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Conversion of polyhydroxybutyrate (PHB) to methyl crotonate for the production of biobased monomers

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ABSTRACT: Within the concept of the replacement of fossil with biobased resources, bacterial polyhydroxybutyrate (PHB) can be obtained from volatile fatty acids (VFAs) from agro-food waste streams and used as an intermediate toward attractive chemicals. Here we address a crucial step in this process, the conversion of PHB to methyl crotonate (MC), which can be converted *via* cross-metathesis with ethylene to methyl acrylate and propylene, two important monomers for the plastics industry. The conversion of PHB to MC proceeds *via* a thermolysis of PHB to crotonic acid (CA), followed by an esterification to MC. At pressures below 18 bar, the thermolysis of PHB to CA is the rate-determining step, where above 18 bar, the esterification of CA to MC becomes rate limiting. At 200°C and 18 bar, a full conversion and 60% selectivity to MC is obtained. This conversion circumvents processing and application issues of PHB as a polymer and allows PHB to be used as an intermediate to produce biobased chemicals. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42462.

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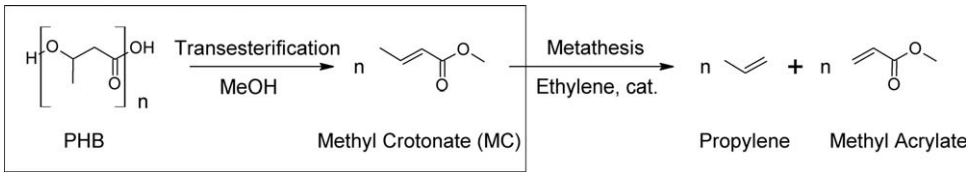
INTRODUCTION

A search for a sustainable alternative for fossil-based chemistry is needed due to depleting fossil resources, geopolitical instability, and global warming. Biomass as a feedstock offers an alternative with a closed carbon cycle. There are two challenges to overcome when using biomass as a feedstock. The first is the heterogeneous nature of biomass, which makes it difficult to isolate desired chemicals. The second is that many biomass streams are dilute, where small amounts of valuable compounds are present in large quantities of water. To overcome these two challenges, microorganisms can be used to uniform a diverse biomass stream by making insoluble polymers. An example is cyanophycin-producing bacteria, which can be used to obtain aspartic acid and ornithine, precursors of biobased acrylamide and 1,4-diaminobutane, from amino-acid-rich waste streams from agro industries.[1] Another example to uniform biomass streams using microorganisms is polyhydroxyalkanoates (PHA), and more specifically polyhydroxybutyrate (PHB). It has been shown that PHB originating from plants can be converted into crotonic acid (CA),[2,3] which can be used as a precursor for biobased propylene and acrylic acid.[2] In both examples, biomass is converted to drop-in chemicals, which are biobased versions of currently used chemicals that can replace their fossil-based counterpart, preventing the need for developing new materials.

PHB can be obtained in several ways since many different groups of bacteria can store carbon from biomass feedstocks to produce PHB.[4] All metabolizable carbon, ranging from CO_2 [5] to crude glycerol,[6] which can be used as a carbon source and PHB can also be produced in plants.[7] On a pilot and large scale, the production of PHB mainly uses glucose, sucrose, fatty acids, and lauric acid as carbon sources[8] and aims to produce materials for packaging, disposables, and biomedical applications. The current global production is 100,000 to 130,000 tons per year and is expected to grow 10 to 30% per year.[9] Commercialization of PHB, however, is difficult due to high production costs originating from using pure cultures and often pure substrates and the necessity to work under sterile conditions.[10,11]

To lower production costs, wastewater-containing volatile fatty acids (VFAs) from several industries (i.e., agricultural, food, and paper) can be treated in a mixed culture fermentation to generate PHB and simultaneously clean wastewater. Using wastewater as a feed lowers production costs by removing the costs for starting material and using a mixed culture removes the need for a sterilization.[10,12,13] An added benefit is the removal of VFAs from wastewater, removing the need for further wastewater treatment facilities. Enrichment of the culture based on natural and ecological selection results in a culture dominated by *Plasticicumulans acidivorans* with a PHB production of over 80% dry weight.[14,15] PHB originating from a fluctuating



