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Atactic, Isotactic, and Syndiotactic Methylated Polyhydroxybutyrates: An Unexpected Series of Isomorphic Polymers

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ABSTRACT: Polyhydroxyalkanoates (PHAs), such as poly[(*R*)-3-hydroxybutyrates] [(*R*)-P3HB], are produced by bacteria and are promising alternatives to nondegradable polyolefin plastics, but their semicrystallinity and high melting points are only maintained at high tacticity, which are commonly seen in other semicrystalline polymers like isotactic polypropylene (*i*PP). We herein report a class of synthetic PHAs, *cis*-poly(3-hydroxy-2-methylbutyrate)s (*cis*-PHMBs), that exhibit tacticity-independent semicrystallinity. The syndiotactic, isotactic, and even atactic PHMBs all share high melting points (T_m > 170 °C) and nearly identical crystal structures. The isomorphism of these polymers across three different tacticities has allowed access to *i*PP-like, high-performance PHMB without the requirement of high tacticity.

Plastics are indispensable in modern society due to their low cost and versatility. Their diverse range of industrial and commercial applications often requires high melting temperatures (T_m) or glass-transition temperatures (T_g), which are critical for their heat resistance and mechanical strength. The world's most widely used plastics, high-density polyethylene (HDPE) and isotactic polypropylene (*i*PP), are examples of semicrystalline polyolefins with high T_m values (HDPE: ∼130 °C; *i*PP: ∼165 °C) due to their high degrees of crystallinity. Their high T_m and semicrystallinity are attributed to their symmetric structures, which favor the compact packing of their chains into highly ordered crystalline phases. For polymers with stereocenters, their crystallinity is further impacted by both the degree and types of tacticity (isotactic or syndiotactic). For instance, although syndiotactic polypropylene is also semicrystalline, it exhibits different physical properties (melting points, solubility, and mechanical strength) than *i*PP due to its different crystal structure (Figure 1a).[1] In contrast, atactic polypropylene is amorphous due to its lack of stereoregularity; similar behaviors have been seen in other atactic polymers.

The chemical inertness of polyolefins is advantageous during use but is a major challenge for plastic waste management and has worsened the plastic pollution crisis.[2] The bacteria-produced polyhydroxyalkanoates (PHAs) are biodegradable polymers that have gained increased attention as sustainable alternatives to polyolefin plastics. Isotactic poly[(*R*)-3-hydroxybutyrate] [(*R*)-P3HB] is the most well-known PHA and exhibits a comparably high melting temperature (∼175 °C) to *i*PP. As is the case for polypropylene, isotactic and syndiotactic P3HBs are semicrystalline with different crystal structures,[3] and atactic P3HB is amorphous. However, its broader use in the market is limited due to its relatively low production volume, thermal instability,[4,5] and brittleness of the isotactic homopolymer. In the chemical synthesis[6] of P3HBs, copolymerization[7−12] and control of tacticity[6a,k,n,13] have yielded tunable materials with improved toughness. However, moderate to high levels of tacticity are always required to maintain semicrystallinity.[7−13]

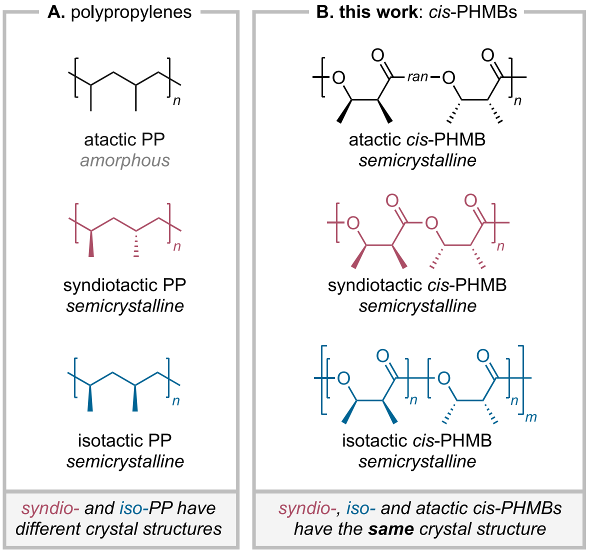

Figure 1. Differences in structure−property relationships between (a) polypropylenes and (b) *cis*-poly(3-hydroxy-2-methylbutyrates) (*cis*-PHMBs).

