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Sustainable and degradable plastics

Sophie M. Guillaume

Plastics developed from renewable resources and able to be recycled are highly environmentally desirable alternatives to current petroleum-based non-degradable polymers. Now, an effective and robust industrially relevant strategy towards high performance biomass-derived degradable poly(γ -thiobutyrolactone)s has been developed.

While plastics are omnipresent in our daily life, one current major objective in polymer science is to tackle the production of plastic waste — through both the synthesis of high performance polymers derived from renewable non-edible resources or wastes rather than from fossil feedstocks, and the design of polymers with improved end-of-life options enabling a more circular economy.^{1,2} New generations of eco-friendly polymer materials thus ideally have to be sustainable and recyclable while remaining economically viable. In this regard, polymers that are degradable back into their original monomer, or into other smaller valuable molecules that can be subsequently used to synthesize new materials, are highly desirable.

Sulfur-containing functional polymer materials have recently attracted increasing interest thanks to their valuable properties. Typically, polythioesters — in comparison to their oxoester analogues, polyesters — exhibit significantly enhanced thermal and mechanical properties as well as biological and chemical resistance, degradability and/or recyclability, thereby offering multi-faceted applications.^{3,4} While the thiocarbonyl moiety has been extensively exploited in radical ring-opening polymerization (ROP) to insert a sulfur-based functional group along the polymer backbone, it is only recently that cyclic monomers containing thionoester functionality ((C=S)–O) — that is, thionolactones — have been explored for their ability to afford degradable (thanks to thioester functions) polymers by radical ROP.^{5,6,7,8}

Miao Hong and colleagues have now synthesized, for the first time, sustainable and degradable poly(γ -thiobutyrolactone)s by the irreversible ring-opening polymerization (IROP) of challenging five-membered thionolactone monomers. This innovation relies on an effective and robust sulfur/oxygen (S/O) isomerization-driven IROP strategy that converts these non-strained cyclic γ -thionobutyrolactones — often referred to as “non-polymerizable” — into high-molar-mass and degradable polythiolactones — containing thioester functionality ((C=O)–S) —, at industrially relevant temperatures of 80–100 °C (Figure 1).

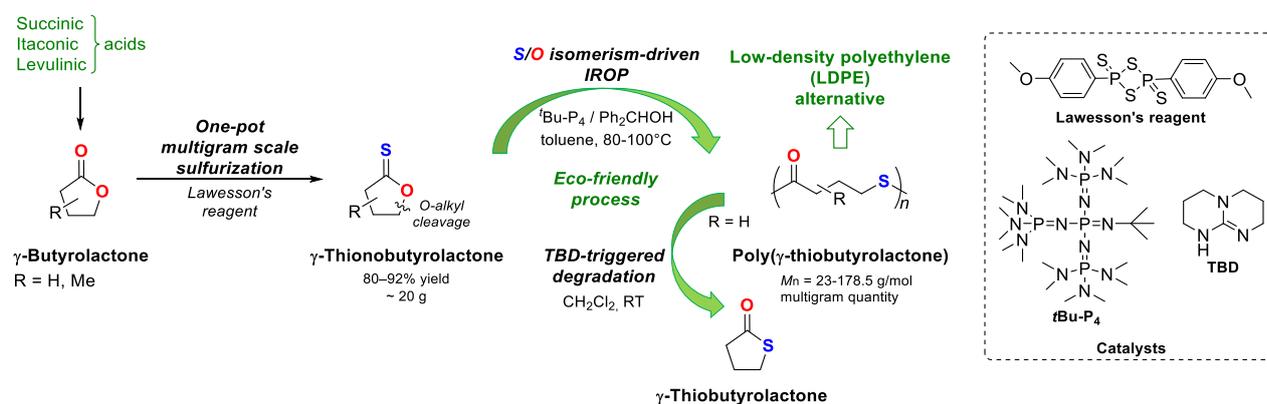


Figure 1. Synthesis and subsequent S/O isomerization-driven irreversible ring-opening polymerization (IROP) of γ -thionobutyrolactones (R = H, Me) and degradation of poly(γ -thiobutyrolactone) (R = H). γ -Thionobutyrolactones can be prepared by sulfurization of the corresponding biomass-derived γ -butyrolactones. Poly(γ -thiobutyrolactone) — a potential substitute for commercial petroleum-based low-density polyethylene — can be degraded to γ -thiobutyrolactone in the presence of TBD.

The primary feature of γ -butyrolactones is that their ROP is generally thermodynamically forbidden at ambient conditions due to insufficient ring-strain in the five-membered cycle of the monomer to drive the polymerization. One approach to overcome this limitation is to perform the ROP at a temperature lower than the ceiling temperature — that is, below the temperature at which the equilibrium between polymerization and depolymerization is reached. However, the usually negative ceiling temperature of unstrained five-membered lactones would require performing the ROP below ambient temperature that is not ideally compatible with industrial implementation.

