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Recent Advances in Polyhydroxyalkanoates Degradation and Chemical Recycling

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Abstract

Plastics are nowadays essential to our daily life for a wide range of applications. In order to face the demand of polymer markets, given the depletion of fossil feed stocks from which they are still most commonly produced, and with the aim to develop more ecofriendly plastic materials, the need for renewable and/or recyclable polymers is huge. Polyhydroxyalkanoates (PHAs) are a class of polyesters that could meet the challenges of such a circular economy, as they currently stand as promising bio-based, degradable and recyclable alternatives to traditional non-degradable commodity polymers that are polyolefins. PHAs typically feature different side-chain substituents on the repeating units, which beside the stereochemistry along the polymer backbone and the intrinsic characteristics of the macromolecules, are key parameters that dictate and enable tuning of their thermal, mechanical, and recyclability performances. PHAs are thus a large family of versatile polymers that are currently of topical interest in light of their end-of-life options. This review discusses the chemical recycling of natural, biosynthetic and synthetic PHAs, mainly focusing on the most common example, namely poly(3-hydroxybutyrate) (PHB), and its related copolymers. The most relevant non-biotechnological approaches, including pyrolysis-type processes, and solvolysis with especially hydrolysis and alcoholysis, whether they are catalyzed or not, are then addressed. The latest advances on the degradation, depolymerization and upcycling of PHAs, show promising outcomes for a close-carbon cycle economy with a favorable environmental impact, as exemplified from the most recent literature.

Keywords

Polyhydroxyalkanoate (PHA), chemical recycling, pyrolysis, hydrolysis, alcoholysis, depolymerization

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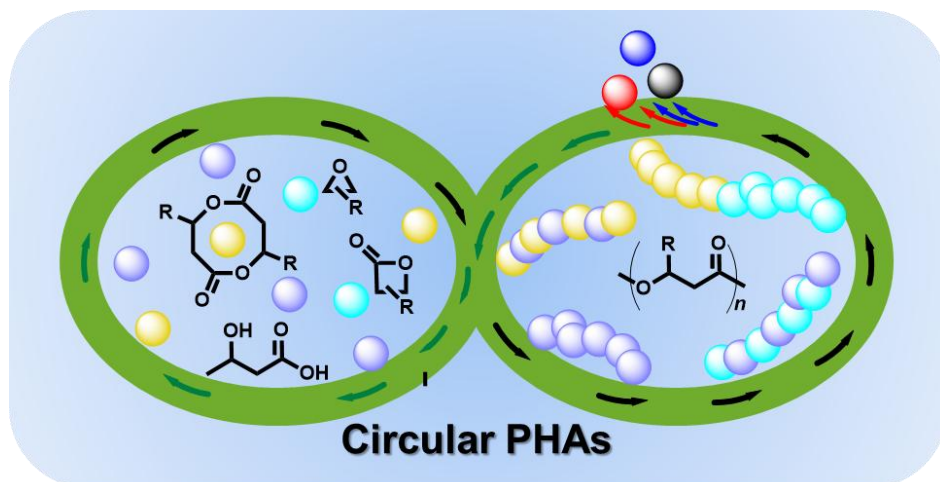
Declaration of Competing Interest

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Funding

References

Graphical Abstract



Abbreviations

AMPL	4-Allyloxymethyl- β -propiolactone
BnOH	Benzyl alcohol
<i>t</i> Bu-P ₄	1- <i>tert</i> -Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidene-amino]2 λ^5 ,4 λ^5 -catenadi(phosphazene)
CA	Crotonic acid
\mathcal{D}	Dispersity (M_w/M_n)
E_a	Activation energy
ϵ_b	Elongation at break
Et3HB	Ethyl 3-hydroxybutyrate, <i>aka</i> ethyl 3-hydroxybutanoate
3HB	3-Hydroxybutyrate
4HB	4-Hydroxybutyrate
3HBA	3-Hydroxybutyric acid, <i>aka</i> 3-hydroxybutanoic acid
3HHx	3-Hydroxyhexanoate
3HO	3-Hydroxyoctanoate
3HP	3-Hydroxypropionate
3HV	3-Hydroxyvalerate
HDPE	High-density polyethylene
IL	Ionic liquid
k_d	Degradation rate constant
3MeBA	3-Methoxybutanoic acid
4MOHB	4-Methyloctahydro-2 <i>H</i> -benzo[<i>b</i>][1,4]dioxepin-2-one
MC	Methyl crotonate, <i>aka</i> methyl-but-2-enoate
Me3HB	Methyl 3-hydroxybutyrate, <i>aka</i> methyl 3-hydroxybutanoate
Me3MB	Methyl 3-methoxybutyrate, <i>aka</i> methyl 3-methoxybutanoate
MeOxPBoc	5-Methyl- <i>N</i> -Boc-1,4-oxazepane-7-one
M_n	Number average molar mass
M_w	Weight average molar mass

2PA	2-Pentenoic acid
P4HB	Poly(4-hydroxybutyrate)
PHA	Polyhydroxyalkanoate
PHB	Poly(3-hydroxybutyrate), <i>aka</i> P3HB
PHBV	Poly(3-hydroxybutyrate- <i>co</i> -3-hydroxyvalerate), <i>aka</i> P(3HB- <i>co</i> -3HV)
PHO	Poly(3-hydroxyoctanoate)
PLA	Poly(lactide)
PLLA	Poly(L-lactide)
poly[(<i>R</i>)-3HB]	Isotactic polyhydroxybutyrate
<i>i</i> PP	Isotactic polypropylene
ROP	Ring-opening polymerization
Sn(Oct) ₂	Stannous 2-ethyl hexanoate, <i>aka</i> tin(II) dioctate
TBL	(<i>R,R,R</i>)-4,8,12-trimethyl-1,5,9-trioxacyclododeca-2,6,10-trione
T_m	Melting temperature
PTSA	<i>para</i> -Toluenesulphonic acid

1. Introduction

For just about a century, plastics have been taking a growing place in our daily life to become nowadays omnipresent and essential.[1,2] Plastics are versatile polymer materials being used in various domains ranging from packaging, building and construction, aerospace and automotive, electric and electronics, medical and healthcare, textile, energy generation and storage. The worldwide production of plastics reached almost 391 million tons in 2021, among which *ca.* 3/4th are polyolefins (polyethylene, polypropylene, polystyrene...) and it is expected to increase by 1.5 times in 2050.[3,4] Thanks to their valuable properties such as high performances, lightweight, chemical resistance, strength and durability, along with their low cost, plastics have long been considered as fantastic. However, their end-of-life should be taken into consideration leading to important changes in current plastic production, in their usage and disposal, so as to achieve the sustainability of plastics. At the very end of their lifetime, plastics are either collected to be taken care of, or they are released in nature, consciously or mistakenly. Plastics entering lakes, rivers and oceans are slowly degrading into macro-, micro- and/or nano-particles that have a profound negative impact on the ecosystems and on human well-being. Contamination by such down-sized plastics has also been reported from plastics being released on land. Plastic waste management is thus the actual challenge that society and scientists have to tackle.[5,6,7,8,9] In addition, being traditionally derived from fossil resources (gas, oil...), their production has revealed limited by the non-renewable depleting feed stock. While the “reduce, reuse and recycle” strategy is under development, rethinking the whole polymer-chain concept from renewable resources to monomer, polymer, polymer materials and recycling, within a closed-loop life cycle via ecofriendly approaches, appears as the best societal and environmental solution. The greatest compromise to address this plastic issue would be to design renewable and recyclable polymers that would be recycled or upcycled within a circular economy to meet the rapidly growing market demand.[10,11,12,13,15,15,16]

Traditionally, plastic waste has been recycled by mechanical recycling, through the physical sorting, grinding, separating, washing, melting, and then cooling back (mainly via extrusion, injection or compression molding) to granulates that can be next reused to manufacture new materials. This process suffers from the required high purity of the input waste with a low level of inhomogeneity and contaminants, a combination difficult to get given the complexity of current plastics materials. Besides, end-products recovered typically display lower thermo-mechanical properties due to impurities which reduces their performances. Other options are the chemical recycling and upcycling of plastics which depolymerizes or degrades them, into the original or new virgin-quality monomeric unit(s) or into some high quality degradation product(s), petrochemical feedstocks, or new molecules of added value, ready to be reconverted into new upgraded polymers and polymer materials, respectively, for an (ideally) indefinite number of recycles. This latter chemical recycling and upcycling approaches promote circularity, and stand as an alternative to landfill and incineration of hard-to-mechanically recycle plastic products such as films or multi-layered plastics. Chemical recycling breaks down the chains in plastics using biodegradation, pyrolysis or solvolysis. Common thermal cracking-type processes include pyrolysis and to a lesser extent thermolysis, depending how much exogenous oxygen (air) is present during the process. Common solvolysis methods are hydrolysis and alcoholysis including most commonly glycolysis and methanolysis, and to a lesser extent aminolysis or phosphorolysis.[17,18,19,20,21,22,23,24,25,26]

Polyhydroxyalkanoates (PHAs) are a wide class of polyesters, with the molecular structure depicted in Fig. 1. PHAs are produced either from nature, biochemically or chemically.[27,28,29] Microbial (also referred to as bacterial) natural or biosynthesized PHAs are produced intracellularly as granules by the polymerization of 3-hydroxy fatty acid monomers from *PHA synthase* enzymes, and they are being used as a mean to store carbon and energy in PHA producing microorganisms.[30,31] Most commonly, the bacterial PHA family includes more than 150 poly(β -hydroxy acid)s (Fig. 1, $x = 1$) differing from the length of their R alkyl side chain, ranging from short-chain-length (C3-C5), to medium-chain-length (C6-C14), to copolymers combining both short- and medium-chain-length

monomers. Alternatively, PHAs can be chemically synthesized either upon copolymerization of epoxides with carbon monoxide, or by ring-opening polymerization (ROP) of four- or eight-membered ring lactones.[32,33,34,35,36,37] These latter synthetic routes provide larger PHAs production volumes at lower cost than conventional fermentation processes. While structural parameters such as the molar mass, dispersity, crosslinking, branching, crystallinity of PHAs do affect their thermomechanical, and degradation or biodegradation performances, the chemical nature of the R substituent provides a valuable handle to tune and enlarge these properties.[38,39] Whereas all bacterial PHAs are purely isotactic ((*R*)-configured), ROP nicely enables to access to PHAs with different stereochemistries, including isotactic, syndiotactic or atactic polymers with different tacticity degrees, provided monomers with different enantiopurities are available and/or a suitable stereoselective catalytic system is implemented. Given the range of synthetically accessible substituted propiolactone and diolide cyclic monomers, onto which the desirable (functional) substituent(s) may be introduced, and given especially the diversity of ROP-monomers in which the functionality of the lactone-side chain can be chemically tuned (Fig. 1), synthetic PHAs thus offer a much wider array of functional polymer materials ranging from thermoplastics to elastomers, subsequently paving the way to more diversified applications. Furthermore, PHAs are attracting considerable and growing attention due to their renewability from oil substrates such as plant oils or waste oils, their biocompatibility, bioresorbability, compostability and biodegradability into nontoxic products under both aerobic and anaerobic conditions.[40,41,42,43,44,45,46,47] Finally, practical recycling strategies for post-consumer PHAs are attractive end-of-life options, making these plastics even more valuable. PHAs thus typically find various user and industrial applications in packaging, agriculture, paints, coatings, adhesives, foams, non-wovens, fibers, 3D-printing, electronics, energy, pharmaceuticals and medical devices.[27,43,48,49]

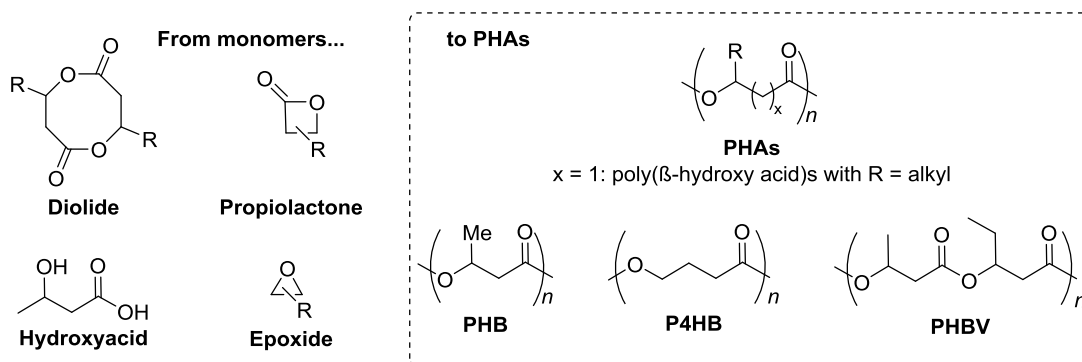


Fig. 1. General structure of PHAs and of the most common ones along with the monomers from which they are derived.

Poly[(*R*)-3-hydroxybutyrate] (poly[(*R*)-3HB]), the most common PHA in nature, which features a methyl group on the repeating unit, is the isotactic linear polymer of (*R*)-3-hydroxybutyric acid, a ketone body present in human tissues (Fig. 1). It is non-toxic, water-insoluble and relatively resistant to hydrolytic attack, and exhibits good ultra-violet (UV) resistance and excellent barrier to oxygen and moisture transport. It has also attracted extensive consideration in light of its material characteristics (glass transition temperature of 15 °C, melting point (T_m) up to 180 °C, tensile strength of ca. 40 MPa) which makes it an alternative substitute to isotactic propylene (*i*PP).[31,36,50] Furthermore, poly[(*R*)-3HB] is biosynthesized from methane and subsequently biodegrades back into biogas (methane and carbon dioxide) thus forming a PHB-methane cradle-to-cradle cycle.[51] While the polycondensation of (*R*)-3-hydroxybutyric acid affords poly[(*R*)-3HB], undesirable side reactions (crotonization, *i.e.*, the formation of crotonate end-groups through transesterification side-reactions or elimination/termination reactions) limit the molar mass of the polymer.[52] Alternatively, the direct copolymerization of propylene oxide with carbon monoxide also forms PHB, yet it gives atactic PHB. On the other hand,

synthetic analogues of this natural PHB are most commonly prepared from the stereoselective or non-stereoselective organo- or metal-catalyzed ROP of β -butyrolactone (2-methyl-2-oxetanone) or dimethyl diolide, returning isotactic, syndiotactic or atactic PHBs.[34,35,37] This chemocatalytic ROP route thus provides access to other-than-isotactic PHB, and polyesters more generally distinct from isotactic PHAs, *i.e.*, the only one(s) obtained from fermentation.

Studies on the chemical recycling of polymers, and especially the degradation or depolymerization of polyesters, are currently prospering.[18,20,21,32,53,54,55,56,57,58] The biodegradation of PHAs, valuable in the event the polymer material accidentally ends-up on land or in lakes, rivers or oceans,[59] that is in an aqueous environment in which it is typically decomposed into CO_2 and H_2O , has however mainly been investigated using various enzymes towards biomedical applications rather than serving as a recycling method, and reviewed elsewhere.[40,60,61,62,63,64] Enzyme-catalyzed recycling processes are not covered in the present review. Mechanical recycling of PHAs, typically impeded by their lack of thermal stability, is similarly beyond the scope of the present review.[25] The present review highlights the main advances in PHAs recycling and upcycling concepts and methods, focusing on pyrolysis and solvolysis (hydrolysis, alcoholysis), including catalyzed approaches (Fig. 2). The various pathways will be discussed by the type of PHA studied, focusing on the most common one, namely the ubiquitous poly(3-hydroxybutyrate) (PHB) (Fig. 3) and its related copolymers, especially poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV). The strengths and opportunities emerging from the most relevant and up-to-date different routes, and the added-value of recycled and upcycled products, are also critically examined with the objective to provide an overall view on PHAs and PHAs-waste feedstock as a potential sustainable source for the next generation of ecofriendly and circular plastics.



Fig. 2. Overview of the chemical recycling of PHAs.

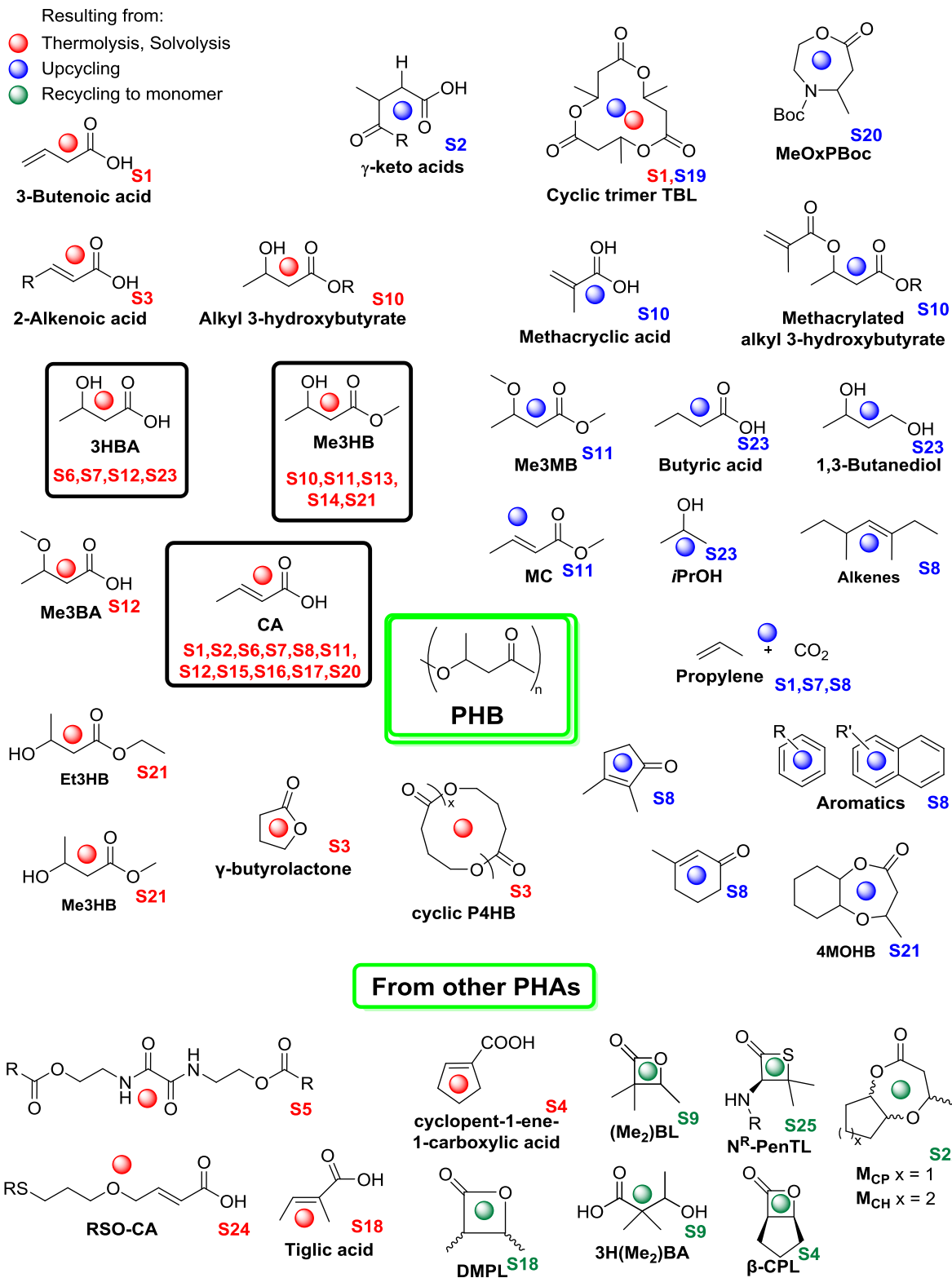


Fig. 3. Major compounds (besides H₂O, gas, char, linear and cyclic oligomers) recovered from the chemical recycling of PHB and from other PHAs, arising from the pyrolysis and solvolysis (red), or from

upcycling (blue) or the recycling back to the monomer (green), as exemplified in the corresponding Schemes referred to as Sx (stereochemistry is unspecified).