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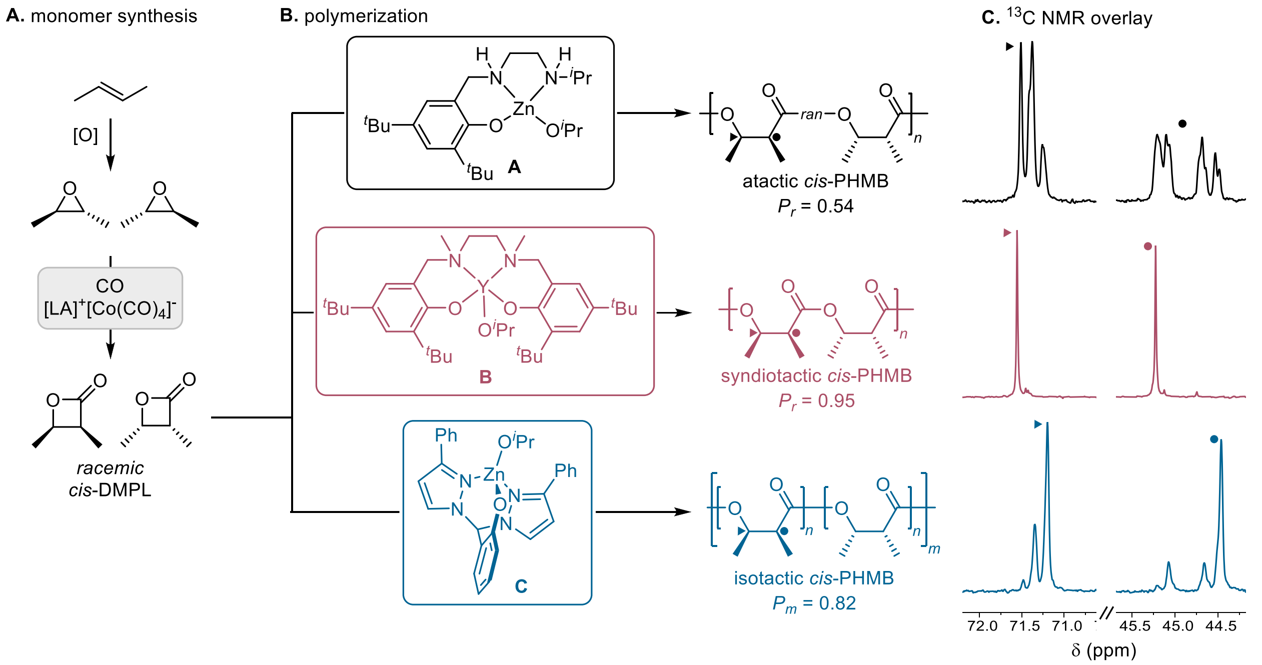

Figure 2. (a) Synthesis of *cis*-DMPL from feedstock chemicals; (b) polymerization of *cis*-DMPL to *cis*-PHMBs with different tacticities; (c) comparison of ^{13}C NMR spectra for the *cis*-PHMBs with different tacticities.