Starting from succinic, itaconic and levulinic acids that are among the US Department Of Energy top 10 value-added biomass-derived compounds, Hong and co-workers prepared a series of sustainable five-membered (α -, β -, or γ -methyl-substituted) γ -thionobutyrolactones in high yields (80–92%) on multi-gram scales (ca. 20 g) via the one-step sulfurization of the corresponding five-membered butyrolactones using Lawesson's reagent. The subsequent controlled ROP of the γ -thionobutyrolactones — catalyzed by the commercially available phosphazene strong organic base $^t\text{Bu-P}_4$ in the presence of an alcohol initiator (Ph_2CHOH) — typically proceeds in toluene at 80 °C within a few hours (15 min at 100 °C) affording poly(thiobutyrolactone)s with a high selectivity (up to 97%). This is in sharp contrast to the commonly observed non-polymerizability of such non-strained five-membered rings at ambient conditions, and to the organocatalytic ROP of larger thionolactones which affords polythionolactones without S/O scrambling.⁹ Remarkably, the recovered polythioesters display absolute number-average molar mass ($M_{n,\text{SEC}}$) up to 178.5 kg/mol with relatively narrow dispersity ($\mathcal{D} = M_w/M_n < 1.6$), while previously reported values, following another approach, did not exceed 6.3 kg/mol (50% yield).

Further mechanistic insights were gained from computational density functional theory (DFT) studies. In addition to confirming the exclusive cleavage of the oxygen–alkyl bond of the γ -thionobutyrolactone rather than of the more commonly opened oxygen–acyl bond, in silico evaluation of the energy profile of the ROP evidenced the formation of the thermodynamically advantageous S/O isomerization product, which provides an overall thermodynamic driving force for the polymerization of non-strained γ -thionobutyrolactones at room temperature or above. Furthermore, DFT calculations clearly indicated that the polymerization is selectively initiated via a kinetically favorable proton-transfer pathway facilitated by Ph_2CHOH mediated deprotonation, while Ph_2CHOH also effectively suppresses back-biting side reactions during propagation by acting as a H-bonding donor to stabilize the $-\text{COS}^-$ propagation species together with $[^t\text{Bu-P}_4\text{H}]^+$, thereby accounting for the controlled polymerization.

The typical polythiolactone obtained from γ -thionobutyrolactone ($M_{n,\text{SEC}} = 162.6$ kg/mol) revealed a semicrystalline thermoplastic (glass-transition and crystallisation temperatures of $T_g \sim -49$ °C and $T_c \sim +74$ °C, respectively) with a high melting ($T_m \sim 100$ °C) and degradation ($T_d^{5\%} \sim 230$ °C) temperature, and a hard, rigid and hydrophilic material (Young's modulus $E = 296.5$ MPa, yield strength $\sigma_y = 15.7$ MPa, tensile strength $\sigma_b = 29.8$ MPa, elongation at break $\epsilon_B = 412.5\%$, and static contact angle $\theta = 78.4^\circ$). Rewardingly, the polyester thus showcases high performances with key thermal and mechanical properties that are advantageously competitive to commercial petroleum-based low-density hydrophobic polyethylene (so called LDPE; $T_m \sim 105$ °C, $E \sim 280$ MPa, $\sigma_y \sim 8$ MPa, $\sigma_b \sim 10$ MPa, $\epsilon_B \sim 200\%$, $\theta \sim 102^\circ$) that is commonly used for flexible bottles, as packaging or as an insulator. Interestingly, the commercially available 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) organocatalyst (0.2 mol%) efficiently prompts the ultrafast degradation (within 15 s) of this poly(γ -thiobutyrolactone) sample at room temperature, quantitatively converting it into the parent γ -thiobutyrolactone.

Hong and coworkers have thus enriched the polythioesters domain by demonstrating the irreversible ROP of γ -thionobutyrolactones as being thermodynamically driven by the S/O isomerization instead of ring strain relief. Catalysis played a seminal role in this achievement. The judicious choice of the highly active $^t\text{Bu-P}_4/\text{Ph}_2\text{CHOH}$ catalytic system in which the alcohol favorably plays an essential dual role, combined with a beneficial high operating temperature of 80 °C, enabled

the first successful straightforward rapid and selective ROP of these five-membered cyclic thioester-based monomers. The external organocatalyst-triggered ultra-rapid degradation of the poly(γ -thiobutyrolactone) into its corresponding cyclic thioester further bestows a valuable end-of-life to such polymers. Starting from monomers derived from renewable resources, the implementation of this remarkably simple and effective out-of-the-box polymerization strategy towards the preparation of robust yet easily degradable polythioesters, holds great promise for the expansion, within a circular economy model, of the next generation of eco-friendly polymer materials with a wide range of notable properties and potential applications.

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