2. Catalyst-Free Pyrolysis of PHAs

Pyrolysis and thermolysis, also commonly known as thermal cracking, of polymer materials are effective methods for the chemical recycling of plastics that refer to their thermal decomposition.[18] While pyrolysis, one of the most significant chemical recycling method (a thermal process in which the organic matter in sludge is broken down in an environment lacking in air compared to the stoichiometry) of PHAs is most commonly reported, thermolysis of PHAs performed in the absence of any exogenous oxygen, is more seldom (only four reported works). Several parameters do affect this degradation process, especially the chemical features of the polymer (chemical nature of the repeating unit(s), molar mass), the catalysts possibly used, the presence or not of oxygen, the temperature and pressure along with the heating rate and residence time. The resulting products are typically gases (CO_2 , CO , H_2), water and simple hydrocarbons, organic vapors that are condensed into pyrolysis oil, and solid residues referred to as char, as exemplified with PHB in Fig. 3. PHAs sensitivity to thermal degradation in the melt is one of the key issues to consider for their broader uptake as commercial materials. Pyrolysis of PHAs has mainly been performed from polymer granules or films, and varied with changes in temperature and reaction time.

Various analytical techniques typically enable to assess the pyrolysis of PHAs and more generally the degradation process, especially size exclusion chromatography (SEC) for the analysis of molar mass changes of residual PHA, thermogravimetry analysis (TGA under nitrogen atmosphere) for monitoring the weight loss, nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopies, gas chromatography (GC), mass spectrometry (MS, including fast atom bombardment MS (FAB-MS), electrospray ionization MS (ESI-MS)), pyrolysis-MS, pyrolysis-GC, pyrolysis-GC/MS, pyrolysis-GC/FTIR, and TG/FTIR, for the analysis of soluble and volatile products, and differential scanning calorimetry (DSC) for monitoring the heat of reaction (Fig. 4).[65]

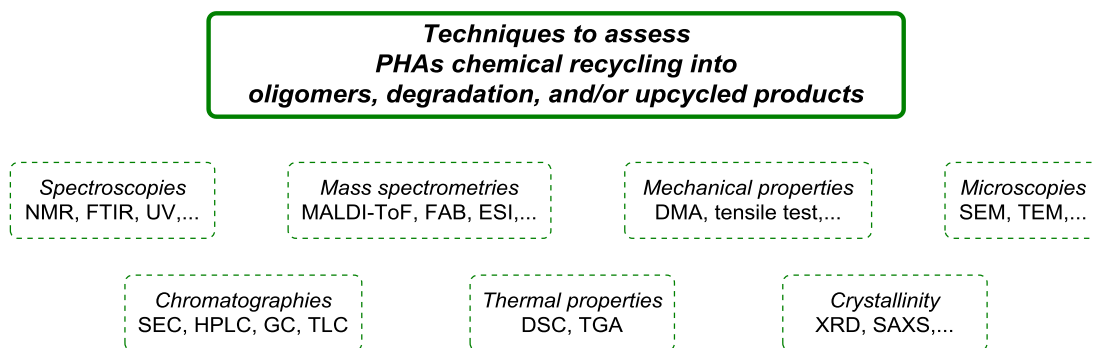


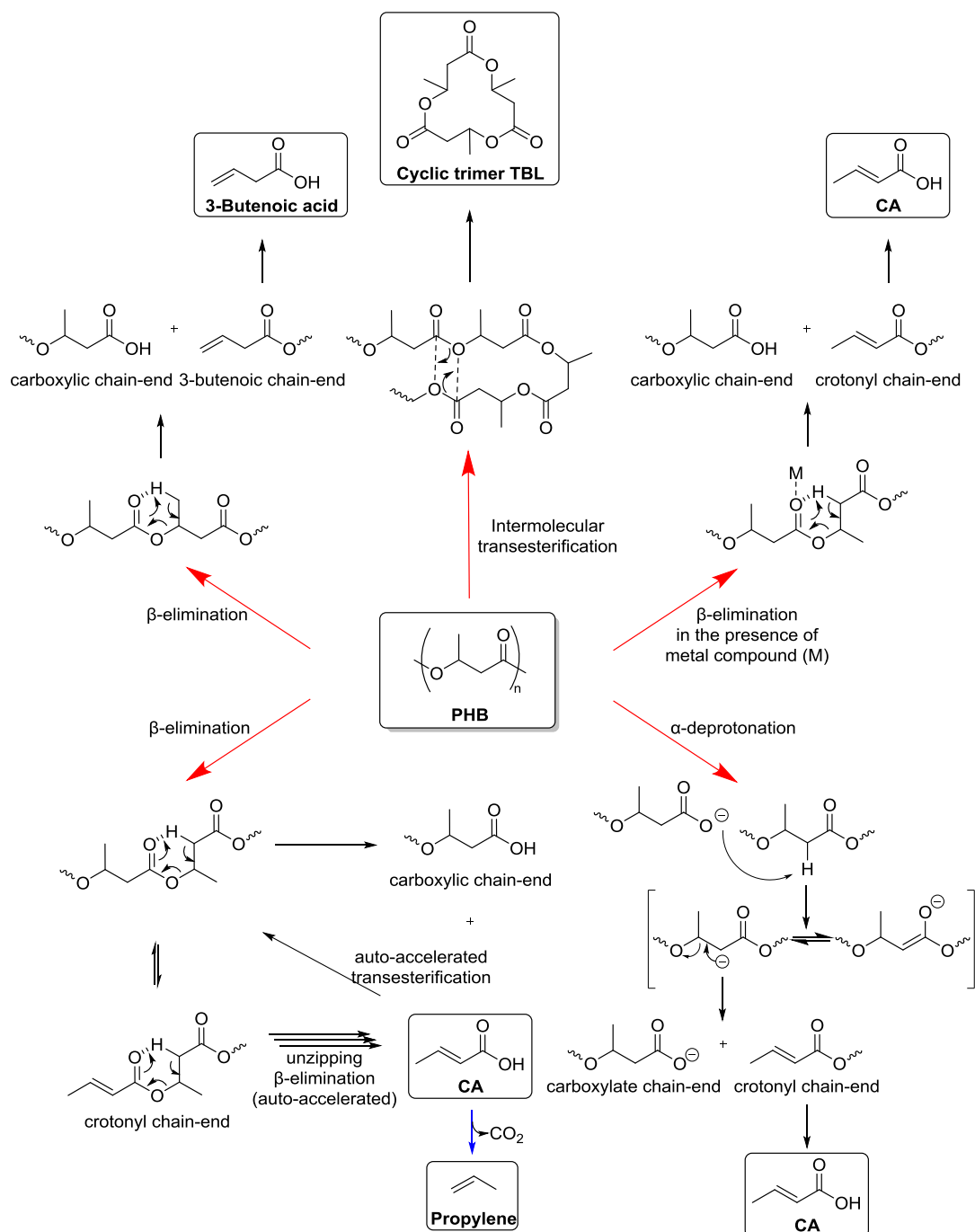
Fig. 4. Analytical techniques commonly implemented for monitoring the chemical recycling of PHAs and characterizing the resulting products.

2.1 Catalyst-free pyrolysis of PHA homopolymers

Typically, PHB, whether it is microbial (T_m ca. 180 °C), biosynthesized or synthesized, is unstable above 160 °C with a thermal decomposition temperature ranging from ca. 225-350 °C. This results in a drastic reduction of its molar mass during melt processing, while significant formation of volatile degradation products is observed above 200 °C. Crude natural PHB derived from biomass is typically less thermally stable than the purified sample (decomposition temperature ca. 235 °C vs ca. 290 °C,

respectively), and different fermentation conditions provide distinct stabilities. The major pyrolysis product of PHB is crotonic acid (CA, *i.e.*, *trans*-2-butenic acid), but significant amounts of PHB oligomers and isocrotonic acid (*i.e.*, the *cis* isomer of CA) were also detected upon heating the polymer to ca. 300 °C. Secondary products such as propylene, 3-butenic acid, ketene, CO₂, acetaldehyde, etc., were also formed by further decomposition of the primary degradation products.

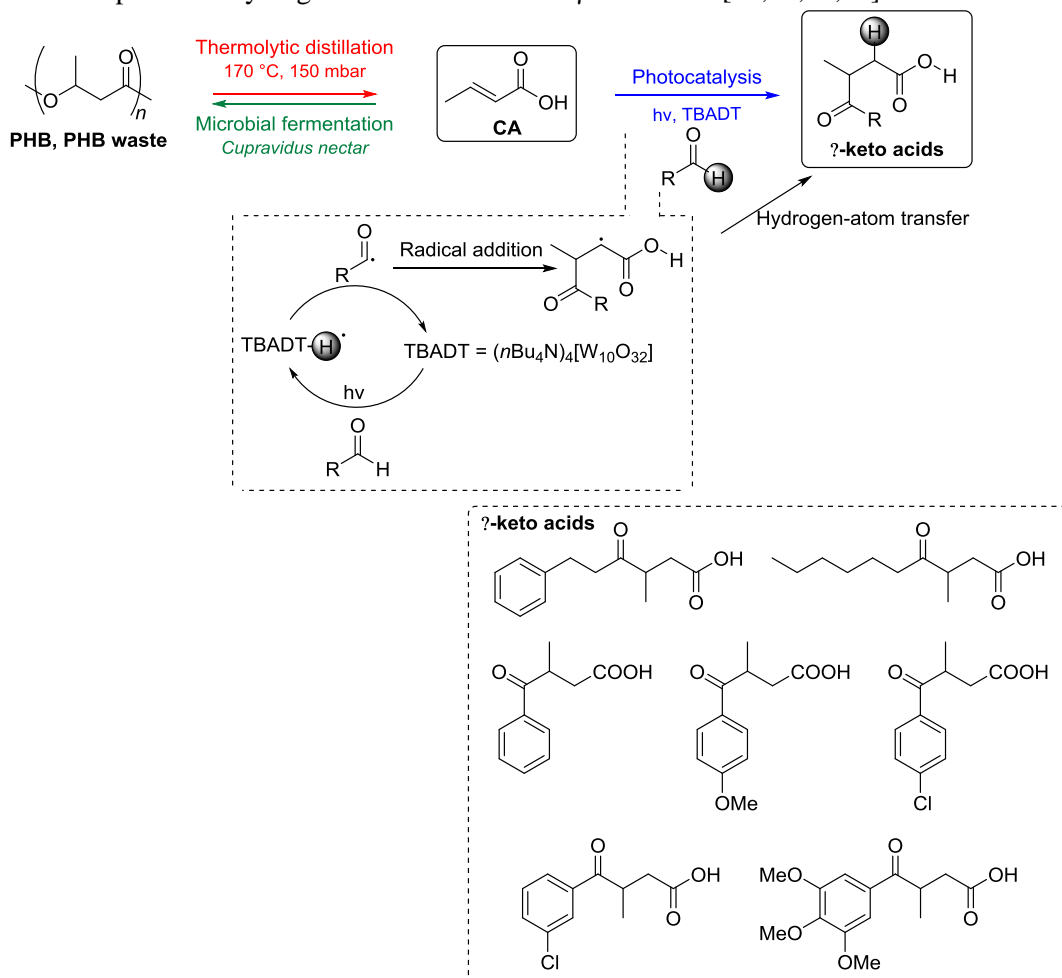
The PHB degradation mechanism has been mainly investigated upon monitoring the decrease of the molar mass over time at different temperatures, and based on the analyses of the main pyrolysis products (CA and oligomers with crotonate and/or carboxylic acid end-groups) (Scheme 1). The degradation behavior of PHB is quite complex, resulting from the contribution of both an auto-catalytic thermal random degradation induced by the β -elimination at the early stage with subsequent auto-accelerated transesterification reactions induced by the formed CA throughout the middle period, along with kinetically favored chain scission reactions occurring at crotonate chain-ends of the formed oligomers. A carboxylate anion mediated α -deprotonation mechanism giving the same product, was also suggested. Unzipping reactions involving ester groups neighboring the crotonate end-groups of the latter oligomers and generating a large amount of CA, were suggested to rationalize the zeroth-order weight loss process. The mechanism is generally accepted to proceed through a transient six-membered ring arising from two neighboring monomeric units of the PHB backbone, resulting in one carboxylic acid and one unsaturated end-groups. The simultaneous or sequential degradation of the oligomers then generates CA. The transient structure is predominantly formed at a temperature around or above the PHB melting point (ca. 180 °C), a temperature at which the PHB backbone is prone to form the planar six-membered ring structure. The activation energy (E_a) of PHB degradation was typically reported in the broad 110–550 kJ/mol range.[65,66,67,68,69,70,71,72,73,74,75,76,77] More recently, propylene, a major commercial hydrocarbon, was obtained in good yields (up to 75mol%) from the depolymerization of PHB performed at 170-250 °C and subsequent decarboxylation of CA, with limitations to the process arising from the rate-limiting decarboxylation step of CA. Investigation by density functional theory (DFT) calculations of the energetics of the PHB depolymerization and the gas-phase decarboxylation of CA, first provided an average E_a value for the cleavage of the RC(O)O–R linkage as 163.9 ± 7.0 kJ mol⁻¹. However, the aforementioned intramolecular auto-acceleration of ester bond cleavage, suggested to occur during the depolymerization of PHB from nearby carboxylic and crotonyl end-groups of fractured PHB oligomers, could not be confirmed by these latter computational insights. On the other hand, these DFT computational results suggested that intermolecular catalysis involving terminal carboxylic groups, showing an E_a of about 20 kJ mol⁻¹ lower than that for the non-catalyzed ester cleavage (144.3 ± 6.4 kJ mol⁻¹), may accelerate the PHB depolymerization. Kinetic models then established that the decomposition of CA proceeds through the initial isomerization of CA to vinylacetic acid which more readily decarboxylates, and that water and likely similar homogeneous catalysts cannot improve the PHB-to-propylene rate of conversion. Finally, the decarboxylation of CA was predicted to follow second-order kinetics with an E_a of 147.5 ± 6.3 kJ mol⁻¹, consistent with the value measured experimentally, 146.9 kJ mol⁻¹. Ultimately, these results indicated that the direct conversion of PHB to propylene should be improved upon facilitating the CA isomerization to vinylacetic acid.[78]



Scheme 1. Overall PHB thermal degradation pathway.

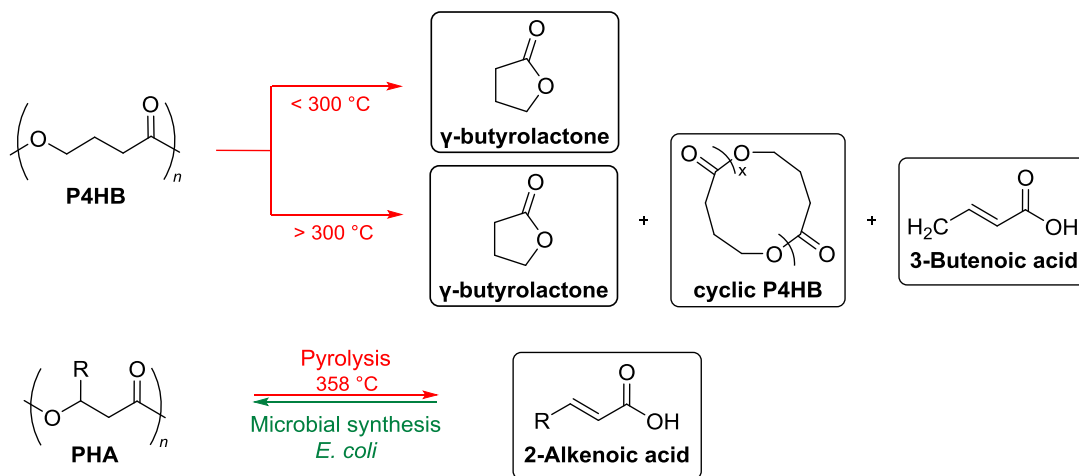
Furthermore, CA was selectively produced from the thermolytic distillation of bacterial PHB (PHB or PHB inclusions inside bacterial cells; $M_{n,SEC} = 800$ kg/mol, $D = 5.9$) under mild optimized conditions (170 °C, vacuum at 150 mbar) with high selectivity (typically up to 98%) in high yield (typically 94%) (Scheme 2). This thermolysis route to CA established a green alternative to the oxidation from crotonaldehyde, avoiding the use of aggressive bases or nucleophiles. CA was next successfully recycled into bacterial PHB ($M_{n,SEC} = 1500$ kg/mol, 60wt% PHB) in an overall tandem “thermolytic distillation-microbial fermentation” process with a 55% overall isolated yield. A recent preliminary evaluation also further unveiled the lower energy consumption (20–25% less) of this thermolytic distillation as compared

to various depolymerization methods, with an acceptable energy demand of 4 MJ/kg(CA) for producing CA from PHB-waste with 50% moisture, in comparison to the 4.4 MJ/kg(sugar) energy that is required to obtain fermentable C-feedstock sugars to be used to feed bacteria that accumulate PHB. It is especially relevant given that CA, as a β -methyl substituted acrylic acid, bearing both a reactive double bond and a carboxylic group, provides access to other useful monomers. This latter technically simple circular approach to PHB thus provides a valuable recycling method of PHB. Such a straightforward cradle-to-cradle strategy thus represents a promising end-of-life management of PHAs waste, further limiting our dependence on virgin C-sources like sugars feedstock. Another study reported that, the mild pyrolysis of blends of switch grass and PHB, which mimic PHB-producing switch grass lines, performed in a pilot scale fluidized bed reactor in the range of 350 to 375 °C, simultaneously returned a switch grass-based bio-oil enriched in CA (yield maximized at 45wt% of the input PHB) and bio-char. Furthermore, the photocatalytic addition of aliphatic or aromatic aldehydes to CA (previously formed from thermolytic distillation), triggered by tetrabutylammonium decatungstate (TBADT; known to cleave the C(=O)–H bond in aldehydes) under solar-simulated light irradiation, induced the hydroacylation via radical conjugate addition, thus generating valuable γ -keto acids in high yield (58-89%, as racemates). Notably, the functionalization of such bio-based CA by photocatalyzed acylation reactions, provides a novel thermochemical-photo catalytic green route to valuable γ -keto acids.[79,80,81,82]



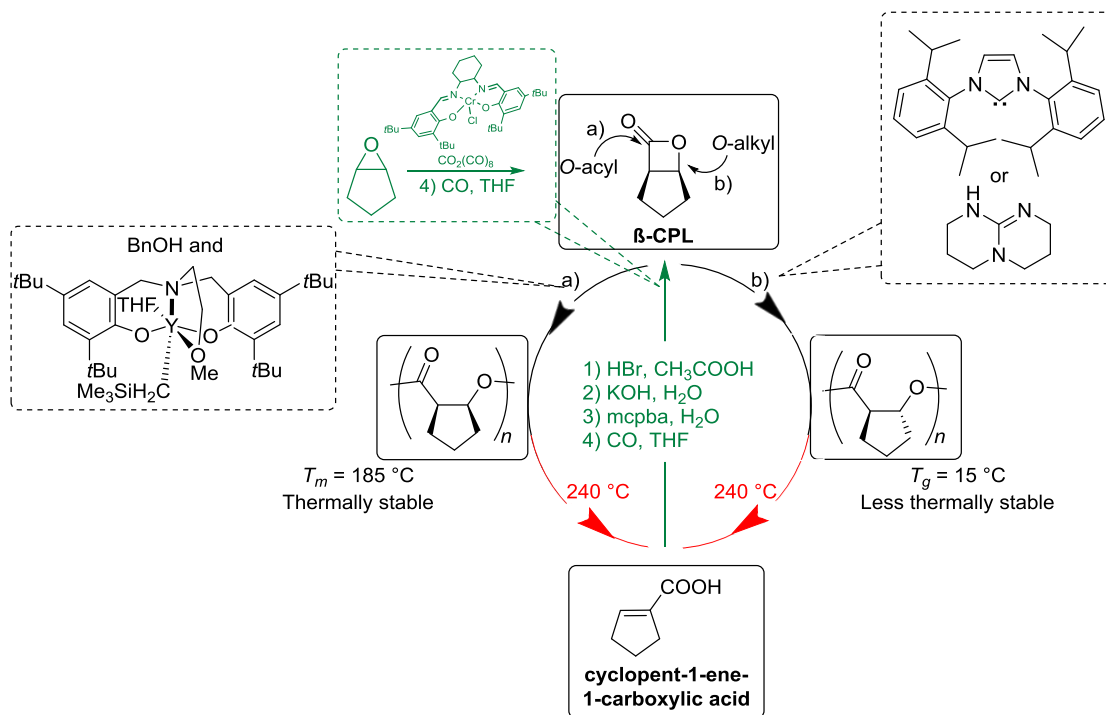
Scheme 2. Thermolytic distillation of PHB into CA and subsequent microbial fermentation of CA back to PHB, and photocatalytic synthesis of γ -keto acids from bio-based CA.

