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Nature-inspired methylated polyhydroxybutyrates from C1 and C4 feedstocks

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Polyolefin plastics are widely used due to their low cost and outstanding properties, but their environmental persistence presents a major societal challenge. Polyhydroxyalkanoates (PHA) are biodegradable substitutes for polyolefins, but their high cost and thermal instability are impediments to their widespread application. Here we report a series of methylated polyhydroxybutyrates, poly(3-hydroxy-2-methylbutyrate)s, which are structurally inspired by natural PHAs. The *cis* homopolymers exhibit tacticity-independent crystallinity, which allows for the discovery of high-melting, thermally stable and mechanically tough copolymers, and a full range of polyolefin-like properties can be further achieved by tailoring the *cis*/*trans* ratio of the repeating units. Moreover, these materials can be synthesized from inexpensive carbon monoxide and 2-butene feedstocks, and they can be chemically recycled or upcycled at their end of life. The versatile properties, abundant feedstocks and end-of-life utility of this family of polyesters will enable a powerful platform for the discovery of sustainable alternatives to polyolefin plastics.

In 2020, the cumulative global mass of synthetic plastics achieved the dubious distinction of exceeding the total combined mass of all terrestrial and marine animals[1]. As an inevitable consequence, the ever-growing amount of plastic waste has become a major threat to the planet, despite governmental action to mitigate plastic pollution[2]. Although mechanical recycling provides a means to collect and sort post-consumer plastics, alternative strategies, such as biodegradation, are needed to tackle plastic wastes that leak into the environment, especially the most common[3] yet environmentally persistent polyolefins, with an estimated 4.8–12.7 million metric tonnes of total plastics entering the ocean in 2010[4]. The biodegradable polyhydroxyalkanoates[5,6] (PHAs), produced by bacteria, continue to attract industrial attention as potential substitutes for polyolefin plastics in packaging and other single-use applications. A major member of the PHA family is isotactic poly[(*R*)-3-hydroxybutyrate] (*R*-P3HB), which may also be produced via chemical synthesis[7–10]. It exhibits low toxicity and has a high melting point (~175 °C) that is similar to isotactic polypropylene (*i*PP), but the low production volumes, brittleness and thermal instability of *R*-P3HB homopolymers have limited their widespread use. Although the mechanical properties of *R*-P3HB may be improved by copolymerizing with other monomers[11–13], or in combination with more elaborate stereochemical and sequence control[14], other problems have not been fully addressed. Major efforts have focused on variations at the C3 position of repeating units, but in this Article we report a family of methylated polyhydroxybutyrates, poly(3-hydroxy-2-methylbutyrate)s (PHMBs; Fig. 1a), that contain an extra methyl substituent and stereocentre at the C2 position. This structural evolution enables us to establish a versatile platform of PHA polymers with enhanced thermal stability, and their melting points and mechanical strength are close or superior to various commodity plastics[15] (Fig. 1b). Such properties can be further tailored by altering the polymer tacticity and the *cis*/*trans* ratio of the monomers.

Although the 3-hydroxy-2-methylbutyrate (HMB) repeating unit has been incorporated into P3HB copolymers via ring-opening copolymerization[16] as well as bacterial engineering[17–21], PHMB homopolymers have only been reported very recently[22,23]. Although *cis*- or *trans*-PHMB homopolymers can be prepared by an efficient one-pot carbonylation/polymerization reaction, the materials were amorphous[22].