Scheme 1. Conversion of PHB to methyl crotonate (MC) as precursor for the productions of biobased propylene and acrylates.

wastewater feed, however, will result in PHB materials with varying properties, which creates challenges in creating markets for these materials. Moreover, the processing conditions of PHB (*ca* 170°C) are close to the temperature where degradation of PHB can be observed (170 to 200°C).[16] A conversion of PHB to chemicals has been proposed by Metabolix, where PHB is converted to CA *via* pyrolysis at 200°C using $Ca(OH)_2$ as a catalyst. The CA produced could be further converted into drop-in chemicals such as *n*-butanol,[17] maleic anhydride, and propylene.[2,3] Converting PHB to chemicals can also be applied at the end of life of PHB products. PHB is unsuitable for landfills where it produces methane and, therefore, has to be collected separately. Instead of composting the waste PHB, it can potentially generate more added value when it is converted to monomers as means of a tertiary recycling process.[18]

The pyrolysis or thermal degradation of PHB to CA has been thoroughly explored to investigate the stability of PHB. It has been shown that PHB will degrade at 170–200°C[16] and above 250°C, CA and oligomers have been observed.[19,20] Little attention, however, has been given to optimize this conversion for the preparative production of CA from PHB. Formation of CA from PHB has been shown[2,21–23] and high conversion and selectivity can be reached when $Mg(OH)_2$ (84% of PHB converted to CA at 260–320°C)[23] or concentrated acid is used (90% of PHB converted to CA at 100°C)[21]. Without the addition of a catalyst, 63% CA can be obtained from pyrolysis at 310°C.[20]

Another well-known conversion of PHB is a transesterification of PHB in acidic methanol or butanol to form 3-hydroxybutyrates, which can be detected by mass spectrometry in order to quantify PHB, i.e., for quantifying PHB production in cells.[24–26] When base or more than 60% acid is used for the assay, crotonates are formed from methyl 3-hydroxybutyrate (M3HB).[24,27] A quantitative transesterification as means to produce methyl crotonate (MC) from PHB is unknown so far.

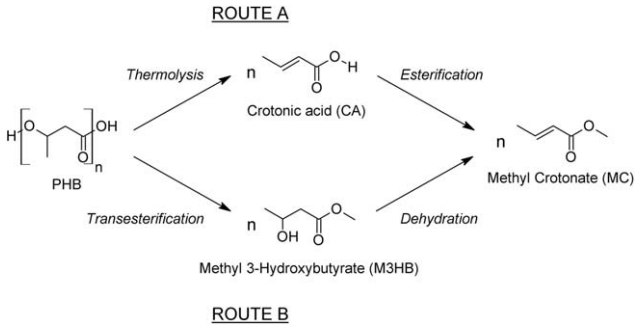
After conversion of PHB to CA, CA can be converted into drop-in chemicals. We previously showed that CA can be converted to acrylic acid and propylene *via* metathesis with ethylene. Metathesis on crotonates may appear to be a challenging reaction due to the near vicinity of an electron-withdrawing carboxylic acid group. However, 45–50% conversion has been obtained under nonoptimized conditions.[28,29] The products of these reactions—acrylic acid (4.5 million ton produced worldwide per year)[30] and propylene (global demand of 50 million tons per year)[9]—are important commodity chemicals for the plastics industry. Current methods to produce biobased acrylates are from the conversion of 3-hydroxypropionic acid, which can be obtained by fermentation, or from the conversion of glycerol to acrylic acid.[9] There are several pathways toward biobased acrylates that include a metathesis step. The metathesis of fumaric acid with ethylene to acrylic acid is patented, but gives low yields.[31] In a patent from Metabolix, biobased acrylates are obtained from crotonates by a metathesis with propylene.[2] Moreover, microbially derived muconic acid can be converted into biobased 1,3-butene and acrylic acid by metathesis with ethylene and has been patented by Amyris.[32] Finally, a reaction of ethylene with cinnamic acid, which could be obtained from rest streams of bioethanol production yields styrene and acrylic acid.[33] Biobased propylene can be obtained from several potential routes and commercialization of biobased propylene produced from sugarcane bioethanol has just begun with Braskem, who built a plant in 2013 with a capacity of 30,000 tons per year.[34]