Investigation of the thermal degradation behavior of bacterial poly(4-hydroxybutyrate) (P4HB; $M_{n,SEC} = 125,000$ g/mol) by ^1H NMR, thermogravimetry and pyrolysis-GC-MS, revealed two distinct processes taking place at temperatures below and above 350°C (Scheme 3). At lower temperatures ($< 300^\circ\text{C}$), unzipping reactions from the ω -hydroxyl chain-end predominantly occurred to form γ -butyrolactone selectively, while at higher temperatures, the *cis*-elimination reaction at the ester bond of 4HB unit (resulting in the formation of olefinic unit) and the formation of cyclic P4HB via intramolecular transesterification both occurred along with unzipping reactions from the ω -hydroxyl chain-end. Finally, at temperatures above 350°C , the thermal degradation of P4HB proceeded by the cyclic rupture via intramolecular transesterification of P4HB along with the release of γ -butyrolactone as volatile product.[83] In a similar approach, pyrolysis of poly(3-hydroxydecanoate) ($220\text{--}670^\circ\text{C}$), a PHA biosynthesized from 2-decenoic acid, dominantly regenerated back its 2-alkenoic acid, thereby exemplifying a closed-loop cycle for a medium chain length PHA.[84]



Scheme 3. Pyrolysis of bacterial P4HB and medium-chain length PHAs, and chemical recycling of medium-chain length PHAs via 2-alkenoic acids.

Recently, the ROP of a β -lactone fused with a five-membered ring at α - and β -positions, namely *cis*-6-oxabicyclo[3.2.0]heptan-7-one (β -CPL) - previously synthesized from the ring-expansion carbonylation of cyclopentene oxide -, was reported from several organic or metallic catalysts, to afford a PHA with linear and/or cyclic topologies. Pyrolysis of the returned poly(β -CPL) ($M_{n,SEC} = 7400$ g/mol, $D = 1.30$) at 240°C under nitrogen atmosphere quantitatively formed α,β -unsaturated carboxylic acid through the random chain-scission of the polymer, rather than regenerating the β -lactone monomer as impeded by the ring strain of the four-membered ring lactone (Scheme 4). The rate of pyrolysis of *trans*-poly(β -CPL) was found more rapid than that of *cis*-poly(β -CPL) (isolated yield: 96% in 6 h vs 88% in 12 h, respectively), thus offering a thermally robust PHA with a *cis*-structure. Transformation of the α,β -unsaturated carboxylic acid into the β -lactone monomers showcases the recyclability, although the proposed route back to the monomer is far from being green. This thus provides one, yet not straightforward, of the few examples of chemically recyclable PHA.[85]



Scheme 4. Multistep chemical recycling of poly(β -CPL), prepared from the regioselective ROP of *cis*-6-oxabicyclo[3.2.0]heptan-7-one (β -CPL), via the corresponding cyclopent-1-ene-1-carboxylic acid.

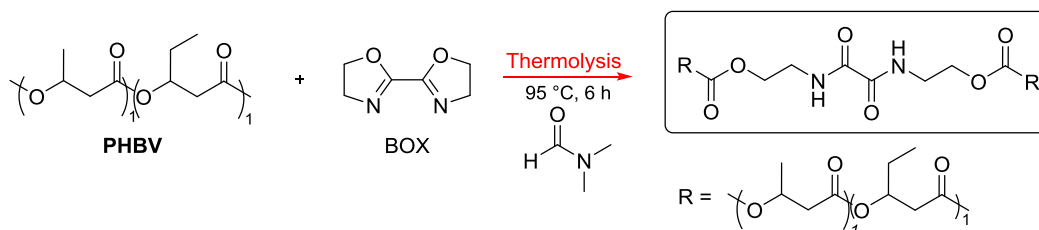
2.2 Catalyst-free pyrolysis of PHA copolymers

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), namely P(3HB-*co*-3HV) or PHBV (3-hydroxybutyrate (3HB); 3-hydroxyvalerate (3HV)), is the most common industrial PHA copolymer. However, it is unstable during melt processing at a temperature above the melting temperature, thereby limiting its practical application as a commodity material. Thus, PHBV (HV = 0-71mol%), as well as P(3HB-*co*-4HB) (4HB = 0-82mol%) copolymers obtained from microbial synthesis, were reported thermally stable up to 160 °C, with a marked drop in molar mass at 170 °C.[86] The time-dependent change in molar mass during the thermal degradation followed the afore-mentioned kinetic model of random chain-scission at ester groups induced by the β -elimination and α -deprotonation. This latter process was found independent on the composition of the copolyesters, yet strongly correlated to the temperature. Mechanistic insights gained from detailed ^1H NMR, MS, pyrolysis GC-MS, TGA and SEC analyses supported the formation of ω -crotonate end-capped PHB oligomers. Typically, the degradation temperature of PHBV decreased with larger 3HV content. These copolymers thus revealed suitable for injection molding (24-71mol% 3HV) and applicable to conventional plastics processing methods such as blown-film processing. More recently, kinetic insights into the thermal degradation behavior of P(3HB-*co*-4HB) (4HB = 16mol%) confirmed that it varies with time and/or temperature, and that it proceeds in at least two steps, with first the initial random degradation and the subsequent zeroth-order weight loss, which indicated unzipping degradation of the 3HB units.[69,75,83,87,88,89,90,91,92,93,94,95]

The pyrolysis of PHBV gives crotonic acid (CA, up to 63%) and 2-pentenoic acid (2PA) as the main pyrolyzates, originating from 3HB and 3HV monomers, respectively. While CA can be further industrially valorized as poly(CA) within adhesives, coatings, binders, paints, textiles, agrochemicals herbicides or cosmetics,[96] the esters of 2PA can be used in flavoring essences or in biomedical applications.[97,98] Establishing a bio-based pathway, easier than their actual complex production routes, would enhance the market of these latter unsaturated carboxylic acids. These two acids were shown to be successfully separated through spinning band distillation operating under reduced pressure (50 mbar,

40–110 °C, for about 5 h). CA with a high purity of > 98% was thus recovered from a synthetic mixture of the two acids with a CA/2PA mass ratio of 80:20, while decreasing the CA/2PA ratio to 54:26 still enabled to isolate 93% of CA. Taking into account that PHB uses are currently limited by its brittleness and thermal instability, the use of PHB or PHB-waste for the production of CA, offers a new route to PHB applications, as an alternative to the petrochemical and more complex one. It was predicted that about 982 ktons of CA could thus be annually produced from pyrolysis of 1.56 Mtons of PHB.[99,100] Correspondingly, the pyrolysis of polyethylene/PHBV blend films (80:20, 70:30), used for packaging for their oxygen-barrier efficiency, performed at 310 °C for 30 min under vacuum, revealed that the PHBV fraction was completely degraded into its volatile dehydrated oligomers (< 24%) and monomers - mainly *trans*-CA (ca. 67%) along with *cis*-CA (< 3%) and 2PA (<7%). This suggests that PHBV can be recycled from such a mixture of polymer wastes, without any PE contamination. This illustrates another advantage of using PHA in packaging and more generally of strengthening the application of PHAs as sustainable plastics on their own, as they could be separated from the omnipresent polyolefins family among commodity plastics.[101]

Overall, due to their thermal instability above ca. 170 °C, that is correlated to the rapid decrease of their molar mass, PHA homopolymers (PHB, poly(3-hydroxyoctanoate) (PHO), poly(3-hydroxyhexanoate) (P3HHx) and their related copolymers, which feature different pending substituents such as alkyl, epoxide, vinyl or hydroxyl groups (P(3HB-*co*-3HV), P(3HB-*co*-4HB), P(3HB-*co*-3HO), P(3HB-*co*-3HP), P(3HB-*co*-3HHx), poly[(3-hydroxyoctanoate)-*co*-(undec-10-enoate)] (PHOU), poly[(3-hydroxyoctanoate)-*co*-(10,11-epoxyundecanoate)] (PHOE), poly[(3-hydroxyoctanoate)-*co*-(10-enoate)] (PHOD)), feature a notably narrow temperature processing window. Incorporation of 3HV (30mol%) or 3HHx (15mol%) into PHB increases the various thermal temperatures (onset temperature of mass loss, temperature at which the mass loss reached a maximum, and the temperature at which degradation was completed) by 3–12 °C relative to those of PHB. PHA copolymers bearing alkyl pendant units decompose in a similar one-step process as PHB. On the other hand, PHO and PHOU flanked with longer average side chains display higher activation energies on their thermal degradation, possibly arising from the steric bulkiness on the formation of six-membered transition structure. PHOE, the partially epoxidized product of PHOU, exhibit a different decomposition profile and is more thermally stable, possibly due to thermal crosslinking between the epoxide and either carboxylic acid or hydroxyl groups, formed during the decomposition reaction. Finally, PHOD, the partially hydroxylated product of PHOU, was found less thermally stable, most likely arising from its side-chain hydroxyl groups which attack the ester linkage in the main chain, acting as nucleophiles.[65-94,102,103,104] Similarly, to improve the thermal stability of PHBV, 2,2'-bis(2-oxazoline) (BOX) was chemically inserted into its backbone so as to better limit the formation, during thermal degradation, of the above-depicted six-membered ring ester (Scheme 5).[105] The optimal reaction temperature and reaction time to thermally degrade this PHBV/BOX were established as 95 °C and 6 h, respectively. As the result of a decrease, both in the negative inductive effect of the neighboring group of methylene groups at the β -position to the ester oxygen, and in the electron-donating effect of substituent group of carbon atoms in α -position of the ester oxygen, the resulting α -hydroxy telechelic PHBVs showed a better thermal stability than the original PHBV, with the initial decomposition temperature thus being raised by 24 °C.



Scheme 5. Chemical modification of PHBV with 2,2'-bis(2-oxazoline) (BOX) to improve its thermal degradation.

Noteworthy, the microwave irradiation performed in the bulk (180-220 °C; 2 GHz, 900 W, up to 15 min) of PHBV (12mol% HV; $M_{n,SEC} = 84,000$ g/mol, $D = 2.4$), or PHOHHx (15mol% HHx; $M_{n,SEC} = 130,000$ g/mol, $D = 1.5$), resulted in their thermal degradation into oligomers ($M_{n,SEC} < 8000$ g/mol; > 94% in 1 s) end-capped with a crotonate and a carboxylic groups. This treatment revealed 100 times faster than the traditional pyrolysis at 190 °C.[106]

3. Solvolysis of PHAs

Chemical recycling of PHAs via solvolytic bond cleavage at ambient to high temperature can be performed in various solvents resulting in degradation or depolymerization into the monomer(s), oligomers or other chemicals. Hydrolysis (using water) or alcoholysis (using an alcohol) of the ester bonds are homogeneously catalyzed processes typically implemented to degrade PHAs. The chemical process as well as the nature of the recovered products are monitored and investigated by various analytical tools, classically including SEC, NMR, FTIR, MS, thin-layer chromatography (TLC), high performance liquid chromatography (HPLC), GC, DSC (Fig. 3, 4).

3.1 Hydrolysis of PHAs

Although PHAs are most commonly water-insoluble, hydrolysis of PHAs remains the simplest, most easily accessible chemical route to implement in order to promote PHAs degradation. It takes place upon the simultaneous diffusion of H₂O into the polymer material and the hydrolysis of the ester bond itself.[18] PHAs hydrolytic degradation has been commonly investigated from solution-cast films (yet also from thread or micro-spheres) in a buffer solution at various pH and/or temperatures. The rates of PHAs hydrolytic degradation essentially vary with the macromolecular features of the (co)polymer, especially the chemical nature of the repeating unit(s), the molar mass and microstructure (*i.e.*, tacticity and related crystallinity) of the polymer, the thickness of the films and the shape of the sample, and also with the experimental conditions, especially the temperature and pH. Although the chemical nature of the resulting degradation products of PHA hydrolysis was not systematically addressed, PHB was shown to hydrolytically degrade into PHB oligomers/fragments and ultimately into CA and 3-hydroxybutyric acid (3HBA) as essentially monitored and established by NMR, FTIR spectroscopy, GC, MS and SEC analyses. Typically, the hydrolytic degradation of PHAs can be enhanced with a higher temperature and/or a more alkaline hydrolytic medium, as both of these promote the solubility of the degradation products.[107,108,109]

3.1.1 Hydrolysis of PHAs at neutral pH

At neutral pH (7.4), the very slow degradation of bacterial isotactic PHB films (poly[(*R*)-3HB], $M_{n,SEC} = 300,000$ g/mol, $D = 2.2$) was reported after 150 days at 37 °C in potassium phosphate buffer (0.01 M), as hardly any weight or molar mass change was recorded. In comparison, a poly(*R,S*-lactide) (PLA, atactic, $M_{n,SEC} = 9000$ g/mol, $D = 2.3$) film degraded more rapidly (ca. 83% weight loss) under the same conditions. Upon blending PHB with such PLA, the hydrolytic chain scission of the PHB occurred more rapidly, as promoted by PLA oligomers. Similarly, from this blend, poly(L-lactide) (PLLA) degraded more rapidly than PHB. While the addition of amorphous atactic (synthetic) PHB ($M_{n,SEC} = 9100$ g/mol, $D = 1.1$) to bacterial isotactic PHB ($M_{n,SEC} = 305,200$ g/mol, $D = 2.1$) enabled to accelerate this relatively slow hydrolysis of PHB – characterized by a half-life in molar mass loss of about 12 months at neutral pH –, the addition of PHB oligomers ($M_{n,SEC} = 2000$ g/mol, $D = 1.5$) did not improve the degradability. On the other hand, addition of a hydrophobic plasticizer such as butyryltriethyl citrate slowed down the hydrolytic degradation, while the water-soluble triethyl citrate plasticizer slightly speeded it up. Amorphous or hydrophilic additives thus prompted the rate of PHB hydrolysis upon promoting water uptake into the polymer matrix. As above-mentioned, hydrolysis is highly dependent on

the tacticity (crystallinity) of the polymer, occurring preferentially in amorphous regions. Thus, bacterial isotactic PHB, due to its higher crystallinity, displayed a slower degradation in comparison to atactic synthetic PHB, while PHBV (10mol% 3HV) which is less crystalline than natural PHB, showcased an intermediate degradation rate at pH = 7.4 in phosphate buffer at 70 °C.[110,111,112,113]

The abiotic hydrolysis of microbial PHBV ($M_{n,SEC} = 22,000\text{-}768,000$ g/mol, $D = 1.9\text{-}3.4$) solution-cast films was further investigated at pH = 7.4 in aqueous phosphate buffer (0.01 M) at 55 °C. The weight of the copolyesters remained unchanged over 58 days highlighting the absence of polymer erosion, while the molar mass value decreased over time supporting a random chain scission of the ester groups. In this case, the rate of hydrolytic degradation was found to depend on the composition (and not on the crystallinity) of copolyesters with P(3HB-co-4HB) (10-27mol% 4HB) films typically degrading faster (rate constant $k_d = 8.3\text{-}17.0 \times 10^{-6}$ /day) than PHBV (45-71mol% 3HV) films ($k_d = 2.3\text{-}4.5 \times 10^{-6}$ /day).[114] In a related study, the hydrolytic degradation of PHB ($M_{n,SEC} = 170\text{-}1000$ kg/mol) and PHBV (20mol% 3HV, $M_{n,SEC} = 1100$ kg/mol) films was investigated, in comparison to PLLA ($M_{n,SEC} = 67\text{-}400$ kg/mol) or PHB/PLLA blend (1:1 weight ratio) over 3 months at physiological (37 °C) or elevated (70 °C) temperatures, at pH = 7.4 in phosphate buffer. Higher molar mass PHB samples displayed better hydrolytic stability as compared to lower molar mass analogues. On the other hand, introduction of 3HV units into PHB resulted in a better hydrolytic stability of PHBV; the larger the hydrophobic 3HV content, the lower the degradation rate. PHBV films thus revealed the most stable, with only 4wt% loss recorded in 95 days. The poor stability of PLLA relative to PHB, as above mentioned, was again demonstrated.[115] The degradation was proposed to proceed stepwise, with PHB fragments being, in the first stage, too large and too hydrophobic to diffuse from the polymer matrix into aqueous media, while in the second stage, when the molar mass PHB intermediates has sufficiently dropped reaching ca. 30,000 g/mol, PHB moieties then dissolve and diffuse out from the polymer into the aqueous medium. The overall trend in hydrolytic stability of these polyesters followed the order: PHBV > PHB > PHB/PLLA blend > PLLA. In this regard, the most stable high-molar mass PHB or PHBV copolymer become appropriate for application in living systems or as the packaging barriers.