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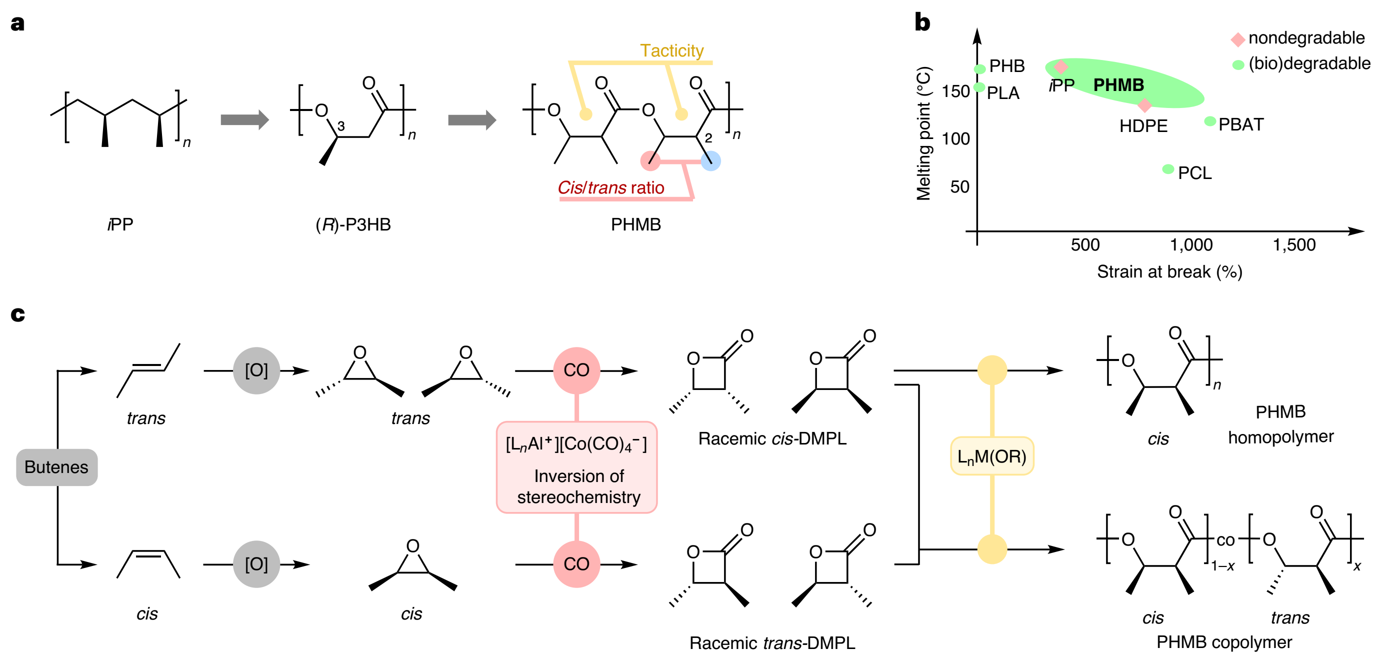

Fig. 1 | General design of methylated polyhydroxyalkanoates and PHMB. **a**, Structural progression from *i*PP, to *R*-P3HB to PHMB. **b**, PHMB exhibits thermal and mechanical properties that are comparable or superior to various commercial polymers, such as (bio)degradable (green) polyhydroxylbutyrate (PHB), polylactic acid (PLA), polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and non-degradable (red) *i*PP and high-density polyethylene (HDPE). **c**, Streamlined synthesis of PHMB from 2-butene via epoxidation, carbonylation and polymerization.