Inspired by the observations of crotonate formation in the transesterification of PHB, we report the investigation of the preparative conversion of PHB to MC, which can act as a biobased substrate for the metathesis to biobased propylene and methyl acrylate (Scheme 1). MC production was performed in methanol in a single step, without the use of additives or a catalyst. The reaction pathway was clarified in order to optimize conversion and selectivity by varying pressure, temperature, and reaction time. Converting PHB from VFA (and sugar)-rich wastewater into drop-in chemicals circumvents process and quality issues associated with PHB from wastewater. Potentially, it could also be applied as a post-use treatment of PHB, circumventing end of life challenges. Moreover, this conversion opens the route to biobased propylene and methyl acrylate, two important monomers for the plastics industry.

EXPERIMENTAL

All experiments were performed in duplicates in 75 mL Parr pressure reactors (Parr multiple reactor system series 5000, 6 × 75 mL, Hastelloy C-276) equipped with glass liners and glass-coated stirring bars. Gas samples were collected from the pressure reactors with 1 L PVF Tedlar Sample Bags. Nitrogen gas (Nitrogen 3.0, purity ≥99.9%) was supplied by Linde Gas Benelux. Anhydrous methanol (99.8%), CA (98%), methyl crotonate (98%), methyl (R)-(-)−3-hydroxybutyrate (99%), and DL−3-hydroxybutyric acid (as sodium salt) were purchased from Sigma-Aldrich; methyl 3-methoxybutanoate was purchased from Ambinter; and PHB was kindly provided by Technical University Eindhoven (2 mol % Polyhydroxy valerate (PHV), Mn = 450 kDa and Mw/Mn = 1.3). All chemicals were used as received.

Starting material of 0.6 g was loaded in a glass liner with a glass-coated stirring bar. The liner was placed in a Parr reactor and the atmosphere was purged with argon. Dry methanol was



Scheme 2. Two possible pathways from PHB to MC.

then added using a syringe while keeping the reactor under an argon flow. The reactor was closed and flushed with nitrogen and pressurized with nitrogen to the desired pressure at room temperature and heating was applied. The heating caused the pressure in the closed reactor to increase to the reported "pressure build-up". Typical heating times up to 200°C took place in 20–30 min. The reaction time started when the temperature reached 200°C. After the allocated reaction time, the reactor was allowed to cool to room temperature before being opened. The crude mixture was worked-up as follows: when solids were present, the suspension was filtered with a Büchner filter. The clear solution was passed through a 0.20 μm single use filter unit and analyzed by HPLC (see Supplementary Information). More details on the analysis methods used can be found in supplementary information.

RESULTS AND DISCUSSION

Thermolysis or thermal degradation of PHB to CA without the presence of methanol has been fully investigated and several mechanisms have been proposed. Grassie *et al.* were the first to propose a chain scission mechanism (CS) in which the ester bond breaks *via* an intramolecular six-membered ring intermediate.[16] Kawalec *et al.* introduced the possibility of an E1cB mechanism where carboxylate end groups act as a base[35] and Ariffin *et al.* concluded that thermolysis of PHB to CA follows a combination of both mechanisms.[36] These studies were performed on degradation of dry PHB, where in our study, we investigated the conversion of PHB in the presence of methanol. The addition of methanol adds an esterification step to the pathway (Scheme 2, route A), resulting in the formation of methyl crotonate (MC). Moreover, the presence of methanol introduces a transesterification pathway, which gives rise to the formation of methyl 3-hydroxybutyrate (M3HB), followed by a dehydration reaction to form MC (Scheme 2, route B). This results in two theoretical reaction pathways from PHB to MC.