In another study, the correlation between the temperature and the hydrolysis rate was investigated on PHBV samples (8mol% 3HV, $M_{n,SEC} = 172,600$ g/mol, $D = 2.3$) in distilled water at 25, 30, 40 and 50 °C. Despite the high crystallinity of PHBV (> 60%), heating confirmed the faster degradation as the result of fostered water penetration, leading to hydrolytic cleavage of the ester bonds, as evidenced by decreased molar mass values. Typically, a reduction of the molar mass of 30 and 40% was recorded at lower immersion temperatures (25 and 30 °C) over 1 year, respectively, while raising the temperature to 40 °C resulted in a drop of about 55% and 70% in 4 and 12 months, respectively. The two-stage profile of the diminution of the molar mass was attributed to water penetration within the amorphous domains followed, by a very slow water attack of crystalline regions. This study provided a tool to assess the lifetime of PHBV materials in distilled water, within the assumptions of this approach.[116]

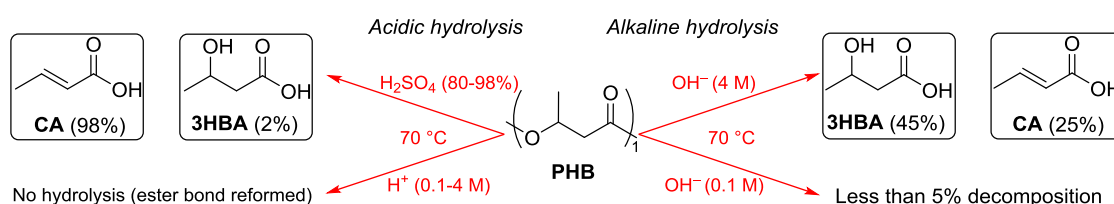
The hydrolytic degradation of PHA homopolymers, distinct from PHB, has been rarely reported. For instance, incubation of bacterial poly(3-hydroxyoctanoate) (PHO) solution-cast films in water or isoosmotic phosphate-buffered saline (0.13M; pH = 7.4) revealed a very slow hydrolysis. This degradation was accompanied with water absorption, a negligible mass loss (< 1wt% in 24 months), and a gradual molar mass decrease, as imparted by the long hydrophobic pendant alkyl side chains. The amorphous regions were found to degrade much more rapidly than the crystalline domains. Also, the degradation was shown to progress from the inside to the outer surface of the PHO films, as monitored by FTIR analyses. Overall, the degradation proceeded faster in phosphate-buffered saline than in water, being promoted by the ionic strength of the medium.[117,118]

More recently, an hydrothermal treatment at subcritical (300°C) and supercritical (375 °C) conditions was successfully applied to PHA-containing sludge (PHA content of 13wt%), to convert most

(> 70wt%) of the bacterial PHA into a high yield of CO₂/alkenes (especially propylene) gas mixtures with high selectivity.[119]

3.1.2 Acidic or alkaline hydrolysis of PHAs

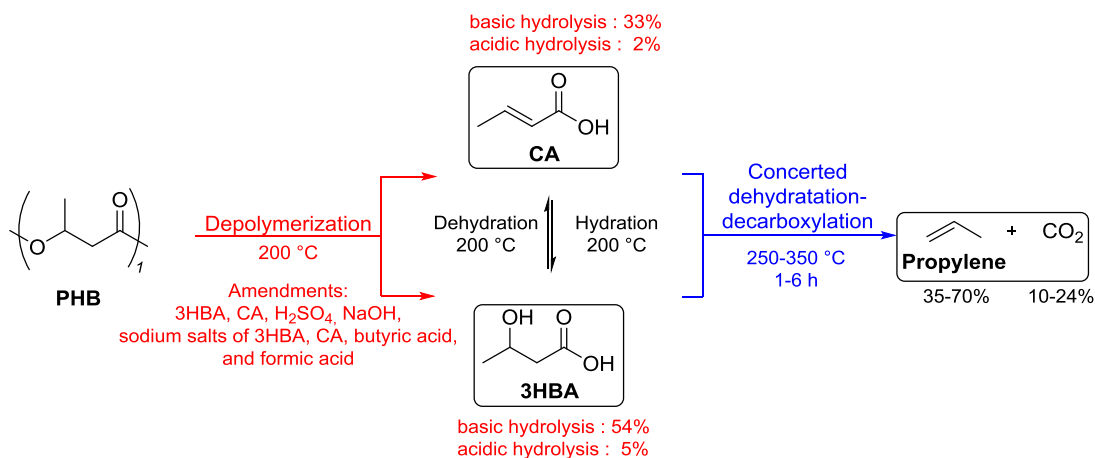
As described above, PHAs hydrolysis at room temperature is rather slow in a close-to-neutral or neutral medium. Changing to acidic or alkaline aqueous media revealed faster kinetics. Indeed, PHB was found tolerant to abiotic hydrolysis (measured by HPLC) under acidic conditions (0.1-4.0 M H⁺), but susceptible to alkaline conditions (0.1-4.0 M OH⁻) (Scheme 6). Poly[(*R*)-3HB] abiotic hydrolysis increased from 5% to 70% when NaOH concentration was increased from 0.1 to 4.0 M at 70 °C. The two major compounds recovered from the alkaline hydrolysis were CA, 3HBA and Me3HB (Fig. 3). In this earlier study, crotonate was shown not be formed by dehydration of 3HBA after hydrolysis - as supported by the parallel increase in 3HBA and CA content over time -, nor by dehydration of 3-hydroxyl groups before hydrolysis, but most likely via a transient six-membered ring involving two neighboring 3HB units. Kinetic insights revealed that hydroxyl anions (OH⁻) very efficiently lowered the *E*_a of PHB hydrolysis. The mass ratio (CA/3HBA = 0.42-0.68) increased with temperature because of the different activation energies, 88.4 kJ/mol and 78.9 kJ/mol for CA and 3HBA formation, respectively. On the other hand, exposure of poly[(*R*)-3HB] to highly concentrated acid solutions (80-98wt% H₂SO₄) generated essentially CA (90% CA, 2% 3HBA) as assessed by UV-visible and ¹H NMR spectroscopies.[120,121,122] More recently, a related work similarly confirmed the concentration- and temperature-dependent kinetics of the alkaline hydrolysis of PHB (*M*_{n,SEC} = 100,000 g/mol) films. The larger the NaOH concentration, the greater the extent of weight loss (2.0, 1.5, 1.0 M; 35%, 26%, 20%, respectively, at 30 °C, 90 h), and degradation proceeded faster at 40 °C than at 30 °C. Furthermore, weight loss monitoring revealed that higher crystallinity of PHB greatly reduced its hydrolytic degradation ability, suggesting that diffusion of hydroxyl ions and the resulting degradation predominantly took place at the surface of the films irrespective of the microstructure, and within the amorphous phase. No significant change in crystallinity was observed upon degradation, as evidenced by time-dependent FTIR spectroscopy. Amorphous PHB was also shown to degrade 30 times faster than its crystalline analogue.[121,123] Another similar study showed that both PHB (*M*_w = 279,000 g/mol) and blended PHBV (20mol% 3HV) samples underwent faster surface hydrolysis in alkaline hydrolytic medium, with complete degradation after 20-30 days (pH = 13, 10, respectively) as compared to minor degradation (10-35% weight loss) in 50 days at pH = 7.4.[124] On the other hand, 92% of a PHB specimen exposed to a concentrated sulfuric acid solution (80-98% H₂SO₄) at 70 °C for up to 14 h, completely decomposed into 3HBA (2%) and CA (98%). The time course of 3HBA indicates that the concentrated acidic solution dehydrates 3HB into CA.[121,125]



Scheme 6. Acidic and alkaline hydrolysis of PHB into CA and 3HBA.

Recent work reported on the hydrothermal depolymerization of waste-water derived PHB was performed in condensed deionized water with different initial reactant loadings (PHB 0.1–1 M) and amendments (acid (H₂SO₄), base (NaOH), sodium salts of carboxylic acids (3HBA, CA, butyric acid, formic acid)). Temperatures ≤ 220 °C (autogenous pressure of ca. 2.3 MPa) resulted (2 h) in a mixture of CA and 3HBA ([3HBA]:[CA] = 2.1-3.1), while longer reaction times and/or higher temperatures (250-

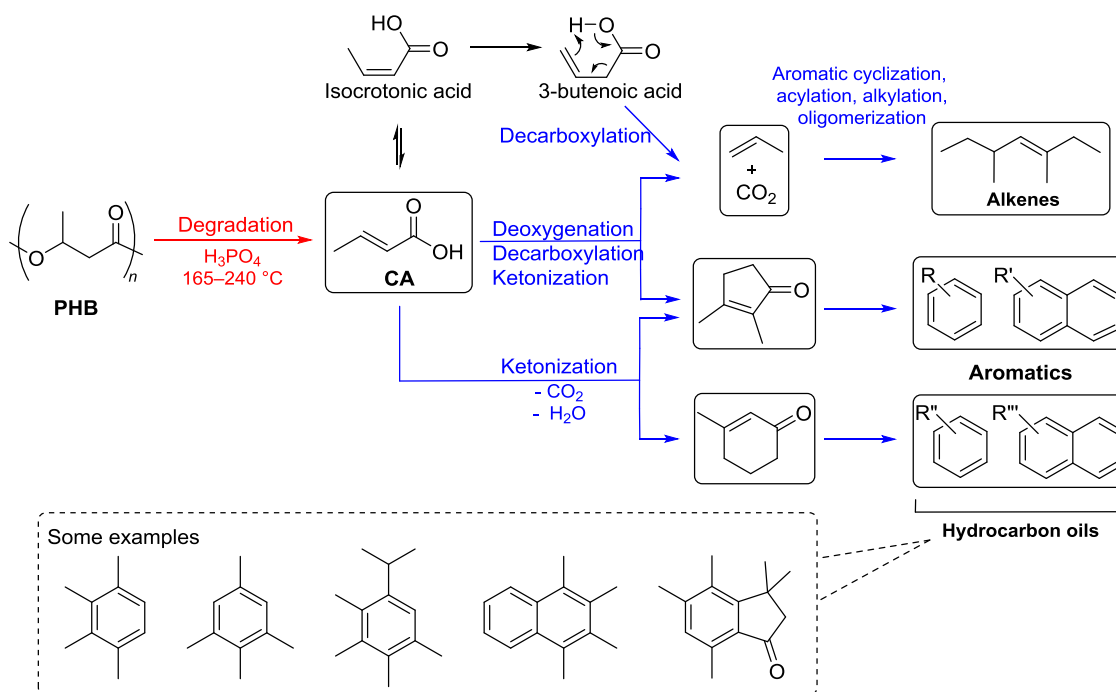
350 °C, 1-6 h) further converted the latter two acids into CO₂ and propylene – a valuable chemical intermediate for the production of liquid fuels that self-separates from water. 3HBA was found to be converted to propylene at lower temperatures and at faster rate than CA. The aqueous reaction medium was shown to significantly impact on the selectivity of PHB depolymerization, independently of the initial PHB loading or reaction temperature. While 3HBA was mainly recovered in water without amendments or with addition of inorganic acids, addition of a mineral base reversed the selectivity with CA then being the major product formed. Hence, the 3HBA/CA ratio could be controlled by adding acids. A new pathway for the PHB hydrothermal depolymerization into a mixture of CA and 3HBA that would next dehydrate and decarboxylate into propylene and CO₂, was then proposed based on kinetic insights. CA conversion to propylene/CO₂ would then proceed mainly through hydration to 3HBA (≥ 200 °C), followed by a suggested concerted dehydration-decarboxylation pathway rather than by direct decarboxylation of CA, a pathway thus differing from the sequential dehydration of 3HBA to CA and decarboxylation of CA to propylene and CO₂, reported for dry thermal conversion (Scheme 7). These findings shed light on the hydrothermal conversion of PHA-enriched biomass for a sustainable and cost-effective production of CA and especially propylene, from which liquid fuels (*e.g.*, C₆–C₁₂ hydrocarbons via oligomerization) or other higher-value chemicals (*e.g.*, cumene, propanediol) [126,127,128] can be subsequently produced. This would thereby offer a promising strategy for the enhanced valorization of waste-water organic components.[129]



Scheme 7. PHB hydrothermal depolymerization into 3HB, CA and ultimately into propylene and CO₂, via the dehydration-decarboxylation pathway.

In another approach exploiting bioPHB as an effective feedstock for the production of high quality renewable gasoline-grade hydrocarbon oils, PHB ($M_{n,SEC} = 53,100$ g/mol, $D = 2.6$) and its major thermal degradation product, namely the aforementioned CA, were deoxygenated in a simple one-pot reaction using phosphoric acid, a cheap reusable catalyst, at 165–240 °C. On the basis of ¹³C NMR, FTIR and GC-MS analyses, a mixture of gaseous and liquid compounds was recovered from PHB, with both CO₂ and propylene as the major gas phase products along with little CO. A hydrocarbon oil made of a mixture of C₄–C₁₆ alkanes, alkenes, benzene, and naphthalenes, was also recovered from PHB in up to 38wt% yield. The composition and yield of the latter oil were significantly influenced by the concentration of H₃PO₄, with “diluted” solutions (50-85wt% H₃PO₄) favoring the formation of acyclic or cyclic alkenes and alkanes (C₄–C₉), and highly concentrated H₃PO₄ (100wt%) promoting the formation of aromatics (C₁₀–C₁₅). Valuably, the acid solution was shown to be successfully used repeatedly over 6 cycles, thereby enabling high yield oil production. In comparison, the highly efficient decarboxylation of CA at 220 °C for 3 h resulted in 71wt% of oxygen depletion as CO₂ and 57wt% of carbon being recovered as hydrocarbon oil.[130] Investigations of the main sequential reaction routes of this H₃PO₄-catalyzed degradation of PHB, through the key intermediates and up to the final hydrocarbons, suggested that, at

200-230 °C, it proceeds in three steps: first, PHB is decomposed into CA as the major monomeric intermediate, followed by CA deoxygenation (namely decarboxylation and ketonization of CA) into CO₂ and H₂O, and finally by combination of the deoxygenated molecules into the final hydrocarbons. The ultimate main aromatic compounds formed in the last third step arise from the two key intermediates that are propylene and 2,3-dimethyl-2-cyclopenten-1-one, themselves originating from decarboxylation and ketonization of CA, respectively. The various recovered hydrocarbons resulted from multiple reactions including oligomerization, aromatic cyclization and alkylation of propylene, as well as from some acylation involving CA and deoxygenation of the O-containing ketones formed during the degradation (Scheme 8). This proposed degradation pathway further supported that the formation of aromatics is greatly impacted by the H₃PO₄ and H₂O concentrations in the reaction medium, both of which thus provide a handle to tune the composition of hydrocarbon oil.[131]

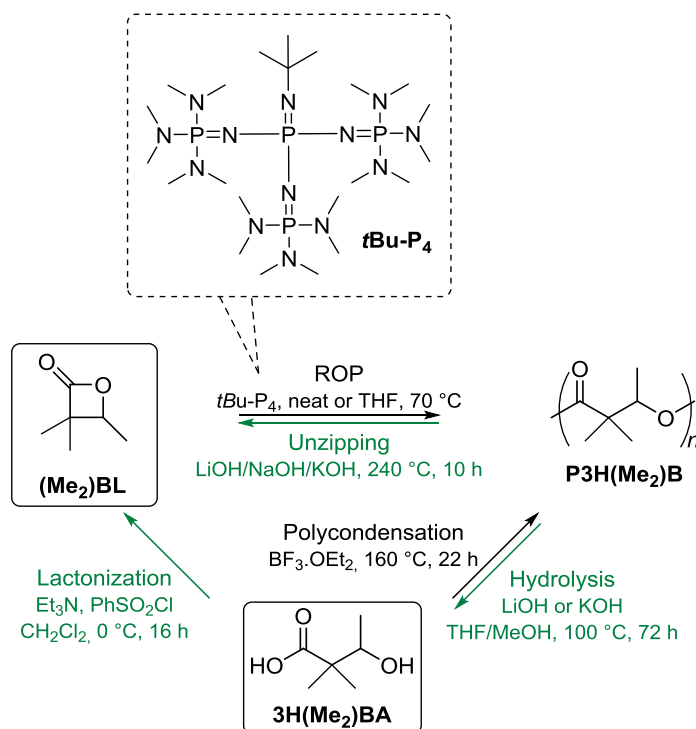


Scheme 8. PHB chemical recycling into hydrocarbon oils.

In order to further probe the role of water in such a bacterial PHB degradation, the aqueous H₃PO₄ solution was replaced by water-free and customizable solid phosphoric acid. PHB ($M_{n,SEC} = 53,100$ g/mol, $D = 2.6$) was thus, in the absence of hydrogen, in a one-pot reaction, similarly degraded, deoxygenated and transformed into CO₂ (gathering ca. 80wt% of oxygen from the decarboxylation of initial PHB), H₂O (7wt%), propylene (7wt%), hydrocarbon oil (C₆–C₁₈, 30wt%) and some char-like solid residues ((C₄H₂)_n, 7wt%), with a total mass recovery of 94wt%. CO₂ and propylene were the major products in gas phase with little CO detected. Remarkably, a crude PHB feedstock of low purity could be used without purification, while the reforming proceeded at a milder temperature (starting at 213 °C and being completed at 240 °C) than that of conventional thermal catalytic treatment of biomass under hydrogen (500-650 °C). The two light- and heavy-hydrocarbon oil fractions separately recovered (23wt%, bp = 40-240 °C and 7wt%, 240-310 °C, respectively) displayed the same elemental composition and high heating value (41.4 MJ/kg and 38.4 MJ/kg, respectively) as an oxygenated commercial gasoline and biodiesel, respectively (41.8 MJ/kg and 39.7 MJ/kg, respectively). Also, both oils returned a high content of alkenes (up to 57%) and aromatics (benzene and naphthalene derivatives, up to 77wt%) depending on the solid phosphoric acid catalyst characteristics (calcination temperature, dosage in the reaction, total acid and

free acid contents, and working time when repeatedly reused). This gasoline- and biodiesel-grade bio-oils thus represent good sources of renewable alkenes and aromatics as promising bio-based alternatives for improved-performance and environmentally friendly fuels for motor engines.[132]

PHAs thermal instability typically arises from the α -hydrogens on the carbon adjacent to the carbonyl group in the PHA backbone that promote the facile *cis*-elimination reaction into an internal alkene and carboxylic acid. Taking this into account, a synthetic PHA platform without such α -hydrogens was recently established (Scheme 9). α,α -Dialkyl substituted PHAs (namely poly(3-hydroxy-2,2-dialkylbutyrate) (P3H(R)₂B with R = Me, Et), were synthesized either by polycondensation of 3-hydroxy-2,2-dimethylbutyric acid (3H(Me)₂BA), or upon ROP of the four membered-ring α,α -dimethyl- β -butyrolactone ((Me)₂BL, previously isolated (92% yield) from the lactonisation of the latter acid 3H(Me)₂BA), catalyzed by BF₃·OEt₂ or *t*Bu-P₄ phosphazene base (1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidene-amino]2 λ^5 ,4 λ^5 -catenadi(phosphazene)), respectively, at temperatures < 160 °C. The resulting PHAs, as exemplified with P3H(Me)₂B, showcased improved thermal stability (T_d = 314-335 °C) and tacticity-independent intrinsic crystallinity (T_m = 167-243 °C), while synergistically combining melt-processability, high ductility and toughness (elongation at break ϵ_b > 200), as compared to the unsubstituted isotactic PHB (T_d = ca 250 °C, T_m = 171-175 °C, ϵ_b = ca 4%). Such performances revealed comparable or even superior to those of *i*PP and high-density polyethylene (HDPE). Rewardingly, simply implementing a base catalyzed process mediated by MOH with M = Li, Na, K (< 5wt%), P3H(Me)₂B was successfully chemically recycled back into its monomer 3H(Me)₂BA (isolated in 99% yield from the depolymerization of P3H(Me)₂B ($M_{n,SEC}$ = 21.9 kg/mol, D = 1.11) in THF/MeOH at 100 °C for 72 h), or α,α -dimethyl- β -butyrolactone ((Me)₂BL, isolated in 60% yield from the depolymerization of P3H(Me)₂B ($M_{n,SEC}$ = 13.1 kg/mol, D = 1.04) at 240 °C for 10 h). Other evaluated catalysts (Mg(OH)₂, KH, CsOH, Ca(OH)₂, Li₂O, LiCl, NaCl, KF, K₂CO₃) remained less effective towards the recovering to (Me)₂BL. These recycled monomers were next shown to reenter a step-growth or chain-growth polymerization cycle, respectively, thus demonstrating the monomer-polymer-monomer closed-loop chemical recyclability of these α,α -dialkylated PHA platform.[133,134]



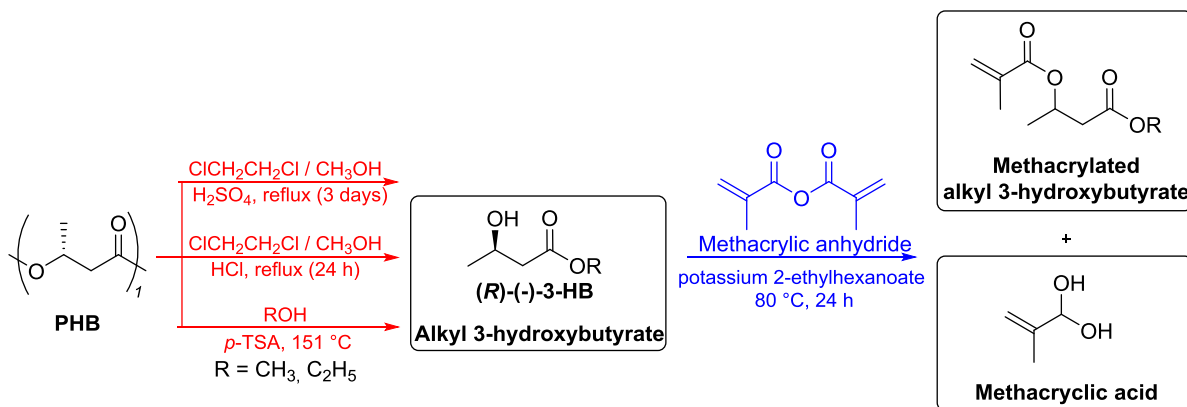
Scheme 9. Synthesis of poly(3-hydroxy-2,2-dialkylbutyrate) (P3H(Me)₂B) by ROP of α,α -dimethyl- β -butyrolactone ((Me)₂BL), or by polycondensation of 3-hydroxy-2,2-dimethylbutyric acid (3H(Me)₂BA), and chemical recycling back to the monomers.