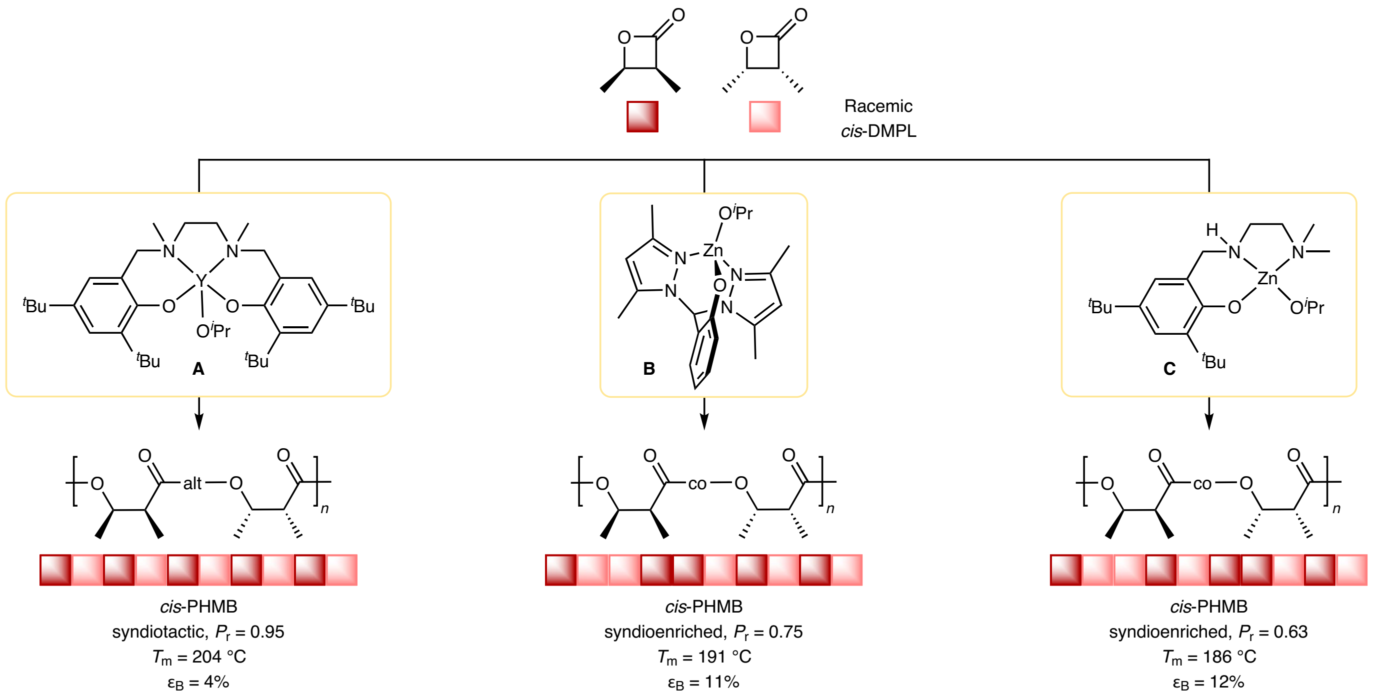

Fig. 2 | Polymerization of *cis*-DMPL by different initiators to give *cis*-PHMB homopolymers with varied degree of syndiotacticity. All the syndioenriched *cis*-PHMB homopolymers have high melting points but are brittle. T_m refers to the major melting peak observed in DSC.

The enantiopure (2*R*,3*R*)-*trans*-PHMB homopolymer can be biosynthesized from gene-modified bacteria[23] and exhibits superior thermal and mechanical properties. However, a systematic evaluation of the full potential of PHMB, especially via chemical synthesis, has not been performed. Based on our previous success in streamlined syntheses of other PHA polymers, such as P3HB[24] and poly(3-hydroxypropionate) (P3HP)[25], we designed a similar strategy that can produce PHMB from 2-butene oxide and CO via carbonylation and polymerization reactions (Fig. 1c). The 2-butene oxide can be industrially produced by the epoxidation of 2-butene[26], an abundant C4 feedstock that can be derived from both fossil-fuel and biorenewable sources[27,28]. Alternatively, 2-butene oxide can also be prepared via dehydration[29] of microbially produced 2,3-butanediol[30]. Catalytic carbonylation of the epoxides with CO in the presence of [Lewis acid]$^+$[$Co(CO)_4$]$^-$ complexes[31–34]

