); thus, consideration of solvation effects through an approximation of the solvent using continuum methods, such as an implicit solvation method, is often warranted. Most critically, calibration of predicted T_c values given a particular DFT method/basis set combination against known experimental values is necessary.

Limited work to date has used DFT to calculate properties of polymers that inform T_c values. Recently, Gilsdorf et al.[42] estimated ΔH_p, ΔS_p, ΔG_p and T_c values of iCPs from DFT (BP86/SVPD) calculations as a series of lactone-based bioplastics, poly(α-methylene-γ-butyrolactone) (PMBL), poly(α-ethylidene-γ-butyrolactone) (PEBL) and poly(γ-methyl-α-methylene-γ-butyrolactone) (PγMMBL), depolymerized more selectively to monomers with higher yields and purity of about 76% isolated yield when compared with 47% recovery in the case of poly(methyl methacrylate) (PMMA). It is important to remember that T_c values are also a function of the monomer concentration. Thus, the T_c values of PMBL and PγMMBL were 305°C and 354°C for 1 M concentration, whereas they were estimated to be 405°C and 502°C for bulk concentrations of 9.36 and 11.4 M, respectively. The predicted T_c values of PMBL and PγMMBL were significantly higher than that of PMMA (~300°C). In contrast to PMBL and PγMMBL, much lower T_c values of 23°C and 80°C were reported for PEBL at 1 M and bulk concentrations, respectively, which suggests superior chemical recyclability at low temperatures. This is due to the introduction of a methyl group substituent at the exocyclic methylene moiety in the lactone-based acrylic polymer. From these calculations, it is evident that there is a connection between structure and T_c values, while the selectivity and higher yields of monomer from lactone-based polymers compared with PMMA are not a strict function of the T_c value but also depend on the geometrical features and the presence of pendant groups in the lactone that lead to kinetic differences as well.

It is possible to glean informative structure/property relationships for potential iCPs from DFT calculations. The structure of lactones, such as the ring size, degree of substitution, and position of the substituent, have a significant impact on the ΔH_p, ΔS_p and associated T_c values that characterize ROP of lactones.[29,30] Generally, the ring size has a dramatic effect on thermodynamic properties through differences in ring strain during ROP. For instance, ΔH_p for the ROP of β,δ,δ-trimethyl-ε-caprolactone and β,β,δ-trimethyl-ε-caprolactone from DFT (B3LYP/6–31g(d,p)) calculations were found to be −22.4 to −19.3 kJ mol^{-1} and −17.3 to −14.3 kJ mol^{-1}, respectively, for the temperatures ranging between −50°C–150°C.[58] The corresponding ΔS_p values ranged between −126.9 to −117.0 J mol^{-1} K^{-1} and −121.0 to −110.9 J mol^{-1} K^{-1}. The DFT values clearly capture the negative ΔH_p values that correspond to the release of ring strain as a result of the ring opening of lactones, while predicting large negative values of ΔS_p that are attributed to the increased order of the