3.2 Alcoholysis of PHAs

A polymer can be depolymerized through alcoholysis when its hydrolyzable bonds are cleaved by a nucleophilic alcohol upon transesterification. While methanol remains the most common alcohol reagent used for such degradation of polymers, including polyesters such as PHAs, both acidic and alkaline alcoholyses have been reported, as well as the use of “greener” or ionic liquid reaction medium.

3.2.1 Acidic alcoholysis of PHAs

Poly[(*R*)-3HB] was efficiently chemically depolymerized to (*R*)-(-)-3HB (93wt% recovered) by acidic alcoholysis using anhydrous hydrochloric or sulfuric acid along with methanol, ethanol or *n*-propanol.[135,136] Further insights into the alcoholysis of PHB catalyzed by *para*-toluenesulphonic acid (PTSA) at 150 °C under high pressure (7-15 bars), revealed that PHB ($M_{n,SEC} = 85,000$ g/mol, $D = 2.49$) depolymerized more rapidly in methanol ($[PHB]_0/[MeOH]_0/[PTSA]_0 = 1:4:0.01$), reaching a rate constant of 0.0103 min⁻¹ and returning methyl 3-hydroxybutyrate (Me3HB) in up to 92% yield in 2 h, as monitored by liquid chromatography (LC)-MS analysis and supported by FTIR, MS, ¹H and ¹³C NMR data. In comparison, the depolymerization performed in ethanol progressed more slowly (same conditions, rate constant 0.0064 min⁻¹) giving ethyl 3-hydroxybutyrate (Et3HB) in 76% yield after 4 h. Subsequent methacrylation of the recovered 3-hydroxybutyrate monoester with methacrylic anhydride produced (catalyzed by potassium 2-ethylhexanoate, at 80 °C for 24 h) the corresponding methacrylated ester (*i.e.*, methacrylated alkyl 3-hydroxybutyrate, > 98% yield), valuable compounds which may next undergo polymerization (Scheme 10).[137]

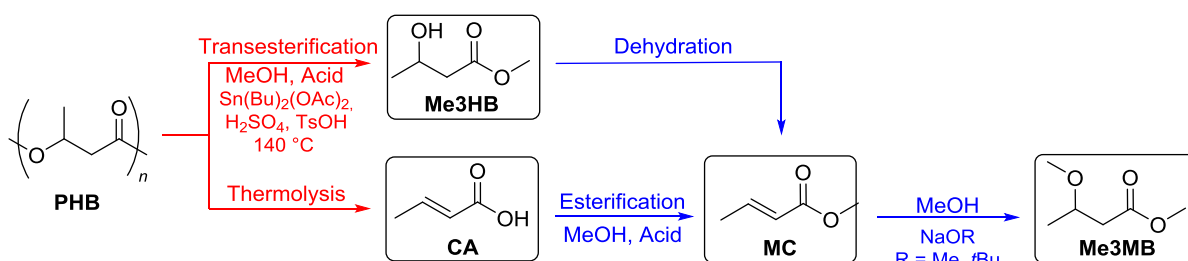


Scheme 10. Acidic alcoholysis of PHB into alkyl 3-hydroxybutyrate.

3.2.2 Acidic or basic alcoholysis of PHAs

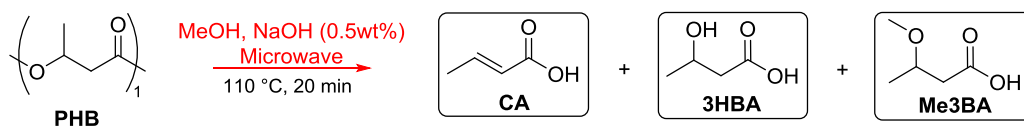
Efforts paid to chemically recycle PHB into Me3HB and methyl 3-methoxybutyrate (Me3MB), was performed using either pure PHB or PHB inclusions obtained from inside bacterial cells, through an acid or base catalyzed methanolysis. Among the various acid catalysts evaluated for the direct preparation of Me3HB from PHB, Sn(Bu)₂(OAc)₂, H₂SO₄, and TsOH, revealed effective (79-95% yield of Me3HB) at 140 °C under autogenous pressure within 7 h, but SnCl₂, CaO, NaOMe, and NaOH, remained inactive. While Me3HB was thus formed from a single-step catalytic methanolysis of PHB in 95% isolated yield, Me3MB was synthesized through a three-step process, successively involving the thermolytic distillation of PHB to give CA (175 °C, 7 h, 150 mbar; 95% yield from PHB), followed by CA esterification into

methyl crotonate (MC) in the presence of a solid acid catalyst (Amberlyst-15H or a sulfonated acidic heterogeneous catalyst derived from potato starch, 130 °C, 7 h; 93% yield), and finally the oxa-Michael addition of MeOH to the MC double bond (3mol% NaOMe, NaOtBu, 23 °C, 50 h) to give Me3MB (ca. 93% isolated yield) (Scheme 11). Thermolysis of PHB to CA is the rate-determining step at low pressure (< 18 bar), and the esterification of CA to MC becomes the rate limiting step at higher pressure. Quantitative conversion of CA with 60% selectivity to MC was achieved at 200 °C and 18 bar. Me3HB enabled to recover up to 96% of PHB, and the Me3MB route allowed to recycle up to 98% of PHB. PHB was thus successfully chemically recycled into these two Me3MB and Me3HB C4 liquid molecules. Subsequently, the latter ones were used as solvent for the extraction of PHB itself. Given the renewability, recyclability, and biodegradability of both bio-based Me3HB and Me3MB solvents, these results establish another route for the chemical recycling of PHB in a circular perspective. Importantly, these works established a renewable pathway to methyl acrylate and propylene, two valuable monomers in the plastic industry, which can be prepared by cross metathesis of ethylene with MC, itself derived from natural PHB. In another study, intracellular PHB obtained by fermentation of industrial waste water, was demonstrated as a potential alternative feedstock to its traditional biopolymer for the production of the two chemical building blocks that are MC and methyl acrylate, both in economic and carbon footprint terms.[138,139,140] Therefore, bacterial PHB which can be biosynthesized from volatile fatty acids starting from agro-food waste streams, appears, alongside PHB, as a valued resource toward attractive chemicals within the concept of fossil resources replacement.



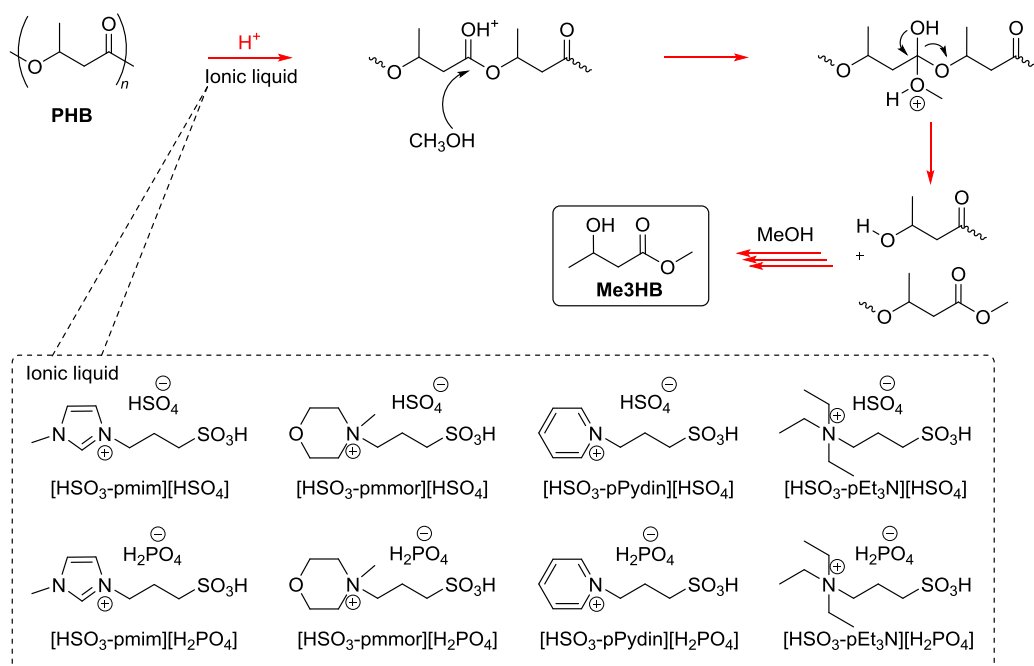
Scheme 11. Acidic alcoholysis of PHB into methyl 3-hydroxybutyrate (Me3HB) and methyl 3-methoxybutyrate (Me3MB) via methyl crotonate (MC) in comparison to the thermolysis route.

More recently, the effective microwave-assisted chemical recycling of bacterial PHB ($M_{n,SEC} = 326,100$ g/mol, $D = 1.8$) was demonstrated in green solvents (water, methanol, ethanol) under alkaline conditions (Scheme 12). The hydrolytic degradation rate increased with higher NaOH concentration, reaching complete PHB degradation into the water-soluble monomeric degradation products, namely 3HBA, 3-methoxybutanoic acid (Me3BA) and CA, within 20 min at 110 °C in 0.5wt% alkaline methanol. Prolonged microwave heating generated larger amounts of Me3BA and 3HBA acids, the former methoxy secondary product being formed by the reaction of the latter 3HBA with alkaline MeOH. On the other hand, a constant amount of CA was observed throughout the heating period, suggesting that CA was generated upon dehydration and hydrolysis of PHB chain-ends and not upon dehydration of 3HBA. Ultimately, the three products were recovered in similar amounts (*i.e.*, *ca.* 33wt%) after 5 h. This microwave-assisted PHB degradation thus advantageously proceeded at a significantly higher rate and lower temperature than the pure thermal degradation of PHB and appears as a promising recycling technique to access functional chemicals.[141]



Scheme 12. Microwave-assisted chemical recycling of PHB into CA, 3-hydroxybutyric acid (3HBA) and methyl 3-methoxybutyrate (Me3BA).

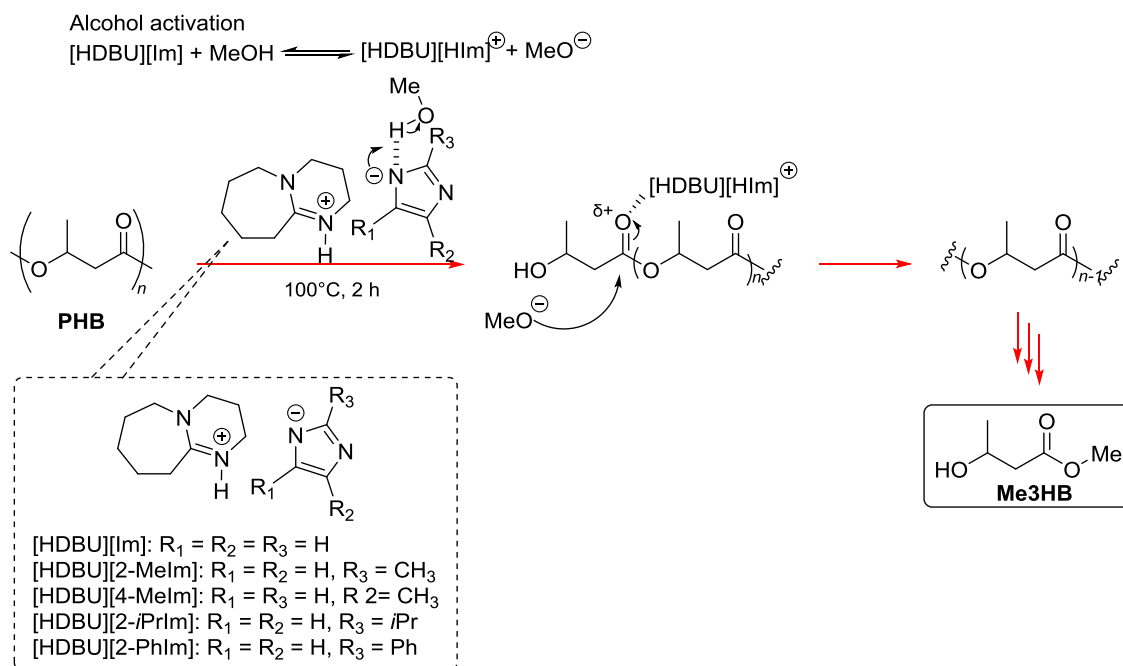
More recently, PHB methanolysis depolymerization has also been investigated in various ionic liquids (ILs), in order to enable the recycling of this polyester into CA and/or Me3HB (Scheme 13). Identification of alternative catalytic systems, in order to avoid the pollution raised by toxic transition metal ions and/or organic solvents residues within the plastic wastes to be ultimately submitted to recycling, was the main driving force of these research works. Thus, 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ($[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$), in the presence of methanol, showed a greater catalytic activity than the above-mentioned conventional acids H_2SO_4 and H_3PO_4 , or other acidic functionalized ILs. Again, Me3HB was recovered as the main product, in yields that were mainly temperature-dependent, while being also increased by larger IL catalyst and methanol loadings, longer methanolysis time, and greater PHB ($M_{n,\text{SEC}} = 204,000 \text{ g/mol}$, $D = 2.11$) conversion. Optimization of these parameters enabled to recycle up to 91% of PHB into up to 84% of recovered Me3HB using a $[\text{MeOH}]_0/[\text{PHB}]_0/[\text{IL}]_0$ loading of 5:1:0.03, at 140°C for 3 h. Noteworthy, under such operating conditions, the IL was reused up to 6 times without any apparent loss of activity (similar PHB depolymerization and yield of degradation product), thus making it a promising substitute to traditional catalysts. Kinetic studies of the PHB methanolysis catalyzed by acidic-functionalized $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ showed a first-order reaction with an E_a of 16.02 kJ/mol . The suggested hydrolysis mechanism classically involved protonation of the carbonyl group upon attack by hydrogen ions in IL, followed by methanol nucleophilic attack resulting in a tetrahedral intermediate that was subsequently decomposed into oligomers, the latter which finally reacted with MeOH to ultimately form Me3HB as the major product (Scheme 13).[142]



Scheme 13. Methanolysis depolymerization of PHB performed in various acidic ionic liquids (ILs).

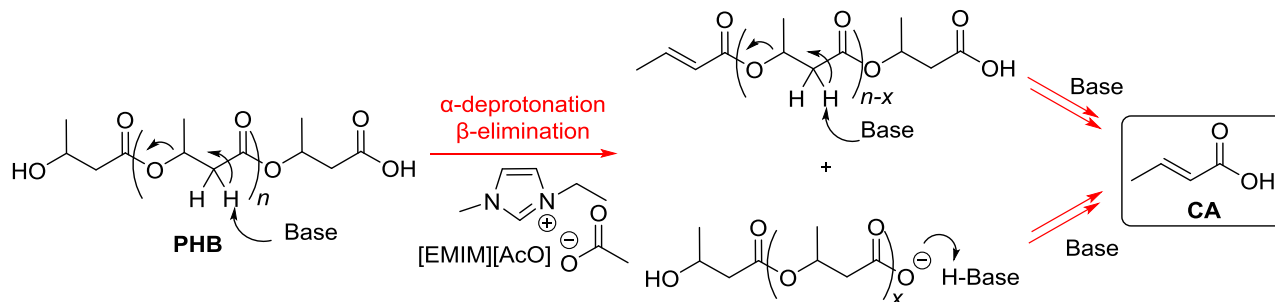
Moving to basic ionic liquids (ILs) with imidazolium cations, a similar activity was generally observed for the methanolysis depolymerization of PHB (Scheme 14). The PHB ($M_{n,\text{SEC}} = 204,000 \text{ g/mol}$, $D = 2.11$) methanolysis was reported using the super Lewis base 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU)/imidazole anion-derived system ($[\text{HDBU}][\text{Im}]$, 100% depolymerization, 33% isolated yield, at 100°C in 2 h) in comparison to the Lewis acidic 1-(3-sulfonic acid)-propyl-3-methylimidazole ferric chloride catalyst ($[\text{MIMPS}]\text{FeCl}_4$, 98% depolymerization, 87% isolated yield, at 140°C in 3 h) at $[\text{MeOH}]_0/[\text{PHB}]_0/[\text{IL}]_0 = 5:1:0.1$. The methanolysis revealed easier in the acid-mediated system, and the

Lewis basic catalyst showed a lower activity under mild operating conditions. The other imidazolium-based Fe-containing IL, 1-butyl-3-methylimidazolium tetrachloroferrate ([BMIM]FeCl₄) displayed excellent catalytic performances in comparison to FeCl₃ or [BMIM]Cl IL, successfully enabling 6 reuse cycles while maintaining the same efficiency in terms of PHB conversion and Me₃HB yield. Kinetic studies indicated that this reaction was first-order kinetic reaction with an E_a value of 27.44 kJ/mol [143,144,145]



Scheme 14. Methanolysis depolymerization of PHB in various basic ionic liquids (ILs).

In the search for highly selective PHB depolymerization catalysts to CA, basic imidazolium acetate ILs were investigated (Scheme 15). These ILs (1-ethyl-3-methyl imidazolium acetate [EMIM][AcO], 1,2-dimethyl-3-ethyl imidazolium acetate [DMEIM][AcO], and 1-butyl-3-methyl imidazolium acetate [BMIM][AcO]) were found to promote the effective and highly selective depolymerization of PHB under mild conditions (140 °C, 90 min), converting 20wt% PHB to CA with 97wt% yield (no added alcohol). The rate of CA formation increased with higher temperatures. On the basis of NMR analyses, the reaction was shown to proceed through intermediates of crotonyl-terminated PHB oligomers, by repeated α -deprotonation and β -elimination mediated by the base catalysis from the IL acetate anion. With a PHB loading up to 40wt%, complete PHB consumption was observed with [EMIM][AcO] applied as solvent and catalyst, in 5 h at 120 °C. Beyond this loading value, partial deactivation of the IL, triggered by hydrogen bonding interactions between the acetate anion of the IL and the carboxylate proton of the CA product formed, was evidenced from combined kinetics, NMR and DSC analyses. Addition of water (25 or 50wt%), which reduced the basicity of acetate anion of the IL and most likely lowered the PHB solubility, revealed detrimental for the PHB conversion. Given that the [EMIM][AcO] IL depolymerization is base catalyzed, the inactivity of the less basic or neutral parent chloride system [EMIM][Cl], was not surprising. Finally, products extraction with 2-methyl tetrahydrofuran biorenewable solvent assisted by brine (saturated aqueous NaCl), allowed the efficient separation of CA and [EMIM][AcO] recovered at high purity with > 90wt%. This single-solvent, metal-free catalysis is a promising process for the recycling of PHB into CA.[146]



Scheme 15. PHB depolymerization using basic imidazolium acetate ILs.