Our group has a long-standing interest in the chemical synthesis of PHAs[6e,14] through carbonylation of epoxides and subsequent lactone ring-opening polymerization (ROP). We recently reported a new class of PHAs, poly(3-hydroxy-2-methylbutyrates) (PHMBs), that can be chemically synthesized from C1 and C4 feedstocks.[15] Using syndioselective polymerization catalysts, we established a versatile platform of PHMB copolymers with high melting points and good mechanical strength. In that work, we observed that even atactic *cis*-PHMB exhibits semicrystallinity. There are only a few reports of atactic yet semicrystalline polymers. Vinyl polymers with small, polar branches[16] are one type of atactic semicrystalline polymers; examples include poly(acrylonitrile),[17] poly(vinyl fluoride),[18] poly(vinyl chloride),[19,20] and poly(vinyl alcohol).[21] More recent examples include some hydrocarbon polymers containing cyclic groups, such as poly(1,5-hexadiene),[22] hydrogenated polynorbornene[23] and related poly(cycloolefin)s,[24] alternating copolymers of cyclic epoxides and dihydrocoumarin,[25] as well as cyclopentane-containing poly(thioester)s,[26] and several acyclic poly(thioester)s[27,28] that are semicrystalline at low or no stereoregularity. Recently, Chen and co-workers developed a synthetic α,α-disubstituted PHA[29,30] that exhibits semicrystallinity while being atactic; it shows similarly high melting points to isotactic P3HB, with better thermal stability and enhanced toughness, and can be further recycled back to its monomer.[30]

We herein report that *cis*-PHMB is an intrinsically semicrystalline polymer exhibiting isomorphism across *all different tacticities* (syndiotactic, isotactic, and atactic, Figure 1b). Isomorphism is a term that has several meanings in the field of materials science. Here we use isomorphism to describe polymers with two or more distinct repeating units in the polymer backbone that crystallize together with the same crystal unit cell.[31,32] In this case, instead of constitutionally different repeating units, the polymers are distinguished by their disparate sequences of enantiomeric monomer units. Owing to the practical synthesis of PHMB from feedstock chemicals (2-butenes and carbon monoxide, Figure 2a) and its facile recycling and upcycling pathways,[15] we envision that these polymers could be promising and sustainable alternatives for commodity polyolefins. This inherent semicrystallinity would further expand the applications of PHMB as high-performance, polypropylene-like materials without the requirement of high degrees of stereoregularity.

We first screened various catalysts for the polymerization of *cis*-(α,β-dimethyl-β-propiolactone) (*cis*-DMPL) to synthesize the corresponding *cis*-PHMB with different tacticities. We previously reported several zinc complexes[15] that were highly active and produced syndioenriched *cis*-PHMB from the ROP of *cis*-DMPL. Further elaboration of ligand substitutions resulted in the discovery of *in situ* formed complex A (Figure 2b, top), which retained high catalytic activity at 0 °C and produced nearly atactic *cis*-PHMB (P_r = 0.54, Figure 2b, top) with high molecular weight (M_n = 103 kDa) and low polydispersity ($Đ$ = 1.04, see Supplementary Table S1).[33] The highly syndiotactic *cis*-PHMB can be prepared from yttrium complex B[15,34] (Figure 2b, middle), and atactic and syndiotactic *cis*-PHMBs are readily differentiated by ^{13}C NMR spectroscopy, as the sp^3 carbons in the polymers' main chains exhibit distinct signals (Figure 2c, top for atactic and middle for syndiotactic).

During the catalyst screening, we further identified that *in situ* formed complex C bearing a C_s symmetric ligand[35,36] (Figure 2b, bottom) initiated the polymerization of *cis*-DMPL to generate stereoregular *cis*-PHMB, which exhibits discrete splitting patterns in ^{13}C NMR (Figure 2c, bottom). However, an elevated temperature (50 °C) and longer reaction times were required for high monomer conversion (see Supplementary Table S1), possibly due to the steric hindrance in complex C from the bulky phenyl substitutions at the pyrazole C3 positions. By further comparing the ^{13}C NMR spectra of this new polymer (Figure 2c, bottom) with a reference sample of isotactic *cis*-PHMB sample prepared from enantioenriched monomers (see Supporting Information for details), we identified that the *cis*-PHMB synthesized with complex C is isotactic[37] with P_m = 0.82. A comparison of the ^{13}C NMR spectra of syndiotactic (Figure 2c, middle) and isotactic *cis*-PHMB (Figure 2c, bottom) at the main chain sp^3 carbon regions confirms that distinctive microstructures are present. This observation provides additional support for the hypothesis that the *cis*-PHMB prepared with complex B is syndiotactic.[15]