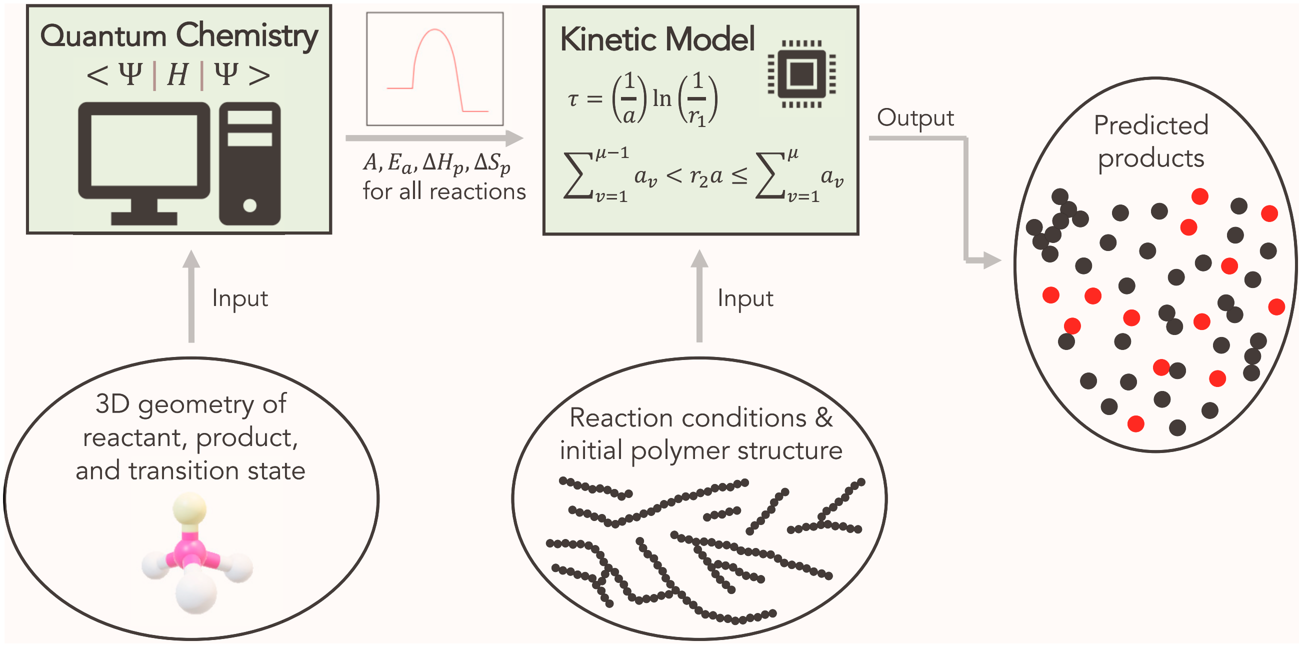

Figure 3. ***In silico*** **prediction of (de)polymerizability**

Given the configurations of reactants, products, and transition states, DFT calculations can determine both the thermodynamics and energy barriers of reactions. These can then be passed to a kinetic model that includes thermodynamically consistent forward and reverse reactions and, given the reaction conditions and an initial polymer structure, can predict the evolution of reaction products.

polymer compared with the monomer when the ring-opened product is formed. Another critical consideration in the application of DFT calculations to predict the properties of polymers is how many monomer units must be simulated to approximate the properties of the polymer. Experiments reveal that the chain length affects the ΔH_p, ΔS_p, ΔG_p, and T_c values, and the goal of the DFT calculations is to obtain the values in the long-chain limit, while still using a mimic of the polymer that is small enough to maintain computational tractability. Thus, calibration of a suitable DFT method must explore not only method/basis set and solvation but also the size of the model system.

Kinetic modeling can complement DFT calculations by offering insight into the rates of reaction and, potentially, the resulting polymer structure and properties that thermodynamics alone does not provide (Figure 3). For optimum recyclability, the rate of the depolymerization reaction must take place on a reasonable timescale and be faster than the rate of any unwanted side reactions due to thermal degradation. However, note that the polymer structure itself can affect the kinetics of both depolymerization and degradation pathways through both intrinsic structural effects, e.g., sequence or physical proximity of reactive moieties, and physical phenomena that result from the structure, e.g., precipitation, bubble formation, crystallinity, or diffusion limitations.[59] Tracking detail of the polymer sequence and structure enables coupling of the description of the depolymerization reaction pathways and kinetics to a model of the physical effects[56] or an adjustment of rate coefficients based on phenomenological correlations to approximate these effects.

Many methods exist for kinetic modeling of depolymerization, including machine learned models, the method of moments, continuum models tracking particular moieties,[60] and kinetic Monte Carlo (kMC).[61] Of these, *k*MC is particularly notable because its stochastic event-by-event formulation enables explicit tracking of the detailed polymer structure.[62,63] By using the *k*MC algorithm or another method that tracks polymer detail, the precise effect of the competing degradation and depolymerization pathways on polymer structure can readily be quantified, and, if desired, coupled to models of physical phenomena.