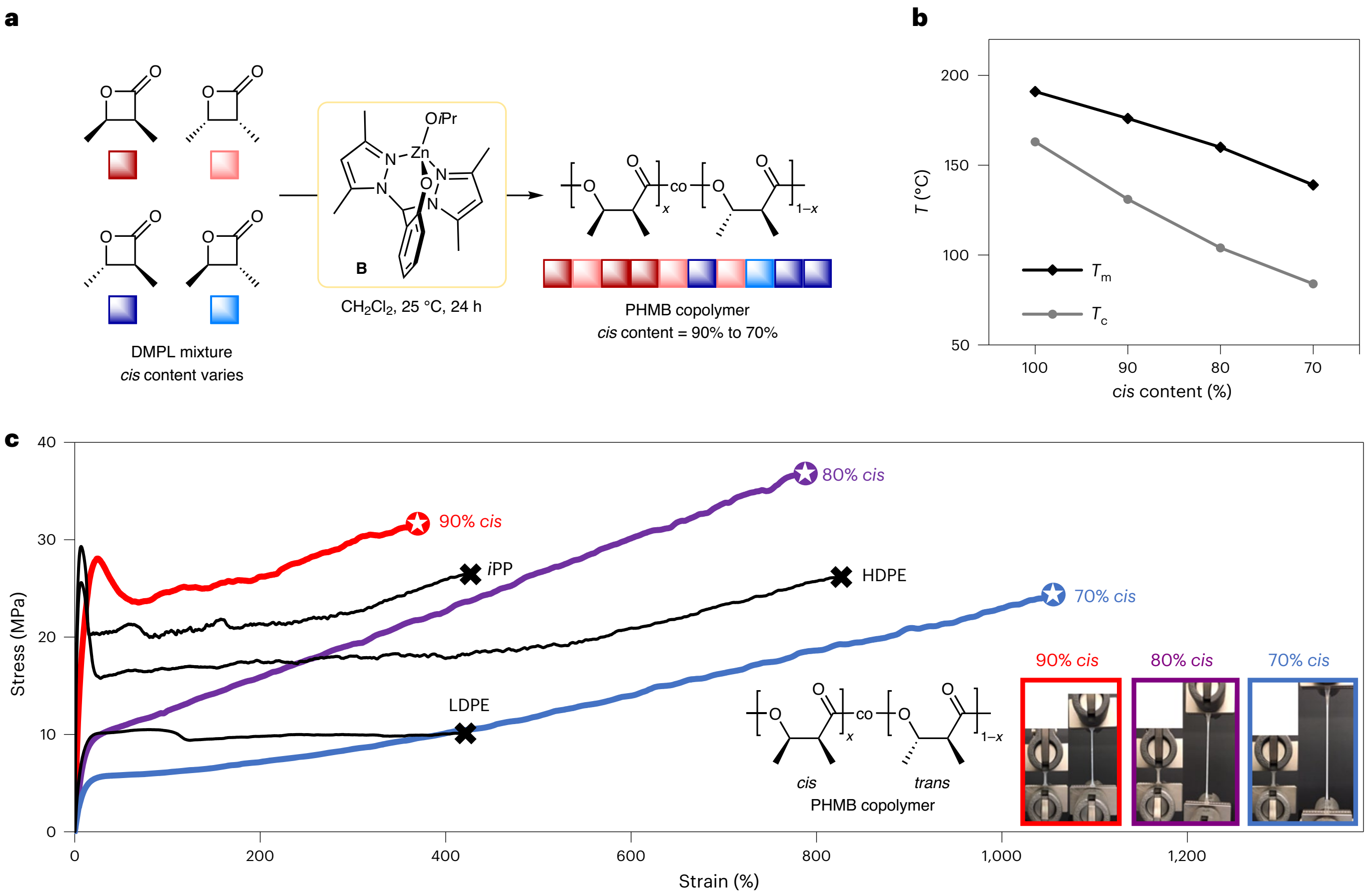

Fig. 3 | Synthesis and characterization of PHMB copolymers with different *cis* content. a, Polymerization of a *cis*/*trans* mixture of DMPL with varied *cis* content. In all cases, PHMB copolymers are obtained with high molecular weight (M_n > 100 kDa) and low polydispersity ($Đ$ = 1.03–1.05). **b**, Thermal properties of different PHMB copolymers. All obtained PHMB copolymers have high melting points. **c**, Representative tensile curves of different PHMB copolymers with 90%, 80% and 70% *cis* blends. All PHMB copolymers are tough, and their tensile properties are comparable to some commercial polyolefin plastics. Their thermal and mechanical properties can be further tuned by the *cis* content of the starting materials. Insets: photographs of the specimens before and after being stretched. T_m refers to the major melting peak observed in DSC and T_c refers to the crystallization peak.