To better understand their thermal properties, we performed DSC analysis of these *cis*-PHMB samples (Figure 3). All the *cis*-PHMB materials tested exhibit double melting transition peaks upon the second heating; similar phenomena were also observed in the synthetic PHAs reported by Chen and co-workers.[30] The presence of two melting transition peaks may be due to the formation of different polymorphs upon cooling or fast recrystallization upon melting.[30] The syndiotactic *cis*-PHMB has the highest T_m (199, 204 °C), and the atactic *cis*-PHMB has the lowest T_m (174, 184 °C). Interestingly, the highly isotactic (P_m = 0.82) *cis*-PHMB only had slightly higher melting points (177, 186 °C) than its atactic isomer. These polymers also show sharp crystallization peaks upon fast cooling (T_c = 148 to 180 °C, see Supplementary Figures S18–S20); such fast crystallization will be beneficial for melt-processing under industrially relevant settings.

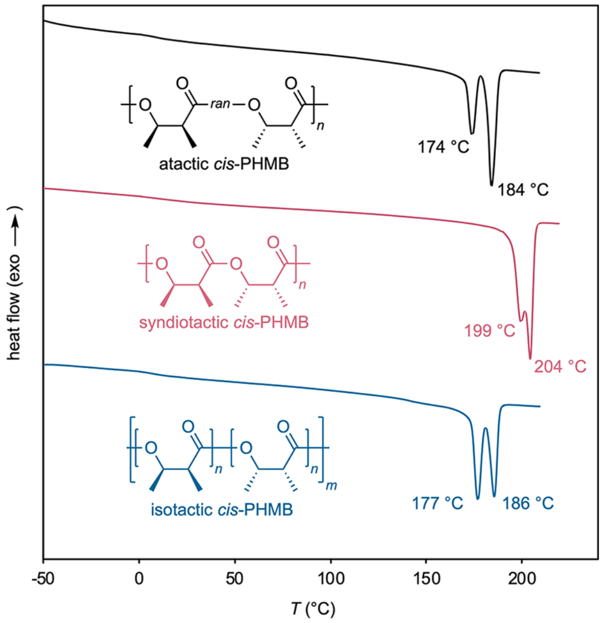

Figure 3. Stacked DSC thermograms (second heating) of atactic, syndiotactic, and isotactic *cis*-PHMB. The double peaks are indicative of polymorphic behavior.

Powder X-ray diffraction (PXRD) analysis was performed on these polymers to determine their semicrystallinity (Figure 4a). Interestingly, the melt-pressed sample exhibited significantly sharper peaks in its XRD pattern than the original, precipitated sample (see Supplementary Figure S16), indicating that melt-processing results in increased crystallinity and larger crystalline domains. By comparing the diffraction patterns of *cis*-PHMBs with different tacticities, we found that they possess nearly the same diffraction patterns (Figure 4a), with intense crystalline diffraction signals at 2θ = 16.9° and 19.0° and minor signals at 11.9°, 14.0°, 20.3°, 23.7°, 25.8°, 28.4°, and 30.5°. The good alignments of these diffraction signals from syndiotactic, atactic, and isotactic *cis*-PHMBs confirm that similar crystal structures are maintained across the full range of tacticity. In contrast, the polypropylene samples with different microstructures clearly show drastically different diffraction patterns[1] (Figure 4b): the syndiotactic and isotactic polypropylene samples have very different peaks, and the atactic polypropylene shows only a broad feature, consistent with the absence of semicrystalline domains.