Moreover, T_c is only defined for polymers following a chain-growth mechanism and must be reported at a reference monomer concentration.[64] For polymers following a step-growth mechanism, equilibrium at a particular temperature depends instead on the relative concentrations of reacted and unreacted functional groups, as well as any by-products that may be formed. For a simple equilibrium of linear polymers consisting of one polymerization reaction in the absence of side reactions, a most probable distribution of chain lengths is obtained. However, for more complicated equilibrium states, such as those involving branched species or polymers consisting of multiple monomer types each with different thermodynamics of reaction, the equilibrium chain length distribution may be more complicated. Since the *k*MC approach enables explicit tracking of polymer structure, there is great potential for future work developing *k*MC models to explore the depolymerization of step-growth polymers as well.

SUPPLY-CHAIN LIFE-CYCLE ASSESSMENT AND TECHNO PRESS-ECONOMIC CONSIDERATIONS

Beyond the fundamental challenges in designing new iCPs, manufacturing and material life-cycle factors must also be thoughtfully considered for realistic implementation of iCPs in the marketplace. This task can be accomplished iteratively and synergistically within the materials development research and development cycle via the judicious application of TEA and LCA. Application of these widely available tools is critical to focus resources on developing iCPs that can realistically and beneficially address the dual problem of today's plastics arising at either end of product life cycles: (1) manufacturing-associated energy use and greenhouse gas (GHG) emissions and (2) the pollution resulting from mismanagement of plastics waste. To that end, this section outlines an analysis framework for the iCP design problem from the perspective of TEA and LCA, relative to the linear supply-chain model in use today for plastics manufacturing, consumption, and disposal. We first discuss synthesis of the virgin monomer and polymer, then the analysis for the closed-loop recycling approach enabled by iCPs and discuss how to compare this with existing, linear polymer life cycles.

As noted above, a central theme to enable iCPs is the design of new monomers that lead to polymers with use-phase properties that match or exceed the required characteristics of today's plastics. Synthesis of both new monomers and the first-life synthesis of iCPs typically implies development of new manufacturing processes, which could source either fossil or bio-based feedstocks. Regardless of the feedstock(s) employed, process modeling tools central to TEA allow researchers to first calculate mass and energy balances for new processes at the chemical process system scale, including compilation of critical inventories encompassing mass flows for raw material inputs, associated product and waste generation outputs, and the need for makeup inputs, such as for recycled or regenerated materials that experience deleterious losses over time (e.g., solvents, catalysts, working fluids, etc.), as well as energy flows required to operate the process, including electricity, process heat, and other energy inputs. From this inventory of mass and energy balances, associated approaches exist for subsequently estimating the baseline capital and operating costs of the process, including across facility scales, often through power law relationships that have been mostly informed from the petrochemical industry. With this approach, researchers can estimate the cost of monomer and iCP synthesis and quantify a material and energy inventory, even of a prophetic process in parallel with experimental research and development. Multiple process simulation tools exist to conduct these types of analyses,[65–67] with many rigorous examples published in this field, especially in the case of bio-based chemical manufacturing approaches.[12,68–70]

With process models and associated materials and energy inventories in hand, immediate application of LCA tools for both monomer and virgin iCP manufacturing is enabled.[71,72] Similar to TEA, there are existing LCA software packages, tools, and databases available to supplement iCP process models for a consistent system boundary.[73–75] The system boundary may be cradle-to-gate (raw material extraction to final product manufacture), cradle-to-grave (raw material extraction through product disposal), or even cradle-to-cradle (when including recycling processes), depending on the focus of the study and data availability on impacts from specific life-cycle phases. The materials and energy inventories compiled in the development of process model (such as in TEA) typically form the primary inputs for LCA, which, in turn, allows for calculation of multiple life-cycle metrics, including energy consumption, GHG emissions, water usage, and many other environmental metrics that may be of interest for a given process.[76] LCA approaches can reveal, similar to TEA, especially intensive elements ("hot spots") of the broader monomer and virgin iCP synthesis system that merit further research and development for process viability from the perspective of environmental impacts.

Oftentimes, especially early in the development cycle of a new monomer and related iCP, it is a useful exercise to assume theoretical yields of the process steps to obtain a "best-case scenario" estimate of both the TEA and LCA outputs for a given product and process. Doing this early in the iCP product development cycle can allow one to compare costs and environmental impacts with those of a conventional baseline synthesis route or monomers and polymers that an iCP is intended to replace (*vide infra*). These types of process design exercises also enable one to readily isolate cost, energy consumption, waste generation, and other metrics for specific unit operations or process areas, and to conduct either single-point sensitivity analyses or multi-dimensional sensitivity analyses (e.g., using Monte Carlo analysis) to understand the effect of changing process variables. Not only can this iterative analytical approach inform process development and improvements, but it is also key input for researchers to identify key gaps and challenges for experimental research and development to enable the realistic and eventual implementation of iCPs.