4. Catalyzed Chemical Recycling of PHAs

Metal residues originating from the cultivation medium of microorganisms used for the fermentation process have been reported as contaminants in natural PHAs that ultimately affect their thermal degradation. This finding prompted further in-depth investigations (in addition to the few aforementioned examples) on the impact of metal species on the degradation of PHAs, both bacterial and synthetic ones.[65] Organocatalysts have been rarely exploited in the degradation of PHAs as compared to other depolymerizations.[147] Opportunely, organo-catalyzed depolymerization of PHAs has been investigated as a new approach to recover metal-free PHAs and ultimately upcycled products without any metal residues. Such metal- and organo-catalyzed chemical recycling of PHAs have only recently been reported, as compared to the pyrolysis and solvolysis approaches that have been developed much earlier.

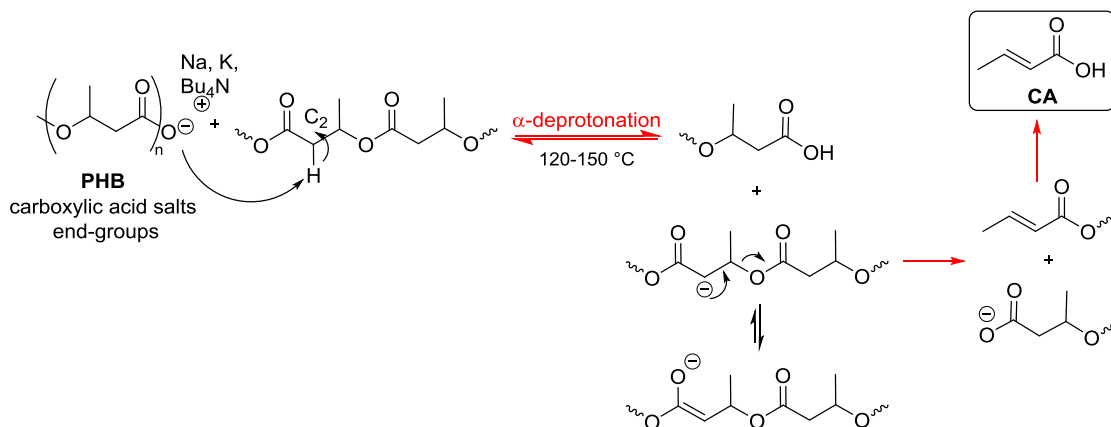
In order to promote the chemical recycling of PHAs, both the thermal degradation and the solvolysis catalyzed pathways, mediated by various metallic salts of organic or mineral acids, or by discrete metallic species, have been investigated. Both homogeneous and heterogeneous catalytic routes have been developed for the degradation of PHAs, the former approach being more often implemented. The recycling was shown to essentially depend, beyond the temperature and the molar mass of the polyester, on the chemical nature of the repeating unit and chain-end groups, and on possible metallic species or metallic residues. Generally, the catalyzed chemical recycling of PHAs proceeds at lower temperature than the uncatalyzed reaction.

4.1 Metal-catalyzed pyrolysis of PHAs

It was generally reported that bacterial PHB ($M_{n,SEC} = 431,000$ g/mol, $D = 2.99$) undergoes a significant thermal degradation in the presence of weak Brønsted chloride, acetic acid or carbonic acid salts of alkali metals (Li, Na, K, Cs), while a less marked effect was observed with alkaline-earth or d-transition metal (Mg, Ca, Al, Zn, Sn) salts. The alkali metal salts (400 ppm), proportionally to their cation radius (effective: Na, Ca; hardly effective: Zn, Al, Sn), revealed as the most efficient to promote a rapid degradation under relatively mild conditions (150-180 °C). Higher rates of degradation were thus observed in the order $Cs > K > Li$, suggesting that an anionic chain scission mechanism is at play. In addition, Ca, Mg, and Zn acetates remained less active, yet still affecting the PHB thermal stability. Other studies showed that, within PHB ($M_{n,SEC} = 198,000$ g/mol, $D = 3.30$) and P4HB ($M_{n,SEC} = 225,000$ g/mol, $D = 1.60$) samples, residual metal traces (arising from the bacterial growing of the PHA, or from purposely-added corresponding metal chloride salts; 2-568 ppm) of the Na, Mg or Ca harder Lewis acids, catalyzed the depolymerization of PHB, while alike Zn, Al or Sn residues hardly affected the thermal degradation. Washing of the polymers with acetic acid enabled to lower the residual metal content and thus to improve their thermal stability. In the case of PHB, while the exact role of the metal species was difficult to unambiguously establish, the Ca or Mg acidic species were proposed to facilitate the β -hydrogen elimination upon interacting with the carbonyl groups. In contrast, the thermal degradation of

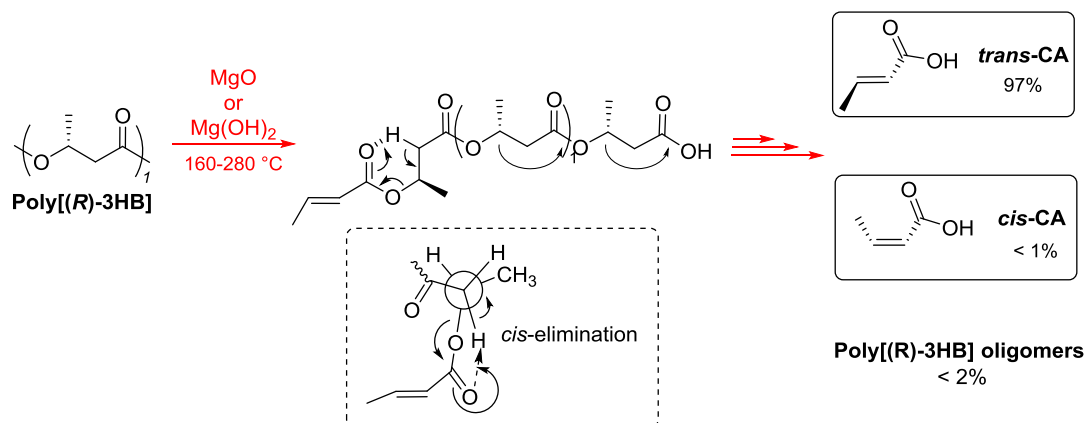
P4HB, effectively promoted by all Na, Ca, Zn, Al, Sn metal chlorides, was demonstrated to involve the cyclic rupture via unzipping reaction from the ω -hydroxyl chain end or/and random intramolecular transesterification at the main chain, with the release of γ -butyrolactone as volatile product.[66,76,94,148,149]

The thermal degradation of different PHB samples ($M_{n,SEC} = 5600$ -131,000 g/mol, $D = 1.60$), either prepared by fermentation, partial saponification of natural precursors, or anionic ROP (initiated by either *tetra*-butylammonium or activated potassium and sodium acetates), has also been reported at moderate temperatures (120-150 °C), similarly induced by other carboxylate salts. The thermal stability (up to the maximum degradation rate temperature) of the samples prepared by ROP ($M_{n,SEC} = 6000$ -10,000 g/mol) was established in the order Bu_4N^+ (224 °C) < K^+ /18-crown-6 complex (228 °C) < Na^+ /15-crown-5 complex (231 °C) < H^+ (291 °C). The mechanism proposed established a relationship between the PHB thermal stability and the chemical nature of the PHB carboxylate salts end-groups (Scheme 16). In particular, it revealed the impact of the counterion size (Na^+ , K^+ , Bu_4N^+), and suggested that the main PHB degradation pathway occurred by the intermolecular α -deprotonation mediated by carboxylates – rather than by the random intramolecular chain scission by *cis*-elimination mechanism as described above. These findings opened the possibility to tune the thermal stability/degradation of PHB and PHB blends by modulating the concentration and/or the counter-anion of COO^- chain-ends. Later on, this pathway was generalized to other PHAs bearing an acidic hydrogen atom at C2 position (*e.g.*, PHBV, PHBHHx) (Scheme 16).[150,151] The thermal degradation of the related bacterial PBHV ($M_{n,SEC} = 250,000$ g/mol, $D = 2.50$), similarly mediated by carboxylate salts, was also described under relatively mild reaction conditions (180 °C). In this case, as established from 1H NMR and ESI-MS data, linear α -unsaturated, ω -carboxylate oligomers were selectively recovered, as opposed to the mixture of γ -butyrolactone along with linear and cyclic oligomers produced from pyrolysis. These well-defined oligomers with controlled molar mass represent potential macromonomers or macroinitiators for the elaboration of more sophisticated polymeric materials.[152]



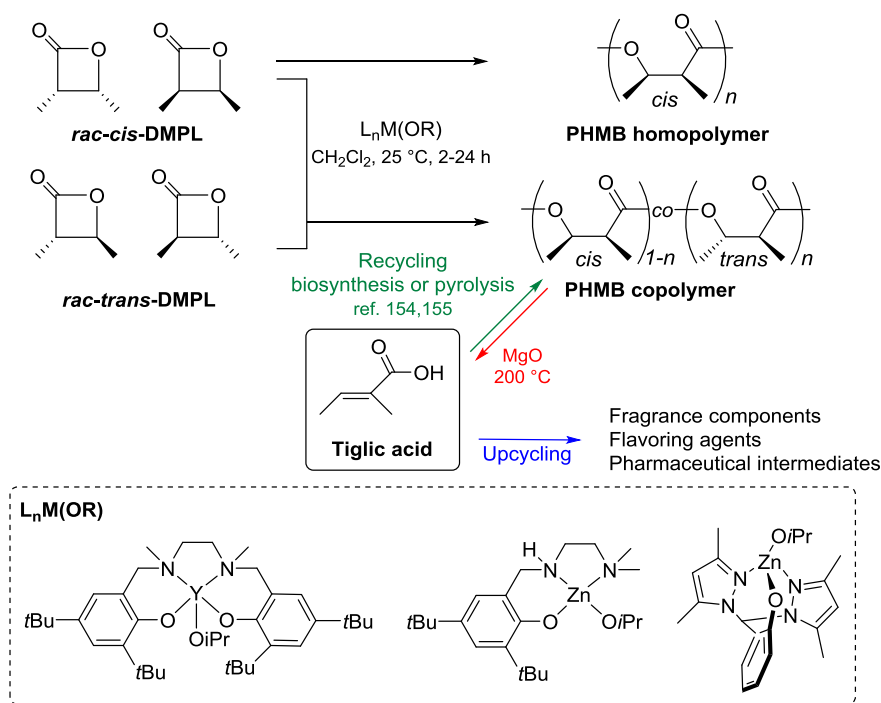
Scheme 16. Proposed degradation mechanism of PHB having a hydrogen atom at the C2 carbon, induced by a carboxylate terminal groups.

The thermal degradation (160–280 °C) of isotactic PHB (poly[(*R*)-3HB], $M_{n,SEC} = 150,000$ g/mol, $D = 3.60$) cast-films, when catalyzed by MgO or $Mg(OH)_2$ (5wt%) that promoted the β -elimination from the early stage of the reaction, enabled to decrease the temperature and E_a value by 40-50 °C and 11-14 kJ mol^{-1} , respectively. It also significantly improved the selectivity of resulting pyrolyzates with up to 97% *trans*-CA obtained from $Mg(OH)_2$, along with *cis*-CA (< 1%) and oligomers (< 2%) (Scheme 17).[153]



Scheme 17. Preferential depolymerization of PHB mediated by MgO or Mg(OH)₂ into *trans*-CA.

Aiming at the preparation of commodity polyolefins alternatives from biodegradable and recyclable or upcycled PHAs with enhanced thermal characteristics and improved mechanical toughness, methylated polyhydroxybutyrate, namely poly(3-hydroxy-2-methylbutyrate) (PHMB), was recently established (Scheme 18). The 2,3-dimethyl- β -propiolactone (DMPL) monomer was first prepared in an easy and scalable (up to 31 g, 79% yield) approach from the industrial C4 feedstocks 2-butene (first epoxidized prior to carbonylation) and carbon monoxide. Subsequent ROP of *cis*-DMPL from metal (yttrium, preferentially zinc) alkoxide catalysts provided *cis*-PHMB homopolymers which exhibited a tacticity-independent crystallinity along with a high T_m (186-204 °C), yet with brittleness ($\epsilon_b < 20\%$). Rewardingly, the copolymerization of both *cis*- and *trans*-DMPL gave tough ($\epsilon_b > 300\%$) and high-melting materials that valuably displayed a full range of polyolefin-like properties as tailored by the *cis/trans* ratio of the repeating units. While at higher *cis*-DMPL content (90%), the copolymer mimicked *i*PP and HDPE (high yield stress = 26.1 ± 1.3 MPa and ductility = $373 \pm 50\%$), the copolymer incorporating 80% of *cis*-DMPL rather resembled low-density polyethylene (LDPE), with a similar yield stress (10.3 ± 0.2 MPa) and Young's modulus ($E = 0.106 \pm 0.003$ GPa). Ultimately, the depolymerization of mixed PHMB samples ($M_{n,SEC} > 100,000$ g/mol) with various *cis*-contents (70-100%), mediated by MgO (1wt%) at 200 °C for 1 h, selectively afforded tiglic acid (93% yield). Profitably, tiglic acid is a value-added C5 feedstock which can be transformed into *trans*-2-butene upon pyrolysis thereby providing access back to the original β -lactone, or into *trans*-PHMB from a biosynthetic route.[154,155] Besides, tiglic acid and its esters are common components entering fragrance and food additives, hence suggesting an atom-economic upcycling outcome of PHMB. This overall strategy thus nicely establishes a opened-loop chemical recycling of PHMB.[156]



Scheme 18. Circularity of PHMB with polymerization from the DMPL β -lactone and subsequent recycling back to the cyclic ester via formation of tiglic acid, the latter that can also be upcycled.

PHBV random copolymers (12-19mol% of HV) were easily thermally depolymerized to versatile vinyl monomers using alkaline earth catalysts. At lower temperatures (160-200 °C, bulk), in the presence of CaO or Mg(OH)₂ catalysts, both CA and 2PA were selectively formed. Of note, the latter catalysts drastically reduced the formation of minor products, as compared to the aforementioned uncatalyzed thermal process. In addition, the catalysts lowered the degradation temperature by 30–40 °C. Subsequent copolymerization of the recovered CA with acrylic acid afforded water-soluble poly(crotonic acid-*co*-acrylic acid) copolymers, leading to many applications such as enzyme-stabilizing agents or hydrogels for biosorbent, wastewater treatment and agricultural applications. This copolymerization of CA derived from PHA pyrolysis provides another illustration of the chemical recycling of PHAs, towards sustainable plastics.[96]

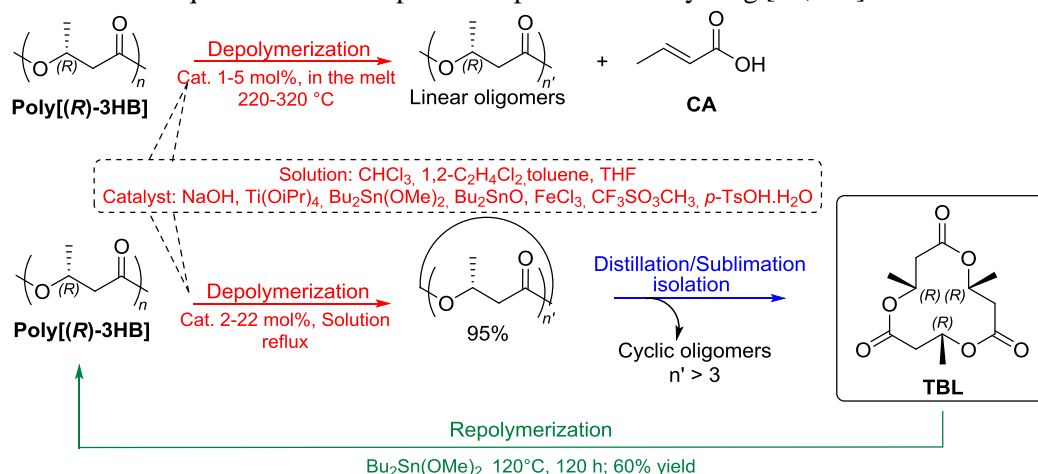
The application of an activated carbon-supported palladium catalyst (Pd/C) for PHB ($M_{n,SEC} = 400$ kg/mol) depolymerization under H₂ atmosphere (employed as the reduction gas, 4.0 MPa, 200 °C, 24 h), similarly led to the formation of butyric acid, butanol, butyrates (46, 24, 8wt%, respectively), and gaseous products (mainly alkanes). Cu/Zn/Al catalysts were more selective towards the formation of 3HBA (70% yield for a Cu-to-Zn ratio of 65:25) as the result of preferential hydrogenation of C=C bonds compared to carbonyl bonds over the Cu surface sites. This heterogeneous procedure established a near zero-waste production of the high-quality C4 derived biofuels from PHB, with up to 99% carbon utilization and 91.5% energy recovery (calculated based on the total consumption of chemical energy of PHB and H₂), via a simple one-pot catalytic hydrogenolysis solvent-free process at 200 °C, *i.e.*, slightly higher than the T_m (180 °C). It may thus pave the way to a green production of biofuels from bioderived feedstocks. Of note, in the absence of hydrogen, CA was the only product recovered in 73wt% in 16 h with Pd/C at 200 °C under N₂ atmosphere.[157]

PHB reforming into gasoline-grade hydrocarbon oil was also established from the use of aluminum dihydrogen phosphate in a one-step reaction at 240 °C for 6 h. Alkenes, ketones, aldehydes, aromatic derivatives, and other cyclic hydrocarbons were essentially composing the recovered oil. In comparison to

the previously mentioned solid phosphoric acid catalysis, this phosphoric acid derived aluminum salt demonstrated, thanks to its weak acidity, excellent catalytic performances (namely up to 37wt% oil yield, a hydrogen/carbon ratio of 1.63, and higher heating value of 42.3 MJ/kg), and good recycling ability (up to 3 cycles), thus making this PHB ($M_{n,SEC} = 400,000$ g/mol) reformed hydrocarbon oil competitive with commercial oxygenated gasoline.[158]

4.2 Metal-catalyzed solvolysis of PHAs

The ring-closing depolymerization of bacterial PHB (poly[(*R*)-3HB], $M_{n,SEC} = 900,000$ g/mol) was performed in the melt (220-320 °C) and in solution (CHCl_3 , 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$, toluene, THF; reflux temperature: 62-111 °C), in the presence of various catalysts (1-22mol%; NaOH, $\text{Ti}(\text{OiPr})_4$, $\text{Bu}_2\text{Sn}(\text{OMe})_2$, Bu_2SnO , FeCl_3 , $\text{CF}_3\text{SO}_3\text{CH}_3$, *p*- $\text{TsOH}\cdot\text{H}_2\text{O}$). Linear poly[(*R*)-3HB] oligomers with crotonate end-groups (up to 70mol% yield) and CA (up to 98mol% yield) - formed through an ester pyrolysis mechanism -, were obtained from the melt depolymerization. On the other hand, cyclic oligomers (up to 95mol% yield) were obtained from the depolymerization performed in solution (Scheme 19). Upon distillation/sublimation of the latter cyclic oligomers, the cyclic trimer of 3HB, namely (*R,R,R*)-4,8,12-trimethyl-1,5,9-trioxacyclododeca-2,6,10-trione (TBL), was isolated in 42-50wt% yield. The TBL triolide was thus successfully prepared in up to 20 g scale. This cyclic trilactone TBL was next successfully repolymerized with tin- or titanium-based catalysts in the melt, into poly[(*R*)-3HB]. The highest molar mass polymer thus prepared (60% yield; $M_{n,SEC}$ ca. 4500 g/mol, \bar{D} ca. 1.6), obtained from the reaction catalyzed by $\text{Bu}_2\text{Sn}(\text{OMe})_2$ (1mol%) at 120 °C for 120 h, yet remained too low to be useful and did not reach the requirements for a opened-loop chemical recycling.[68,159]



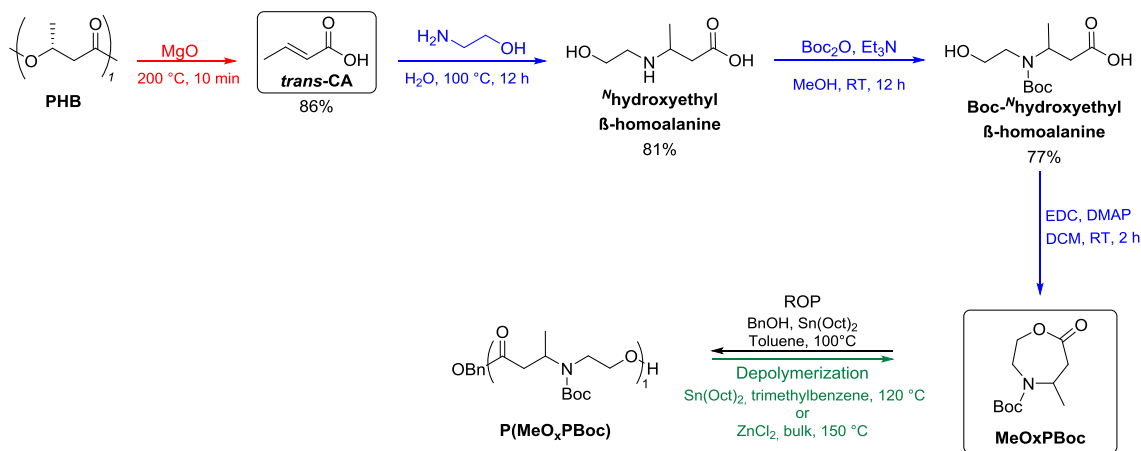
Scheme 19. Chemical recycling of poly[(*R*)-3HB] by depolymerization to linear and/or cyclic oligomers and the cyclic trimer TBL, next repolymerized into poly[(*R*)-3HB].