To get insight in the influence of reactor to methanol volume ratio on the conversion of PHB to MC, initial experiments were performed with a varying amount of methanol. The amount of PHB was varied, while the ratio of PHB to methanol was kept constant (Figure 1). In a closed reactor, liquid methanol at 200°C has a vapor pressure of 39 bar and under these conditions, the ideal gas law predicts that *ca* 3 mL methanol will be in vapor phase in a reactor volume of 75 mL. This results in a different gas-to-liquid ratio when various amounts of methanol

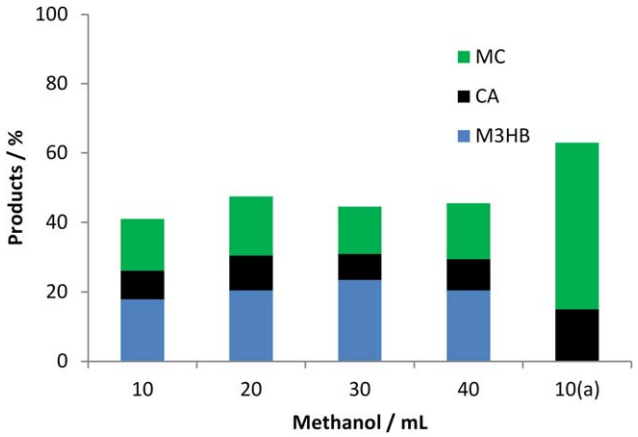


Figure 1. Conversion of PHB in methanol with varying amounts of methanol. Reaction conditions: 0.6 g PHB per 10 mL MeOH, $t = 6$ h, pressure build-up of up to 39 bar, for 10 and 20 mL nitrogen gas was added to reach 39 bar. Average of duplicate experiments. (a) $p = 7$ bar. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are present in the reactor. Since the reactor head is cooled to 25°C, the methanol is able to condense and flow back down to the heated part of the reactor. When the amount of methanol is reduced to 10 mL, there is not sufficient methanol present to flow down to the bottom of the reactor and a system where the methanol refluxes in the reactor head is created. In this system, 3 mL methanol is in gaseous state and the remaining 7 mL is present as liquid in the dead volume of the reactor head. The highest temperature at which liquid methanol is present determines the vapor pressure, and therefore the pressure in the system reaches only 7 bar. In order to circumvent this lowering of the pressure, nitrogen can be added at the beginning of the reaction. Additional nitrogen results in a system where 10 mL of methanol can be used and liquid methanol is present at 200°C, which results in a pressure of 39 bar. Pressure versus temperature data can be found in Supplementary Information.

The conversion of PHB to MC is independent on the volume of methanol used, reaching 15% MC in all reactions at 39 bar

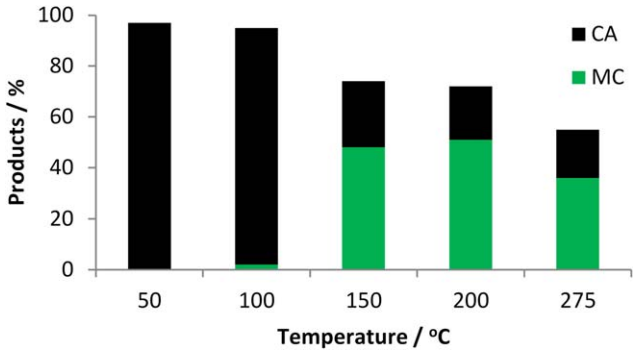


Figure 2. Catalyst-free esterification of 0.6 g CA in 10 mL methanol at various temperatures for 6 h, reactors closed at atmospheric pressure (pressure build up to 7–9 bar). Average of duplicate experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