Taken together, the process modeling steps described earlier will enable estimates of the economics and environmental impacts of *de novo* monomer and iCP manufacturing. At this point, the analyst must decide whether to calculate impacts for a specific iCP substitute product (relative to a specific conventional product) or for the entire iCP manufacturing system (multiple product lifetimes). The latter of these options may be chosen to avoid the allocation problem, in a framework known as system expansion.[77] System expansion is an approach employing cradle-to-grave life-cycle thinking, which compares the impacts associated with an entire system of multi-functional products (in this case, the initial and subsequent closed-loop recycled iCP product lifetimes, including their eventual disposal, if applicable) with the impacts associated with manufacturing and disposal of an equivalent quantity of linear plastics product lifetimes. It requires data on impacts associated with the collection and recycling of an iCP in addition to the end-of-life collection and disposal (the latter of which can take many forms, such as landfilling, combustion for energy recovery, or even other recycling technologies) of the analogous conventional polymer. If the use and collection phases are equivalent to an existing, linear plastic, these components of the life cycle will likely be similar from a cost, energy, GHG emissions, and potentially from a broader environmental impacts perspective. For simplicity and ease of comparison in highlighting the differences between the systems, identical components of the reference and iCP systems can be omitted from a system expansion analysis (i.e., "pruned" from the system boundary of each). This pruning has the added benefit of reducing data requirements necessary for the system expansion approach, which can become extensive.

Central to the iCP concept is the idea that iCPs are ultimately intended to undergo true closed-loop recycling through a depolymerization/repolymerization loop at the end of each functional life to keep the materials in the economy. For process modeling and TEA, again, process simulation tools, similar those described earlier, must also be applied to evaluate the economics, energy consumption, GHG emissions, and other metrics for a given iCP recycling approach relative to incumbent technologies. Although not directly applied to iCPs, Singh et al. recently presented the detailed analysis framework regarding how to treat closed-loop recycling of poly(ethylene terephthalate).[78] This framework is generalizable to iCPs or any indeed, other material that is intended to be closed-loop recycling, as previously outlined by Nicholson et al.[79] We strongly urge the adoption of this approach to fully capture both the process economics from a TEA perspective and the environmental impacts via LCA related to iCPs over multiple product life cycles.[75,76]

The outputs from both TEA and LCA are critical to evaluate a given iCP synthesis and recycling approach and to identify key gaps that merit further research and development to overcome. As importantly, the outputs from TEA and LCA can and absolutely should be used to compare with the economics, energy use, GHG emissions, and other environmental impacts of today's plastics that are overwhelmingly fossil-based, linear, and not readily recyclable or biodegradable, as mentioned earlier. Several studies have been reported that benchmark the manufacturing and consumption of current plastics for these key variables, which can be used as resources to this end.[3] Industrially informed data such as these are crucial for direct comparisons of key circularity drivers.

SUMMARY AND OUTLOOK

The development of iCPs, inspired by the circular materials economy approach toward sustainability, offers a feasible solution to address the plastics pollution crisis while also preserving finite natural resources. Highlighted success achieved so far has led to formulations of a set of the guiding principles discussed herein for designing iCPs from four elements of consideration, which are intended to aid future sustainable development of iCPs. Many challenges, thus future opportunities, still remain, including:

(1) "Energy inputs" for both polymer de/reconstruction processes—how to minimize energy inputs while maximizing atom and energy efficiency in both processes?
(2) "Selectivity" in de/polymerization—how to maximize selectivity, thus minimizing separation/purification needs and materials loss?

(3) "Depolymerizability/performance trade-offs"—how to overcome traditional trade-offs by rendering iCPs with not only full chemical recyclability but also properties rivaling or exceeding today's most useful polymers?