Ruthenium(II) PNN pincer complexes (pre-activated by $\text{KO}t\text{Bu}$) have been shown to selectively depolymerize poly[(*R*)-3HB] and P3HP ($M_{n,SEC} = 135,000$ g/mol, $\bar{D} = 1.3$) into butyric (88%) and propionic (90%) acid, respectively, by catalytic hydrogenation ($([\text{PHB or P3HP}]/[\text{Ru catalyst precursor}]/[\text{HO}t\text{Bu}] = 50:1:2, \text{THF/anisole}, 54.4 \text{ bar H}_2, 160 \text{ °C}, 48 \text{ h})$). Surprisingly, these PHAs that feature two methylene units between ester linkages depolymerized to carboxylic acids rather than diols (1,3-butanediol, propanediol), as recovered from the other polyesters such as PLA or polyethylene terephthalate (PET).[160] Of note, Brookhart's iridium(III) cationic pincer complex $[\text{Ir}(\text{PCP})\text{H}(\text{THF})][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{PCP} = 1,3\text{-}(t\text{Bu}_2\text{P})_2\text{C}_6\text{H}_3$) failed to catalytically depolymerize PHB in the presence of Et_3SiH (90 °C, $\text{C}_6\text{H}_5\text{Cl}$), regardless of the quantity of reductant, the temperature and the

reaction times (up to 2 weeks), whereas PLA or PET were successfully converted by hydrosilylation into silylethers and alkanes.[161]

The simple, nontoxic/biocompatible zinc bis[bis(trimethylsilyl)amide] ($\text{Zn}(\text{HMDS})_2$) has been reported as an efficient catalyst for both the synthesis and the degradation of polyesters. In the presence of $\text{Zn}(\text{HMDS})_2$ as catalyst and BnOH as initiator, a PHB oligomer ($M_{n,\text{SEC}} < 5000$ g/mol, $D = 1.16$) was synthesized by ROP of β -butyrolactone, and subsequently depolymerized upon transesterification reaction in methanol (1mol% $\text{Zn}(\text{HMDS})_2$, 25 °C, 24 h) into Me3HB with excellent yield (93%). Although a single experiment was mentioned, this is actually the lowest temperature reported so far for the effective PHB depolymerization.[162]

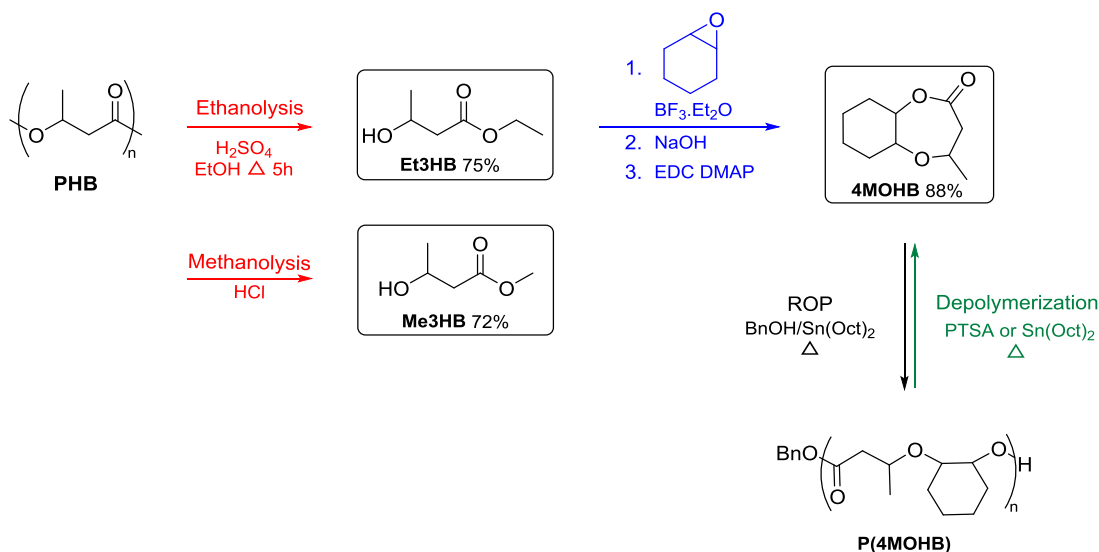
Efforts to achieve the chemical upcycling of PHB waste into valuable synthons resulted in the preparation of the *N*-heterocyclic lactone, 5-methyl-*N*-Boc-1,4-oxazepane-7-one (MeOxPBoc). As much as tens-of-grams of high-purity MeOxPBoc were easily obtained from PHB waste in 80% yield in a four-step procedure involving i) formation of *trans*-CA from the selective pyrolysis of PHB using MgO as catalyst at 200 °C for 10 min, ii) nucleophilic aza-Michael addition in water of CA with aminoethanol to form the *N*-hydroxyethyl- β -homoalanine, iii) protection of the secondary amine group, and finally iv) cyclization into MeOxPBoc. The subsequent living and controlled ROP of MeOxPBoc catalyzed by tin octoate ($\text{Sn}(\text{Oct})_2$) in the presence of benzyl alcohol as an initiator in toluene, gave the corresponding poly(amine-*alt*-ester) P(MeOxPBoc), a potential precursor of drug delivery and gene transfection carriers. Rewardingly, the latter P(MeOxPBoc) copolymer was ultimately depolymerized back to its pristine monomer either in bulk (150 °C, ZnCl_2 as catalyst) or in solution (trimethylbenzene, 120 °C, $\text{Sn}(\text{Oct})_2$ as a catalyst). Following a simple purification by recrystallization of the thus chemically recycled MeOxPBoc, it was successfully repolymerized to produce virgin-quality polymers, thereby establishing a closed-loop life cycle (Scheme 20).[163]



Scheme 20. Chemical upcycling of PHB into MeOxPBoc and its corresponding polymer.

Recently, the facile upcycling of a bacterial sample of PHB ($M_{n,\text{SEC}} = 540,000$ g/mol) into a value-added bicyclic ether-ester monomer, subsequently polymerized into degradable and recyclable polymers with a closed-loop life cycle, was demonstrated. The sulfuric acid (98wt%)-catalyzed ethanolysis converted PHB into ethyl 3-hydroxybutyrate (Et3HB) in high yield (75%), which then upon reaction with cyclohexene oxide (CHO) gave ethyl 3-((2-hydroxycyclohexyl)oxy)butanoate (3-(2-HCH)OBEt, 68%). The ethanolysis performed with other acids (FeCl_3 , HCl) remained less efficient than the H_2SO_4 route (39%, 11% yields of Et3HB, respectively), while the methanolysis catalyzed by HCl returned up to 72% of Me3HB. Subsequently, cyclization of the latter butanoate - through the prior formation of the butanoic acid intermediate by saponification (85%) -, next afforded the bicyclic seven-membered ring cyclic ester 4-methyloctahydro-2*H*-benzo[*b*][1,4]dioxepin-2-one (4MOHB, 88%), which

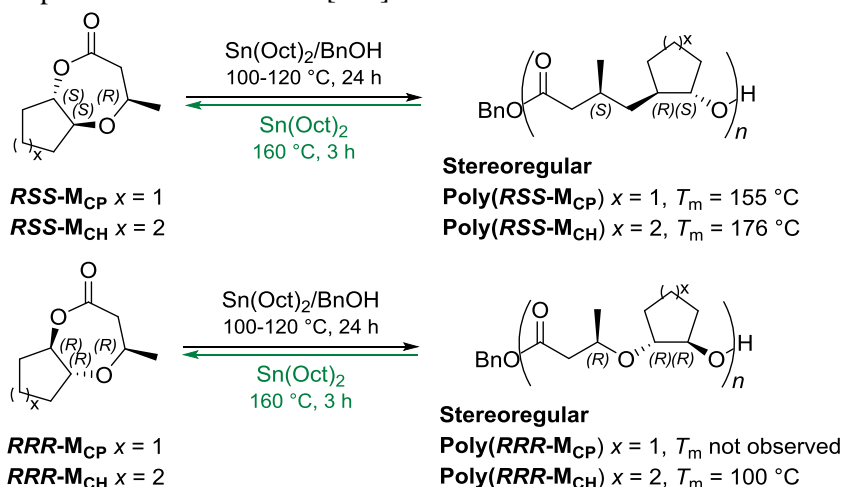
was finally melt-polymerized into the corresponding atactic and amorphous polyester, poly(4MOHB). Interestingly, upon pyrolysis using PTSA (80 °C) or the same catalyst as for the ROP, namely Sn(Oct)₂ (BnOH, 140 °C), the resulting polymer could be depolymerized back into its pristine monomer (79%). The alike thermal degradation of poly(4MOHB) catalyzed by ZnCl₂ (180 °C) revealed less effective (33% yield of 4MOHB). The similar H₂SO₄-catalyzed depolymerization of P(3HB-*co*-4HB) copolymers in ethanol returned a mixture of Et3HB (66%) and γ -butyrolactone, the latter being formed upon the more favorable cyclization of the 4HB moiety. This is another example of a chemical upcycling of PHB into Et3HB, 4MOHB, poly(4MOHB) (Scheme 21).[164]



Scheme 21. Chemical recycling of PHB into the 4MOHB bicyclic monomer, next ring-opened polymerized back into poly(4MOHB) (EDC = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, DMAP = 4-dimethylaminopyridine).

Following this report, closed-loop recyclable PHAs with improved thermal properties were further developed from enantiopure *trans*-cyclohexyl (M_{CH}) or *trans*-cyclopentyl (M_{CP}) fused bicyclic ether-ester monomers, by upcycling of the resulting PHAs (Scheme 22). The monomers were synthesized from the corresponding cyclohexene or cyclopentene oxide, upon reaction with *R*-methyl 3-hydroxybutyrate (*R*-Me3HB). Stereoretentive “living” and controlled ROP of the enantiopure monomers, catalyzed by Sn(Oct)₂ in the presence of BnOH, afforded at 100-120 °C over 24 h, well-defined crystalline polyesters with high melting temperatures. Remarkably, the stereoregular PHA (poly(*RSS*- M_{CH}); $M_{n,SEC}$ = 6.4-22.5 kg/mol, D = 1.06-1.15) obtained from the enantiopure *trans*-cyclohexyl fused bicyclic ether-ester diastereoisomer with *RSS* stereoconfiguration (*RSS*- M_{CH}), revealed semi-crystalline; it exhibited a T_m ranging from 165 °C up to 176 °C, that is higher than that of *i*PP (165 °C) or of HDPE (130-137 °C) commodity polyolefins.[165,166] The cyclohexyl or cyclopentyl fused-ring thus introduced along the PHA backbone significantly improved the PHAs thermal stability, with the onset decomposition temperature ($T_{d-onset}$) of atactic polyesters prepared from racemic monomers unexpectedly displaying improved stability (e.g., $T_{d-onset}$ of poly(*rac*- M_{CH}) = 296 °C) as compared to the stereoregular ones (e.g., $T_{d-onset}$ of poly(*RSS*- M_{CH}) = 286 °C) regardless of the cyclic substituent on the repeating unit. The recycling of these PHAs by depolymerization into the pristine enantiopure monomers, respectively, was accomplished by thermolysis. The depolymerization of poly(*RSS*- M_{CH}) performed in diluted trimethylbenzene solution as catalyzed by Sn(Oct)₂ (5mol%) at 160 °C within 3 h, selectively returned the original *RSS*- M_{CH} monomer (87% conversion) without racemization, following a first-order kinetics relative to monomer concentration, most likely proceeding via an unzipping pathway from ω -terminal hydroxyl group. Also, PTSA enabled the solution (toluene) depolymerization of poly(*RSS*- M_{CH}), showcasing a higher catalytic activity (88% conversion at 80 °C for 12 h) than Sn(Oct)₂. However, it gave

dispersed oligomers, thus hinting at a random chain scission or macrocyclization depolymerization route. Alternatively, the bulk thermolysis at 180 °C under reduced pressure (ca. 200 Pa) in the presence of ZnCl₂ (5mol%) revealed less effective, returning 56% of RSS-M_{CH} in 6 h. Rewardingly, the repolymerization of the thus recycled enantiopure cyclohexyl and cyclopentyl monomers returned stereoregular PHAs with virgin macromolecular features (*M_n*, *D*, stereoregularity). Such a recycling approach of PHAs back to pristine monomers establishes another closed-loop life cycle of PHAs featuring high melting temperatures, thereby paving the way to potential applications similar to commodity plastics, such as hot beverage cups or disposable food containers.[167]

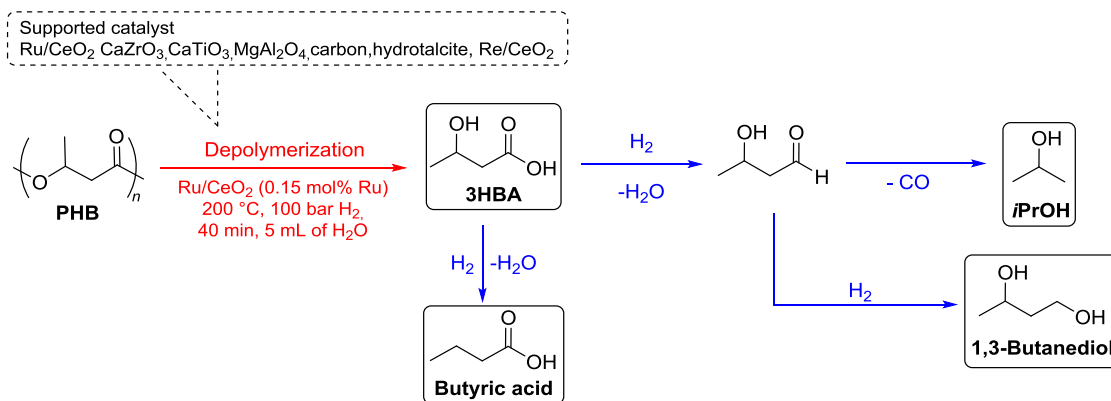


Scheme 22. Closed-loop life cycle of PHAs derived from *trans*-cyclohexyl or *trans*-cyclopentyl fused bicyclic ether-ester monomers (M_{CH}, M_{CP}) by upcycling.

The one-step catalytic reforming of bacterial PHB by cerium oxide (CeO₂) enabled its conversion to oils and propylene (35 and 17wt%, respectively) ([CeO₂]₀/[PHB]₀/[water]₀ = 1:1:4, 240 °C, 9 h), by completely inhibiting the formation of solid residues. The recovered oils contained ketones, esters, hydrocarbons, ethers, alcohols, and an *N*-containing compound. In addition to its low-cost, good catalytic activity, excellent stability and environment-friendliness, CeO₂ exhibited a nearly perfect 5-cycle reusability without requiring any regeneration. However, its equimolar-to-PHB loading should be first optimized to possibly envision industrial application.[168]

Various Ru or Re supported catalysts (Ru/CeO₂, /CaZrO₃, /CaTiO₃, /MgAl₂O₄, /charcoal, /hydrotalcite, Re/CeO₂) have been screened for the heterogeneous degradation of PHB in aqueous phase under different conditions (reaction time, temperature, hydrogen pressure, polymer concentration) (Scheme 23). The Ru deposited on ceria (Ru/CeO₂, 50 mg of catalyst with 5wt% metal loading and 138 mg PHB, (ca. 0.15mol% Ru)) showcased the highest activity and selectivity (200 °C, 100 bar H₂, 40 min, 5 mL of H₂O), enabling a full conversion with a 3HBA selectivity over 84%, and a 69wt% yield of 3HBA, and 31wt% yield of butyric acid. The reaction temperature revealed decisive with no product being formed at 150 °C and the onset of monomer formation was established at 170 °C, close to the *T_m* value (180 °C). Hence, the optimized temperature of ca. 200 °C enabled to avoid detrimental dehydration and/or decarboxylation reactions. Prolonged reactions or higher reaction temperatures detrimentally induced the decarboxylation of the monomer acids into *iso*-propanol. The presence of H₂ was shown to be crucial as no significant amounts of 3HBA or CA (< 4% each) were observed without it. Regardless of the catalyst, the amount of 1,3-butanediol (< 5wt%) remained lower than that of isopropanol (up to 27wt%). Also, water was essential, with the 3-HBA selectivity increasing with higher amounts of water. Transposition of the process to the recycling of a mixture of PHB, PLA and PET (5 mg Ru/CeO₂, 45.7 mg PHB, 38.2 mg PLA, 101.9 mg PET (0.53 mmol each), 200 °C, 100 bar H₂, 5 mL H₂O, 500 rpm), was also presented with a comparable outcome, returning 3-HBA (48%), butyric acid (21%), lactic acid (82%) and

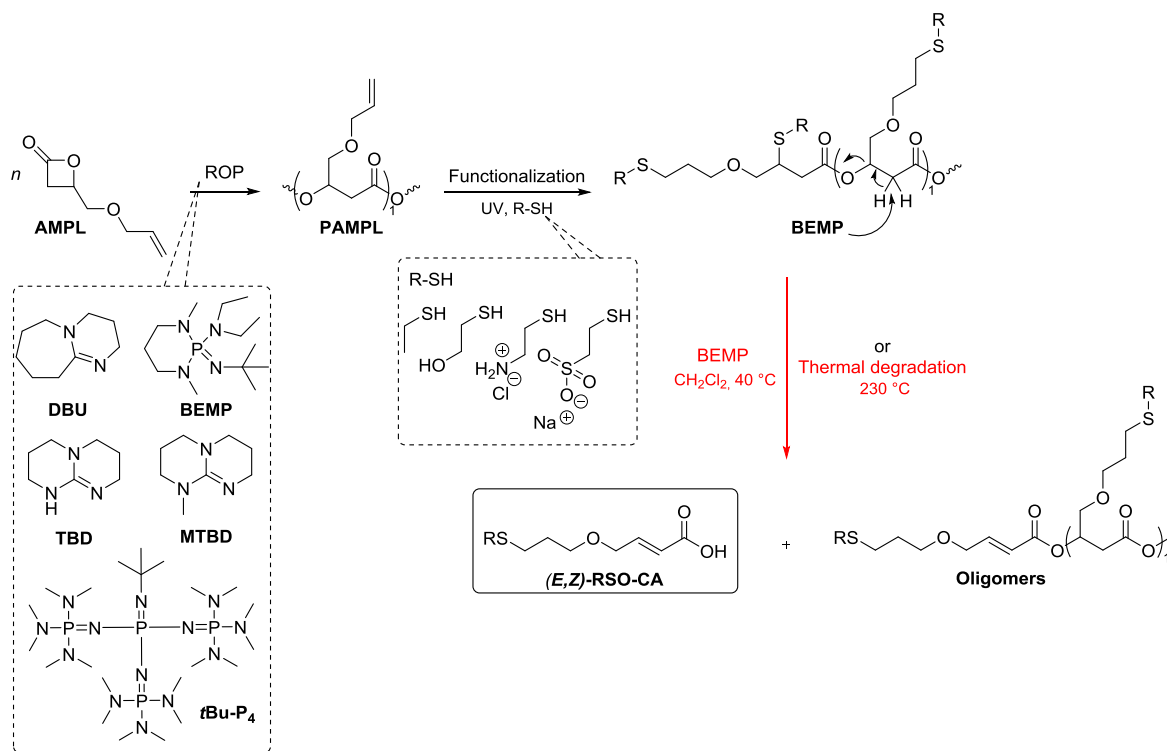
minor amount of iso-propanol, propionic acid and 1,2-propanediol arising from PHB and PLA, while PET largely remained intact (96% recovered after filtration). These findings highlight the feasibility of the chemical recycling of mixed waste streams made of these latter three polymers that facilitate high monomer yields recovery for repolymerization and improved circular value-chains.[169]



Scheme 23. PHB chemical recycling over ceria-supported Ru catalysts.