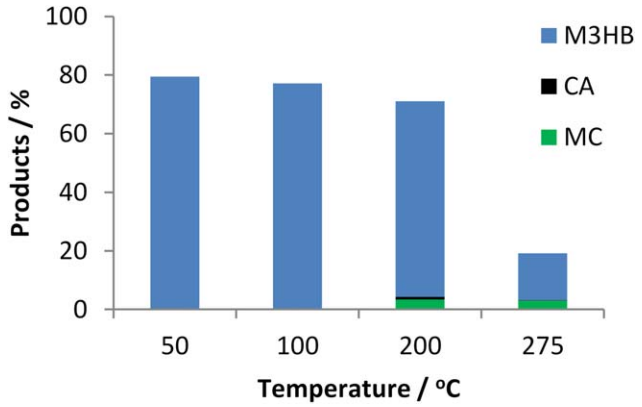


Figure 3. Reactivity of 0.6 g M3HB in 10 mL methanol at various temperatures for 6 h, pressure build-up of 7–9 bar. Average of duplicate experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Figure 1). However, when 10 mL of methanol is used without added pressure and the methanol is present only in the reactor head, less M3HB is observed and the conversion to MC becomes three times higher, rising from 15 to 48%, which indicates that the pathway *via* M3HB (Scheme 2, route B) is unfavorable. Based on the high conversion of PHB to MC at 10 mL methanol without added nitrogen, these conditions were further investigated.

To investigate the possibility of a catalyst-free esterification step, which is necessary for formation of MC from PHB in methanol *via* the thermolysis route (Scheme 2, route A), CA was reacted in a closed reactor in methanol at various temperatures (Figure 2). The reactors were closed at an atmospheric pressure of nitrogen, which resulted in a pressure of 7–9 bar at the reaction temperature, this build-up of pressure is from now referred to as pressure build-up.

Figure 2 shows that CA does not undergo esterification below 100°C. At 150°C, a conversion to MC was observed, but increasing the temperature further had little effect on the conversion. The catalyst-free esterification of CA has not been reported in literature so far. However, the catalyst-free reaction of free fatty acids to esters in vegetable oils has been reported at temperatures of 200°C,[37] which is in the same temperature range of the current findings. Next to the conversion to MC, about 30% of mass was unaccounted for by HPLC. This mass can most likely be contributed to gaseous products such as propylene and CO_2 originating from the decarboxylation reaction of CA, which has already been reported to take place at 310°C.[38] Further discussion of such degradation reactions are addressed later (Figure 5). To investigate the possibility of a transesterification–dehydration reaction pathway (Scheme 2, route B), M3HB was also subjected to the same reaction conditions (Figure 3).

Figure 3 shows that conversion of M3HB to MC or CA under these conditions is less than 5% and therefore can be neglected. The only significant conversion occurring is the degradation of M3HB to gaseous compounds, especially above 200°C. At 50°C, about 80% of the M3HB is recovered and at 275°C, only 16% of the M3HB could be recovered and still less than 5% crotonates are formed. The fact that no significant amounts of CA or MC can be formed from M3HB has been observed before in experiments with M3HB in gaseous form[39] and in a solution of *m*-xylene.[40] Degradation of M3HB follows a six-membered ring intermediate which leads to the formation of C_2 species instead of MC.[40] Our observation that also no crotonates are formed in methanol suggests that conversion of PHB to MC cannot take place *via* a transesterification–dehydration route, and therefore that the conversion of PHB to MC has to occur *via* a thermal conversion of PHB to CA followed by a catalyst-free esterification to MC.

With the pathway known, the conversion of PHB to MC can be optimized. From the reactivity of CA in Figure 2, it is clear that no esterification takes place below a temperature of 150°C; therefore, the investigation of the temperature dependence takes place from 150°C, which was performed in methanol in a closed reactor without additional inert gasses (Figure 4).

In Figure 4, it is shown that conversion of PHB starts at temperatures as low as 150°C, a clear trend can be observed where formation of MC increases with rising temperatures up to 200°C. Reactions at temperatures above 200°C, however, showed a lower product formation.

