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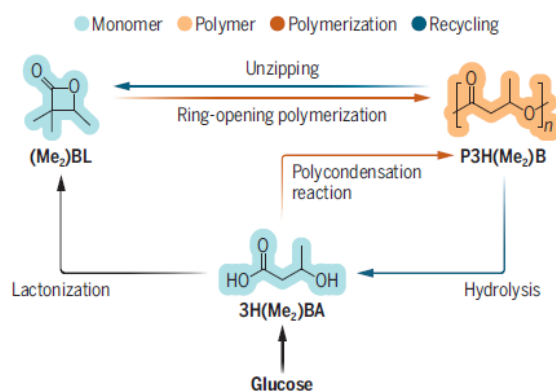
Enhancing thermal stability of polyhydroxyalkanoates for their closed-loop chemistry

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Chemistry that allows plastic recycling

Two synthetic pathways can produce a stable α,α -disubstituted polyhydroxyalkanoate P3H(Me₂)B polymer. One route involves a polycondensation reaction from the dimethylbutyric acid [3H(Me₂)BA] monomer. The other route uses ring-opening polymerization of the α,α -dimethyl- β -butyrolactone [(Me₂)BL] monomer. This monomer itself is derived from the lactonization of 3H(Me₂)BA. The resulting polymer can undergo base-catalyzed hydrolysis or depolymerization, regenerating the monomers and closing the life-cycle loop.



Polyhydroxyalkanoates (PHAs), a class of polyesters discovered nearly a century ago (1), have recently gained renewed industrial and academic interest because of their renewability, biocompatibility, degradability, and recyclability (2). Diverse PHAs are biosynthesized in nature from microorganisms. They also can be synthesized through chemical reactions, creating forms with greater variability with respect to polymer chain length, microstructure, post polymerization reactivity, and functional properties (3, 4). However, PHAs suffer from mechanical brittleness, thermal instability, and lack of the desired closed loop chemical recyclability, which limit their widespread applications. On page 64 of this issue, Zhou *et al.* (5) describe a synthetic strategy based on designing PHAs with enhanced mechanical toughness and thermal stability. Moreover, the process is circular, enabling PHAs to be recycled.

An ecological circular plastics economy requires renewable and recyclable plastics as alternatives to fossil fuel-based nondegradable polymers that currently dominate the markets. Eco-designing polymers from biobased feedstocks with improved end-of-life options is nowadays mandatory to secure a sustainable future (6–9). In this context, PHAs are promising alternatives to common plastics such as polystyrene, polypropylene, and poly(ethylene terephthalate), with

applications that range from packaging to biomedical and pharmaceutical devices (2). However, the broad commercial use of these polymers is impeded because they are mechanically brittle, not melt-processable, and not chemically recyclable to monomers (3, 4). In contrast to bacterial routes, synthetic chemical (abiotic) pathways can produce functional reactive PHAs that are endowed with tunable thermomechanical and degradable or biodegradable properties. These pathways include the polycondensation reaction of substituted hydroxyacids, or the ring-opening polymerization of either substituted cyclic four membered ring β -lactones or eight-membered ring diolides (2).

Fine adjustment of PHA characteristics can be specifically achieved with ring-opening polymerization of the functional cyclic esters or diesters, performed in the presence of a stereoselective catalytic system (organic or metal-based). Thus, PHAs with precise chain length, β -pendant substituents, chain end-groups, and stereomicrostructure that can be controlled in a specific manner (tacticity) — features not available with natural PHAs — can be achieved (10–12).

Zhou *et al.* tackled the thermal instability of PHAs by designing a polymer from α,α -dialkylated β -lactones. The straightforward substitution of the two α -hydrogens with alkyl groups prevented a facile *cis*-elimination reaction that is detrimental to thermal steadiness. This simple approach makes use of either a glucose-derived hydroxyacid {3-hydroxy-2,2-dimethylbutyric acid [3H(Me₂)BA]} or an α,α -dimethyl- β -butyrolactone (Me₂BL) monomer. The latter cyclic ester is obtained from the former hydroxyacid through direct lactonization, in which the *gem*-disubstituent favors ring closure and stabilization of the strained ring (13, 14). Subsequent polycondensation of 3H(Me₂)BA or controlled ring-opening polymerization of (Me₂)BL, catalyzed by commercially available reagents under mild conditions (<160°C for ~20 hours), generated the desired α,α -dimethylated PHA—poly(3-hydroxy-2,2-dimethylbutyrate), or P3H(Me₂)B—of short, medium, or long chain length (see the figure). Increasing the synthesis of the monomers [up to 362 g of 3H(Me₂)BA and 232 g of (Me₂)BL] afforded as much as 115 g of pure P3H(Me₂)B (92% yield) through ring-opening polymerization under industry-relevant conditions (55 parts per million loading of a catalyst under solvent-free conditions at 70°C for 28 hours). The demonstrated compatibility of the method with other α -dialkylated monomers or a mixture of such monomers further broadens the scope of possible PHAs.

All P3H(Me₂)B samples synthesized by Zhou *et al.* were semicrystalline regardless of their tacticity (atactic or isotactic). This is a rare example of polymers exhibiting tacticity-independent crystallinity and provides a highly valuable strategy for preparing high-performance PHAs without requiring the more delicate stereocontrolled ring-opening polymerization that relies on specifically designed stereoselective catalysts. Furthermore, the P3H(Me₂)B samples exhibited thermal robustness with high melting and degradation temperatures (T_m = 167 to 243°C and T_d = 314 to 335°C) at 68°C and 85°C, respectively, higher than those of the most ubiquitous isotactic PHA, (*R*)-polyhydroxybutyrate. Additionally, these P3H(Me₂)B polymers showed high mechanical performances and enhanced melt processability and ductility (elongation at break > 200%). Even more rewarding, P3H(Me₂)B could be chemically recycled back to its starting monomers upon either depolymerization to 3H(Me₂)BA or chain unzipping into (Me₂)BL, establishing the highly sought monomer-polymer-monomer closed-loop chemical recyclability of PHAs.

The pathways described by Zhou *et al.* exemplify how polymers can be improved by revisiting some fundamental chemistry concepts rather than establishing complex chemistry models. Their reversible polymerization routes stand in contrast to past strategies that focused on either varying the steric, electronic, and chemical environment of the β -substituent on the lactone monomer, or on the composition, stereochemistry, and structure of the main-chain backbone, or even on the polymer topology. Furthermore, the method enables the introduction of other chemical groups at the α -position, which opens the possibility of pushing PHAs toward more diversified functional materials. Together with the scalability of the polymerization and depolymerization steps, the findings of Zhao *et al.* constitute a notable step in the PHA domain to advance sustainability and circularity of polymers and could have profound implications for the next generation of industrial plastics.

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