yields 2,3-dimethyl-β-propiolactone (DMPL) with inversion of stereochemistry at the site of ring-opening. With this method, *cis*- and *trans*-DMPL can be easily produced on a decagram scale in the laboratory (see Supplementary Information for details). PHMB can thus be prepared with tunable microstructures from both DMPL isomers in the presence of suitable metal-alkoxide catalysts. We decided to initially pursue the homopolymerization of *cis*-DMPL, as it is derived from the more accessible, thermodynamically more stable *trans*-2-butene and *trans*-2-butene oxide feedstocks[26,35].

Results and discussion

Inspired by the seminal discovery of syndiotactic β-butyrolactone (BBL) polymerization using single-site yttrium complexes[36–38], the polymerization of *cis*-DMPL using complex **A**[39] was investigated (Fig. 2 and Supplementary Table 1). The polymerization was complete within 2 h, resulting in high-molecular-weight (M_n > 100 kDa) PHMB with excellent syndiotacticity (P_r = 0.95, 95% *racemo* diad). The polymer obtained is semicrystalline and has a high melting temperature, (T_m, >200 °C). Although the syndiotactic *cis*-PHMB's physical properties are promising, the scarcity and high price of yttrium limit the industrial-scale production of the material. We therefore investigated zinc-based catalysts, which are earth-abundant and highly active for BBL polymerization[24,40]. Mehrkhodavandi and others recently reported a series of zinc phenoxide catalysts that initiated polymerization of BBL with an extremely high turnover frequency[41] to give syndioenriched P3HB. Prompted by these studies, we found that in situ-generated complexes **B**[42] and **C** both produce *cis*-PHMB with high molecular weight (M_n > 100 kDa), narrow dispersity ($Đ$ < 1.1) and >99% conversion in 24 h (Supplementary Table 1). Complex **B** gives higher syndiotacticity (P_r = 0.75), possibly due to the presence of a C_s symmetrical bispyrazole-phenoxide ligand backbone (Supplementary Fig. 16). Complex **C** induces similar degrees of syndiotacticity (P_r = 0.63) in *cis*-PHMB compared to previous P3HB synthesis[41] with similar catalysts. Both PHMB polymers, however, are semicrystalline with high T_m, and their melting temperatures decrease slightly with decreasing tacticity. Surprisingly, completely atactic *cis*-PHMB is also semicrystalline with a high melting point (Supplementary Table 1). Similar powder X-ray diffraction (PXRD) patterns were observed for all *cis*-PHMB samples, regardless of stereoregularity (Supplementary Fig. 24). The tacticity-independent crystallinity[43–47] and extremely high melting points were unexpected and may permit the use of *cis*-PHMB as a versatile crystalline component in PHA thermoplastics. However, all these materials are brittle, with strain at break (ε_B) not exceeding 20% (Fig. 2). The brittleness across these materials severely limits their further applications and suggests that simply adjusting the tacticity is insufficient to improve their mechanical properties. We thus embarked on other structural modifications to solve this limitation.