From an iCP monomer's perspective, the scope of the monomers designed for iCPs is largely limited as most readily available, abundant monomers are unsuitable due to the lack of a sufficient enthalpic driving force for polymerization or a range of difficulties regarding efficient/selective depolymerization under cost-effective conditions. An Achilles' heel for the new iCP monomers, which are typically demonstrated only at small, laboratory scale, is that they currently lack commercial availability and/or demonstrated cost-competitiveness and scalability required for further industrial consideration. Nonetheless, we stress that monomer design is the cornerstone of discovering new iCPs and the currently most effective strategy, when employed together with engineering of reaction/processing conditions, to regulate the de/polymerization dynamics, while targeting desired thermal and mechanical properties. Moving forward, while we should continue to promote fundamental discovery via innovative design of monomer and polymer structures, such research endeavors should also consider the sourcing of their raw materials (ideally from bio-based renewable feedstocks or recaptured intermediates from deconstruction of today's waste plastics), developing more environmentally benign and efficient processes (e.g., catalytic, solvent-free reactions), and demonstrating scalability (analysis-guided R&D efforts).

For the molecular modeling of iCPs using DFT, a community standard DFT method, i.e., exchange-correlation functional (mostly hybrid method) and basis set combination, based on benchmarking against known thermodynamic parameters for a variety of different polymer types would be highly valuable. Computations in both vacuum and solvent need to be evaluated to better understand the ability of DFT to assess the (de)polymerization of iCPs. Effects of chain length on the thermodynamic quantities should be thoroughly understood since the growing polymer chain produces significant steric hinderance, which could dramatically affect ΔH_p and ΔS_p. Scaling of ΔH_p and ΔS_p for small systems against experimental values for a series of diverse polymers is possible to improve computational efficiency but may not capture important entropic effects. The main advantage of DFT simulations is to predict ΔH_p, ΔS_p, ΔG_p, and T_c, and kinetics for any arbitrary iCP without any prior experimental information but various methods may need to be explored to ensure that even relative trends are recapitulated.

While *k*MC is a versatile method that is highly applicable to exploring (de)polymerizability as a function of conditions and in the face of detrimental side reactions, there is a relative lack of "plug-and-play" *k*MC (de)polymerization codes, which perhaps is due to the diversity of reaction mechanisms, polymer structures, and accompanying physical phenomena. These physical changes are particularly challenging to model from first-principle approaches, but the possibility of scale-bridging approaches allows one to envision a simulation approach in which kinetic and physical models can be coupled using a variety of methods, including molecular dynamics simulations, machine-learning approaches, and computational fluid dynamics.

Many critical gaps and opportunities exist from an analysis perspective as it relates to iCPs, plastics circularity broadly, and generally the concept of the circular economy. First, it is well accepted that improvements are needed in identification of metrics for circularity, and this represents a major research frontier at the intersection of economics, engineering, industrial ecology, and social science that will very likely require a transdisciplinary approach to develop for the global economy.[80–83] Additionally, the importance of both carbon intensity for resource extraction, manufacturing, and materials use and end-of-life management, as well as carbon emissions as GHG emissions to the atmosphere and solid plastics into the environment, are both now well recognized as a dual problem of broad human concern. Indeed, these considerations are clearly becoming a critical factor for businesses, consumers, policymakers, and governments to take action toward. To that end, there is a clear opportunity for the community to develop more holistic analysis tools that will enable quantitative approaches to internalize these externalities, such that quantitative decision-making and policy development can proceed in a way that is beneficial for all. Ultimately, judicious application of these tools in a rigorous, transparent, and self-consistent manner, especially when comparing with the amortized plastics manufacturing industry, will be critical to push the materials economy toward a more circular—and quantitatively informed by analysis—a more cost effective, energy efficient, and environmentally benign approach to humankind's design and use of plastics.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Requests for further information should be directed to and will be fulfilled by the lead contact, Eugene Y.-X. Chen (eugene.chen@colostate.edu).

Materials availability

This study did not generate new unique materials.

Data and code availability

All data needed to evaluate the conclusions in the paper are present in the paper.

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AUTHOR CONTRIBUTIONS

E.Y.-X.C. conceived the idea and outlined the draft. C.S. wrote an initial draft, which was substantially revised and supplemented with contributions from all authors who co-wrote subsequent versions.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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