We then measured the tensile properties of the *cis*-PHMB homopolymer samples (Figure 5). We previously found that the highly syndiotactic *cis*-PHMB (P_r = 0.95, sample 1) was

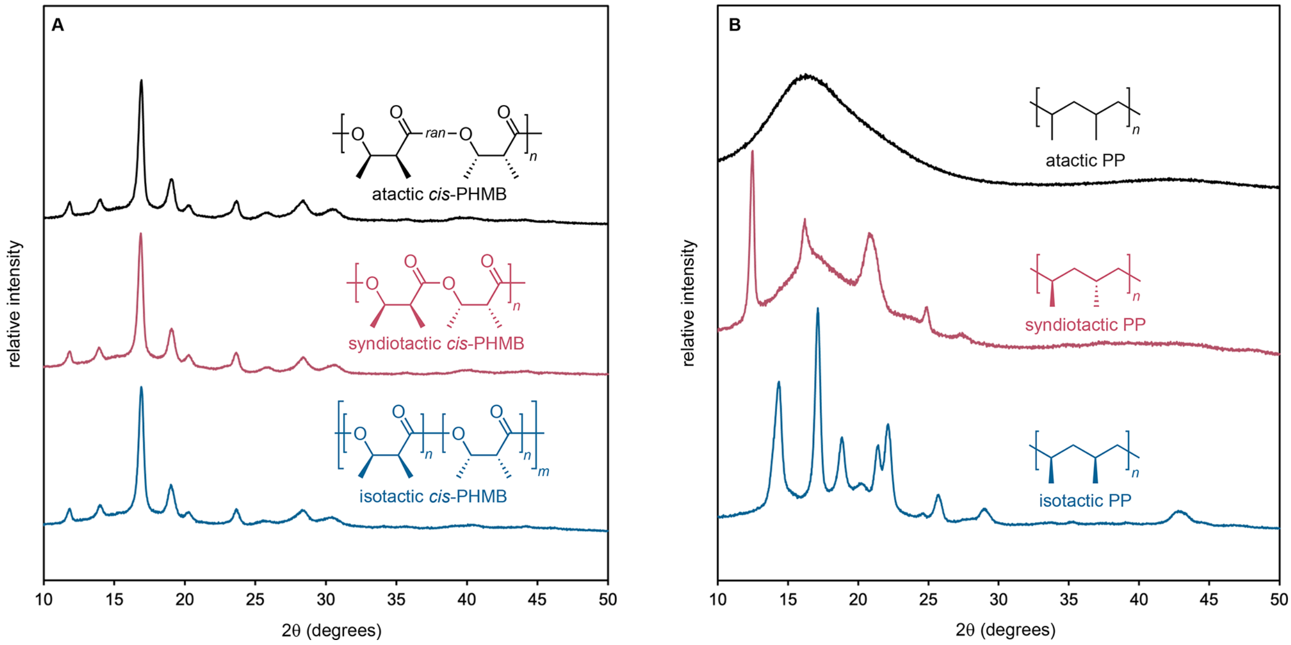

Figure 4. Comparisons of powder X-ray diffraction patterns of (a) atactic, syndiotactic, and isotactic *cis*-PHMB and (b) atactic, syndiotactic, and isotactic polypropylene.