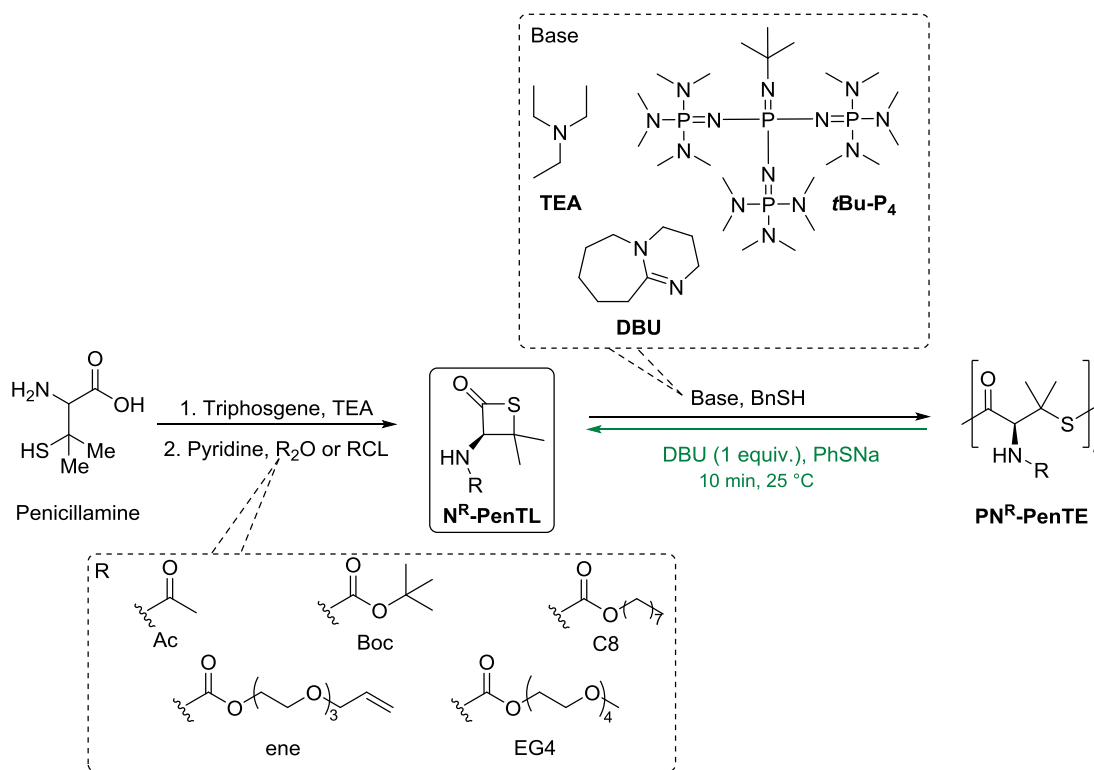
4.3 Organobase-catalyzed chemical recycling of PHAs

Recently, 4-allyloxymethyl- β -propiolactone (AMPL) – previously prepared by carbonylation of allyl glycidyl ether – was successfully ring-opened polymerized into poly(AMPL) using catalytic amounts (0.02-0.002 equiv.) of common guanidine, amidine, phosphazene organocatalysts, namely 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), or the *t*Bu-P₄ phosphazene superbase (Scheme 24).[170] While BEMP and *t*Bu-P₄ acted as a base, DBU, TBD, and MTBD displayed a dual activity behaving as both a base and a nucleophile involving both alkyl-oxygen and acyl-oxygen bond cleavage of AMPL. BEMP revealed as the most effective catalyst to promote a controlled anionic ROP of AMPL. Subsequent photoactivated thiol-ene reaction on the pendant allyl moieties with thiol-based molecules (ethanethiol, 2-mercaptoethanol, cysteamine hydrochloride, and sodium 2-mercaptoethanesulfonate), afforded functionalized poly(AMPL) with various side-chain substituents, which displayed distinct solubility, thermal and degradation profiles. Ultimately, the BEMP (15 equiv. with respect to a functionalized PAMPL) mediated chemical degradation of the thus functionalized poly(AMPL) ($M_{n,NMR}$ up to 15,700 g/mol, $D = 1.15$) performed in dichloromethane at 40 °C, generated *E*-RSO-CA comprising 87% of the total degraded PHA, along with 13% of functionalized *Z*-RSO-CA (RSO-CA: (*E/Z*)-4-(3-mercaptopropoxy)but-2-enoic acid). The excess of BEMP behaves as a base and abstracts the α -proton from the poly(AMPL) backbone to give a crotonyl chain-end via β -elimination. In comparison, the thermal degradation of poly(AMPL) at 230 °C proceeded almost exclusively via a random chain cleavage upon β -elimination, giving crotonyl chain-end moieties and anhydride (formed by the condensation of two carboxylic acids), as observed by ¹HNMR and FTIR spectroscopies. Cross-linked poly(AMPL) films were next found to degrade spontaneously in a BEMP solution (0.10 M in CH₂Cl₂), while only a mass loss of 62 and 13% was observed in NaOH (0.10 M) or in HCl (0.10 M), respectively, after 1 month, as BEMP enabled easier access to the hydrophobic poly(AMPL) film.



Scheme 24. Representative degradation mechanism mediated by BEMP of functionalized poly(AMPL) and the resulting products.

Polythioesters, the sulfur analogues of PHAs, have recently gained renewed attention as attractive sustainable PHAs, thanks to their dynamic thioester bonds in their backbones which make them more reactive than their oxo analogues. Various penicillamine-derived *gem*-dimethyl substituted β -thiolactones with different side-chains (N^R -PenTL) monomers were ring-opened polymerized by organobase catalysts (triethylamine (TEA), DBU, *t*Bu-P₄) in the presence of benzyl mercaptan as initiator under mild conditions (in bulk at room temperature) (Scheme 25).[171] Stronger bases promoted faster ROP within the general trend TEA < *t*Bu-P₄ << DBU. Subsequent post-polymerization modification of the chain-end group of the resulting poly(N^R -PenTL) easily enabled to introduce end-functionalities in addition to tunable side-chain groups. All polythioesters were efficiently depolymerized by DBU back to pristine enantiopure β -thiolactones, at > 95% conversion from minutes to a few hours at room temperature (*e.g.*, in 4 h with 0.1 equiv DBU relative to the number of poly(PN^{C8}-PenTL₄₀) ($M_{n,SEC}$ up to 20,100 g/mol, $D = 1.21$). Lowering the recycling temperature and increasing the catalyst loading effectively prevented racemization as revealed by the complete depolymerization without racemization of poly(PN^{C8}-PenTL₄₀) achieved within 10 min with DBU (1 equiv.) at -25 °C. These experimental data combined to theoretical calculations suggested a fast, selective, and highly controlled domino-like unzipping depolymerization process, where the geminal dimethyl group was shown for the first time to be playing a crucial role. Such polythioesters pave the way to high-value, recyclable polymers with a wide range of applications such as self-immolative materials, covalent adaptable networks, sacrificial domain for composites and nanolithography, or responsive biomaterials.



Scheme 25. The closed-loop polymerization/depolymerization cycle of *gem*-dimethyl substituted β -thiolactones promoted by organic bases.

5. Concluding Remarks and Perspectives

Within the current awareness of the plastics environmental and societal issues, thanks to their easy (bio)degradability, PHAs have recently gained increasing attention while stimulating renewed insightful research into their recyclability. Beyond mechanical recycling and enzymatic catalysis, several pathways for the chemical recycling of PHAs have been established in the emerging field of plastics sustainability. While the PHA intrinsic parameters (typically its chemical nature and molar mass, physical state/morphology) are essential for their recycling fate, end-products of the degradation process are very much dependent on the method used, be it pyrolysis, thermolysis, hydrolysis, or alcoholysis, uncatalyzed or catalyzed, and the related operating conditions as well. The present review has addressed the recent advances in PHAs chemical recycling according to these latter strategies.

The thermal degradation of PHAs and PHA copolymers typically proceeds at high temperature (160-375 °C). PHA pyrolysis classically generates gaseous products, liquid oil and some solid residue. Typical PHB pyrolysis products recovered include CO_2 , H_2O , propylene, ketene, acetaldehyde, β -butyrolactone, *trans/cis*-CA, 3-butenic acid, linear oligomers, as well as cyclic trimers (Fig. 3). CA, and more precisely *trans*-CA, a versatile monomer for many applications, is recovered from the thermal breakdown of PHB as the major value-added product (Fig. 3). Other products such as γ -butyrolactone or 2PA are typically recovered from pyrolysis of P4HB or PHBV, respectively. The pyrolysis mechanism, although somewhat complicated, has now been established, proceeding almost exclusively via a random chain scission (*cis*-elimination) towards the formation of CA acid and its oligomers. Low-energy thermolysis processes have also been established, especially from waste-PHA plastics. Also, the high efficiency of the now-established pyrolysis process enables the production of bio-based CA, a valuable versatile precursor to a chemical platform including polymeric materials such as poly(CA) and its

copolymers (*e.g.*, with vinyl acetate). The pyrolysis of biomass-, chemical-, waste-PHAs or mixed-PHA waste revealed as an effective chemical recycling method, providing circular products (naphtha, distillates or waxes) that are of suitable grade for end-use applications, thereby providing one promising approach to step into a PHA circular economy. Pyrolysis technology, enabling to convert PHAs to higher value products, can thus be part of a biorefinery model to provide recycling options to both.

Whereas the pyrolysis of PHAs has been investigated for quite some time, the chemical recycling of PHAs through a solvolysis pathway has only recently emerged, prompted by the search for plastics circularity. Hence, besides pyrolysis, both hydrolysis and alcoholysis concepts have been investigated as a mean to degrade PHAs. Implementation of such processes are not technically complicated, requiring most often mild operating conditions such as room temperature for hydrolysis, alcoholysis being usually performed at higher temperature (80-175 °C) than hydrolysis (most often < 40 °C), and aqueous or neutral reaction medium. The use of higher temperature or of some readily available acidic or basic catalyst, generally enabled to accelerate the degradation process. However, the drawback in using such soluble acids or bases is that complex separation technology is subsequently required. The tacticity of PHAs drives their crystallinity, which in turn impacts their hydrolytic degradation ability, as the diffusion of reagents within the polymer is facilitated within amorphous. Also, the introduction of 3HV into PHB prompted hydrolytic degradation. Other reaction media have also been established such as in particular IL, including acidic and basic ILs. Rewardingly, PHAs have revealed chemically recyclable by hydrolysis or alcoholysis, efficiently returning CA, 3HBA, Et3HB, γ -butyrolactone, MC, Me3HB, Me3MB, 4MOHB, CO₂ and propylene or other hydrocarbon oil (alkanes, alkenes, phenyl and naphthyl aromatics), or other chemicals that are valued for their reconversion into PHA in a closed loop cycle, into other polymers upon further reaction, or even into competitive gasoline- and biodiesel-grade hydrocarbon bio-oils (Fig. 3). Important progress has thus been achieved unveiling promising PHAs green circularity.

Various metal-based catalytic systems have been established for the thermal and solvolysis recycling of PHAs in both homogeneous or, to a lesser extent, heterogeneous processes. Regardless of their nature, the catalysts generally promote the formation of higher quantities of degradation products (mainly CA, along with some 3HBA, butyric acid), with a better selectivity, at a lower reaction temperature (typically by 30–40 °C), and reaction time. These reactions were usually performed in solution (organic solvents, water) or as bulk, solid mixtures to facilitate their separation, recovery, and/or recycling. Either alkali (Li, Na, K, Cs), alkaline earth (Mg, Ca), transition (Ti, Fe, Cu, Ru, Ir) and post-transition (Al, Zn, Sn) metals have been commonly used, most often as alkoxide, carboxylate or oxide derivatives, generally requiring to recover the metallic species for cost and/or environmental issues. Heterogeneous systems operating at high temperature in the range of 160-200 °C generally revealed less selective than homogeneous ones, the latter yet showcasing better efficiency (activity and selectivity) under milder operating conditions.

Organocatalyzed unzipping of PHAs and their polythioester congeners, although hardly reported, has been exemplified at temperatures close to ambient conditions (25–40 °C), significantly milder than other pyrolysis or solvolysis temperatures. While CA, similarly as from pyrolysis, hydrolysis or alcoholysis, was recovered as the major degradation component from the poly(AMPL) polyester, the poly(N^R-PenTL) thio-series enabled to regenerate back their pristine β -thiolactone monomers with good efficiency. The organocatalyzed depolymerization of poly(thio)esters appears as an easy recycling approach to implement chemical recycling. However, this depolymerization pathway is only in its infancy and requires deeper investigations.

While PHAs are biodegradable thanks to their ester functions throughout their backbone, their thermal stability impeding melt processability, their brittleness and their unattained recyclability remained, until recently, the major drawbacks for their wider industrial and consumer implementation and applications enabling them to compete and replace traditional non-degradable carbon-backed commodity plastics. Noteworthy, the penicillamine-derived *germinal*-dimethyl β -thiolactones, initially

opened the possibility of establishing a circular economy for PHA materials, as reported by Er-Qiang Chen and Hua Lu.[171] The latest advances simultaneously (on April 05-07, 2023) and independently reported by Geoffrey Coates,[156] Eugene Chen,[133] and Zhibo Li,[167] all tackled these issues upon developing either α -alkyl or α,α' -dialkyl substituted four-membered β -lactones, and bicyclic ether-ester seven-membered ring monomers flanked with *trans*-fused cyclohexyl or cyclopentyl moieties, respectively, that all subsequently underwent ROP into the substituted corresponding PHAs with such improved and desired properties. Indeed, these latest unveiled alkylated PHAs featured polyolefin-like performances, thereby representing promising *i*PP, HDPE or LDPE substitutes to traditional petroleum plastics. In addition to providing more thermally stable and more malleable polymers than the so-far established PHAs, all these newly designed monomers are biobased, and the polymers are industrially scalable. Finally, these new class of PHAs were shown to be chemically recyclable back to their pristine monomer, respectively, thanks to a favorable equilibrium between polymerization and depolymerization, as well as a balance between material performance and recyclability. Remarkably, these latter pioneering works relying on the monomer design, set the basis of a sustainable and circular PHAs value chain that unveils an important breakthrough in the plastics field, and that may reveal in the near future, a new polymer era following the first one witnessed some 70 years ago with the polyolefins birth.[172]

Taking into account their biodegradability, PHAs are also polyolefin alternatives towards valuable single-use plastics for usages as straws, bottle, food packaging or bags. While PHAs will not substitute any traditional petroleum plastics, their potential market is very large and diversified. The industrialization of the PHA platform initiated some twenty years ago has now reached an early-growth stage with several small-to-larger companies expanding their manufacturing capacities. Europe (France, Germany, United Kingdom) is currently dominating the global PHA market, but the present fastest growing market is Asia Pacific. Key PHAs market players include among others: Bio-on SpA (Italy), Danimer Scientific (USA), Kaneka (Japan), PolyFerm (Canada), Tianjin GreenBio Materials Co., Ltd (China). As the demand for eco-friendly materials is rising, the PHA market, estimated at \$ 57.8 million in 2022 and predicted to reach \$ 98.5 by 2028, is correspondingly expected to increase within the next five years, from 32.13 ktons to 92.4 ktons with a compound annual growth rate of 23.52%. PHAs are a distinctive family of plastics that can be recycled in many different ways, be it a closed- or opened-loop cycle : reuse in another way, incineration, environmental home or industrial composting, nutrients for living organisms, raw materials as renewable carbon feedstock, or back to the original pristine monomer. PHAs do meet the challenging essentials of all-known end-of life options, thus standing amongst the leading polymers of the future.[173,174]

Within the objective to design a PHA closed-loop chemistry, in spite of the recent progress as reported in the present review, the overall environmental performances of the chemical recycling approaches still have to be assessed and optimized, especially in comparison to mechanical recycling which still dominates in this regard. Chemical recycling and upcycling yet provide an attractive end-of-life option to PHAs, as recyclates therefrom recovered display a lower environmental impact than virgin plastics while performing like virgin materials. Besides, chemical recycling of PHAs and PHA-wastes can avoid the negative impact of emissions accompanying incineration and energy recovery process. Latest reports showcase the possibility to recover, from PHAs and even from PHAs waste or PHAs waste mixtures, either the pristine monomer or added-value products of industrial interest, thereby getting closer to a monomer-to-polymer-to-monomer circular closed- or opened-loop life cycle while tackling the plastics sustainability and end-of-life concerns (Fig. 3). In this regard, although one could tackle PHA closed-loop recycling upon implementing various approaches, obviously, the simpler the route, the better. Ideally, redesigning PHAs such that they are easily recycled, regardless of the stimulus, be it preferentially a self-immolative process, or possibly a catalyzed one, would provide a good option. Nevertheless, no single route can provide a universal solution to PHAs (as well as to plastics) recycling. Chemical recycling of PHAs as reviewed herein should serve as a further incentive to elaborate a circular value chain for sustainable plastics from such polyester materials. Computational inputs may also further

provide a better understanding into the degradation and depolymerization reactions at play. Nevertheless, the life cycle assessment of the various chemical recycling reported strategies of PHAs, remains to be fully established for consolidated PHAs circularity with viability and sustainability metrics of both environmental benefits, and economic feasibility.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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- [17] The meaning of chemical recycling, as used in our manuscript, and as understood from the open literature, is the implementation of a chemical process, be it pyrolysis (also to a lesser extent thermolysis) or solvolysis (this includes hydrolysis, alcoholysis -essentially glycolysis and methanolysis-, and aminolysis or phosphorolysis), through which the polymer is degraded, upcycled, depolymerized or unzipped into individual building blocks. The chemical recycling process thus ultimately returns through depolymerization, degradation or upcycling, a monomer identical to the initial one, a new monomer distinct from the one initially used to prepare the polymer, or a different compound that is subsequently valuably reused as raw reagent in some other process. The chemical recycling is different from the enzymatic recycling (a process mediated by enzyme) and from the mechanical recycling (which returns a material of the same chemical structure as the initial polymer), the latter two processes not being addressed in the present review.
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