The toughness of *R*-P3HB can be improved by copolymerization with different comonomers bearing similar chemical structures[10,11]. With this strategy, *trans*-DMPL may be an ideal comonomer due to its

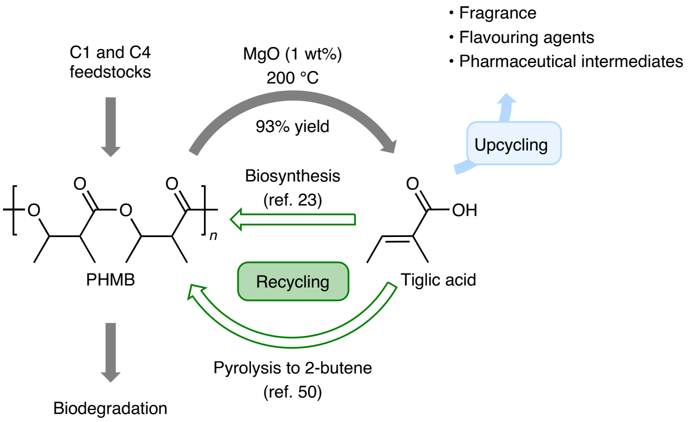

Fig. 4 | Potential chemical recycling and upcycling of PHMB. In addition to potential biodegradation, PHMB can be depolymerized to tiglic acid under catalytic MgO with near-quantitative yield. Tiglic acid is a value-added C5 feedstock and can also be pyrolysed to generate *trans*-2-butene, which would permit the potential chemical recycling and upcycling of PHMB.

structural resemblance to the *cis* isomer. In addition, the comonomer stream could come from a mixture of 2-butene without laborious separation of the two stereoisomers, which would greatly enhance its industrial practicality. Because the copolymer would probably have diminished crystallinity and thermal behaviours, we chose complex **B** for further studies, hoping that the higher syndiotacticity it provided in *cis*-PHMB could offset the decreased T_m from stereodefects introduced by the comonomer. When the mixtures of DMPL isomers with varied *cis* content (90%, 80% and 70%) were polymerized by complex **B**, high-molecular-weight copolymers of PHMB were obtained (Fig. 3a and Supplementary Table 2). All three copolymers exhibit semicrystallinity, albeit with moderate tacticity for the major *cis* composition. Although their T_m and T_c (the crystallization temperature) decrease with lower *cis* content (Fig. 3b), these copolymers still maintain high melting points ($T_m > 130$ °C). Unlike *R*-P3HB[48], a minimal decrease in molecular weight or broadening of dispersity was observed when the selected PHMB copolymer was heated at 170 °C (Supplementary Fig. 44). Similar enhancement in thermal stability was also reported for biosynthesized *trans*-PMHB[23]. Further kinetic experiments showed that the *cis*-DMPL was consumed faster than the *trans* isomer ($k_{cis}/k_{trans} = 4.0$; Supplementary Figs. 45 and 46) in the copolymerization, indicating that the copolymers are tapered rather than completely random. Given the lower melting points and attenuated crystallinity of the copolymers, we expected that the copolymerization strategy might improve the ductility and toughness of the materials.

We then measured the tensile properties of the three copolymers (Fig. 3c). Encouragingly, all copolymers are tough materials with ε_B greater than 300%. At higher *cis*-DMPL content (90%), the copolymer behaves very similar to *i*PP and high-density polyethylene (HDPE), with a high yield stress ($\sigma_Y = 26.1 \pm 1.3$ MPa) and ductility ($\varepsilon_B = 373 \pm 50\%$). Although it is less stiff than the hard polyolefins, with a Young's modulus (E) of 0.34 ± 0.01 GPa, it possesses a higher stress at break ($\sigma_B = 30.7 \pm 1.3$ MPa). Upon lowering the *cis* content to 80%, the copolymer becomes softer and resembles low-density polyethylene (LDPE), with a similar yield stress ($\sigma_Y = 10.3 \pm 0.2$ MPa) and Young's modulus ($E = 0.106 \pm 0.003$ GPa). Moreover, it is more ductile ($\varepsilon_B = 783 \pm 7\%$) and tougher, exhibiting a much higher stress at break ($\sigma_B = 36.6 \pm 0.1$ MPa) than LDPE. If the *cis*-DMPL percentage is further decreased to 70%, the copolymer is even softer and can be stretched to ~10 times its original length ($\varepsilon_B = 1{,}020 \pm 55\%$). The ductility of these copolymers is further illustrated by photographs taken before and after being stretched (Fig. 3c). All the copolymers obtained here exhibit high tensile toughness (~96–177 MJ m^{-3}) that is close to or higher than the reference polyolefin samples. These results demonstrate that a full spectrum of different polyolefin-like materials, from hard to soft, can be easily obtained by simply adjusting the *cis*-DMPL content in the comonomer mixture, which can be precisely controlled by the *trans*/*cis* ratio of the starting 2-butene and 2-butene oxide.