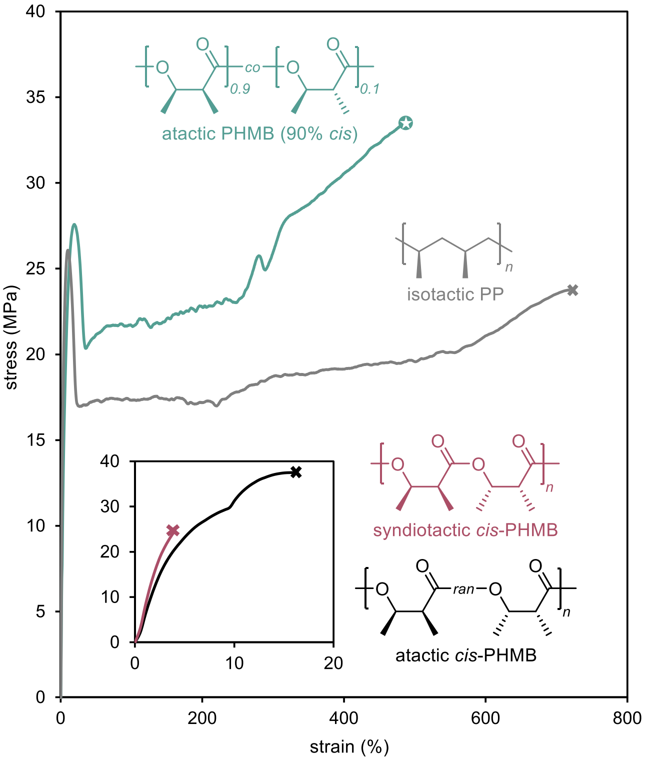

Figure 5. Tensile stress−strain curves for syndiotactic and atactic *cis*-PHMB (inset) and atactic PHMB copolymer (90% *cis*) and *i*PP.

very brittle,[15] with a strain at break (ε_B) of 4%. Atactic *cis*-PHMB exhibits an increased ductility ($\varepsilon_B = 15.7 \pm 0.4\%$) while retaining a similarly high Young's modulus ($E = 0.662 \pm 0.009$ GPa), but it is still brittle, indicating a high degree of semicrystallinity in spite of its barely stereoregular microstructures. The isotactic *cis*-PHMB is unexpectedly tougher (ε_B > 100%, see Supplementary Figure S26); however, the relatively low activity of complex C is a disadvantage. Motivated by our previous copolymerization strategy,[15] we introduced *trans*-repeating units into the polymer chain to break up the high degree of semicrystallinity of atactic *cis*-PHMB. Complex A maintains high activity in the copolymerization to afford the corresponding atactic PHMB copolymer with 90% *cis* content. Despite its reduced stereoregularity, this atactic PHMB copolymer exhibits excellent thermal and mechanical properties that are very similar to those of *i*PP (Figure 5), with high melting points (T_m = 160, 173 °C) and high thermal stability ($T_{d,5\%}$ = 297 °C), and is both hard ($E = 0.467 \pm 0.008$ GPa, yield stress σ_Y = 26.8 ± 0.5 MPa) and tough ($\varepsilon_B = 446 \pm 24\%$, ultimate stress σ_B = 31.3 ± 1.3 MPa, tensile toughness U_T = 110 ± 9 MJ/m^3). Its PXRD patterns also overlap with the *cis*-PHMB homopolymers bearing different microstructures (see Supplementary Figure S17), indicating that isomorphism is also present in this atactic copolymer. This finding clearly demonstrates the versatility of *cis*-PHMB as an atactic yet semicrystalline polymer, and such features will facilitate the discovery of high-performance PHMBs without the limitation of high tacticity.

In conclusion, we report a class of PHA, *cis*-PHMB, that has universal semicrystallinity and near-identical crystal structures across all different tacticities (syndiotactic, isotactic, and even atactic). The semicrystallinity of atactic *cis*-PHMB endows it with a high melting point and good mechanical strength, allowing a wider range of PHMB copolymers to be used as high-performance materials that are not constrained by tacticity requirements. Along with their practical synthesis from feedstock chemicals and versatile recycling and upcycling pathways, the development of PHMBs as sustainable alternatives for traditional polyolefin plastics will be further accelerated by their tacticity-independent semicrystallinity. We are currently studying the possible origin of the inherent semicrystallinity of *cis*-PHMBs and how tacticity may influence their other physical properties and biodegradation. We believe this finding will expand the scope of atactic yet semicrystalline polymers and provide valuable guidance toward the design of new polymer materials with high degrees of semicrystallinity at low tacticity or no tacticity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c10944.

General information, experimental details, NMR spectra, GPC chromatograms, DSC and TGA thermograms, PXRD data, and tensile test data (PDF)

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Notes

The authors declare no competing financial interest.

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