Finally, we carried out a preliminary depolymerization study of PHMB to tiglic acid[23,48,49] (Fig. 4). In the presence of MgO (1 wt%), PHMB can be depolymerized cleanly at 200 °C to give pure tiglic acid with 93% yield. Because tiglic acid was used as a feedstock for the biosynthesis of *trans*-PMHB[23], this process offers potential open-loop chemical recycling of PHMB. Through further pyrolysis of tiglic acid into *trans*-2-butene[50] and *cis*/*trans* isomerization of 2-butenes[35], this approach could also permit alternative closed-loop chemical recycling of PHMB. In addition, tiglic acid and its esters have been commonly used in fragrance and food additives, suggesting that PHMB may also be upcycled to value-added products in a green, atom-economic manner. The facile post-consumer transformations of PHMB will permit additional avenues for their waste management.

In conclusion, we have discovered a class of synthetic PHA materials—PHMBs—that can be easily synthesized from the industrial C4 feedstocks 2-butene and carbon monoxide in a practical and scalable manner, and may biodegrade, be recycled or be upcycled. The *cis*-PHMB homopolymers exhibit tacticity-independent crystallinity and high melting points, and by copolymerizing both *cis*- and *trans*-DMPL, we can obtain a full range of tough and high-melting copolymer materials that mimic commodity polyolefin plastics in a well-controlled and predictable manner. The study of the biodegradability and industrial composting ability of these polymers is ongoing, and we also plan to study their compatibility as blending materials to improve the properties of other biodegradable polymers. These materials could provide a promising platform for sustainable alternatives to polyolefin plastics, and their facile synthesis, renewable sourcing and potential biodegradability may provide an additional way to mitigate plastic pollution.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41557-023-01187-0.

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Methods

General carbonylation procedure

In a glovebox, the selected carbonylation catalyst was dissolved in tetrahydrofuran (THF) and cooled to −35 °C. In a separate container, the corresponding *cis*- or *trans*-2-butene oxide and THF were combined and cooled to −35 °C. The solutions of catalyst and epoxide were combined in a pre-chilled (−35 °C) autoclave, which was then sealed and brought out of the glovebox. The reactor was pressurized with CO (~700–900 psi) and heated (~50–65 °C) for ~16–20 h. The reactor was cooled and then vented carefully and opened. After removal of THF from the reaction mixture, the residual mixture was distilled under vacuum to give pure *trans*- or *cis*-DMPL, respectively.

General polymerization procedure

In a glovebox, to a solution of DMPL (in pure form or as *cis*/*trans* mixtures) in CH_2Cl_2 was added a solution of selected initiator (complex **A**, **B** or **C**) at 25 °C. The resulting mixture was kept at 25 °C for ~2–24 h. The reaction mixture was then removed from the glovebox, precipitated from mixtures of hexane and diethyl ether, and dried under vacuum to give the corresponding polymer.

Detailed synthetic methods, depolymerization procedures and characterization data are available in the Supplementary Information.

Data availability

The data supporting the findings of this study are available within the paper and its Supplementary Information. Crystallographic data for the structure of B-HMDS reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under deposition no. CCDC-2135622. Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/. Source data are provided with this paper.

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Author contributions

Z.Z. and A.M.L. designed and performed all experiments. G.W.C. directed the research. All authors prepared the manuscript.

Competing interests

Z.Z., A.M.L. and G.W.C. are inventors on US provisional patent application 63/220,301, submitted by Cornell University, which covers the synthesis and characterization of PHMB. T.D.S. declares no competing interests.

Additional information

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