The observed starting temperature of conversion (150°C) is much lower than the minimum temperature of 270°C reported for pyrolysis.[20] Conversions of PHB at low temperature can be achieved in watery systems with a concentrated acid or dilute base. With acid, a full conversion to CA has been observed, where base leads to a mixture of 3HB and CA.[41] In methanol, the conversion of PHB has been performed at −18 to −24°C using NaOH, which results in PHB oligomers.[42] However, no conversion of PHB has been reported below 190°C without the use of an acid or base, although a lowering of the average molecular weight has been observed at these temperatures.[16] Our lower thermolysis temperature could be an effect of the

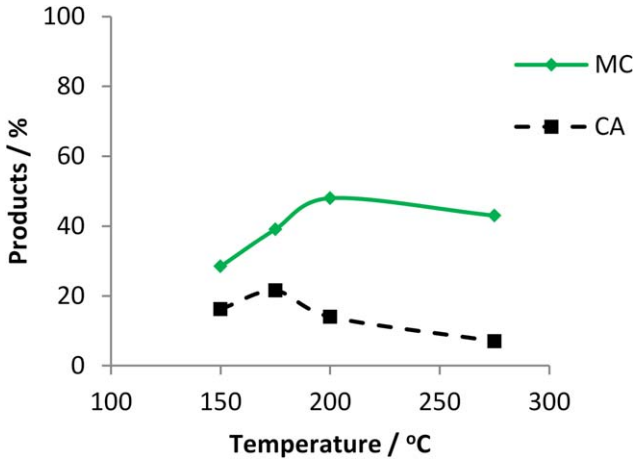


Figure 4. Temperature dependence of the conversion of PHB to CA and MC. Reaction conditions: 0.6 g PHB, 10 mL MeOH, pressure build-up of up to 8 bar, $t = 6$ h. Average of duplicate experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

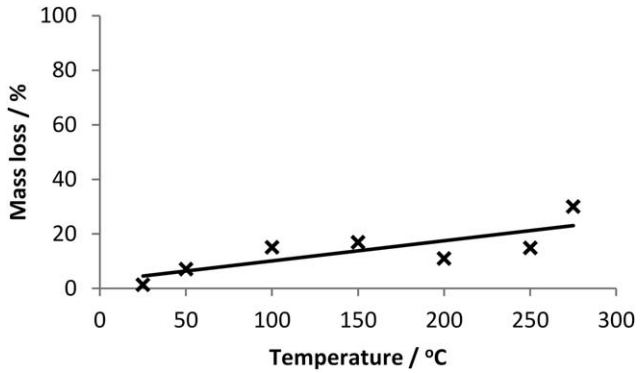


Figure 5. Control reaction of MC stability in methanol with a pressure build-up of 1–8 bar at different temperatures. Reaction conditions: 0.6 g MC, 10 mL MeOH, $t = 6$ h. Average of duplicate experiments.

higher pressure (8 bar) or the presence of methanol, since a lowering of the degradation temperature has been reported at atmospheric pressure in the presence of glycerol.[43] The lowering of degradation temperature in the presence of glycerol is explained by an alcoholysis, which is unlikely in our system due to the low amounts of M3HB formed (10%).

The rising of the conversion between 150 and 200°C indicates a higher conversion of oligomeric PHB to MC and CA at higher temperatures, where the decrease in conversion above 200°C can be explained by an increasing rate of decarboxylation of monomeric PHB fragments into gaseous compounds.

No insoluble PHB was observed after the reactions, which indicates that all PHB has been converted into small, soluble organic molecules and oligomers. At the optimal temperature of 200°C, no oligomers were observed by the analysis of the reaction mixture with HPLC with MS and MALDI-TOF, where no oligomers were found (see the section entitled "Experimental"). As a reference, a reaction of PHB in methanol at 100°C for 67 h showed a PHB conversion of 15.5% to oligomers consisting of up to 15 monomer units (see MALDI-TOF in Supplementary Information). In a GC-MS analysis of gas recovered from the reactor head after reaction, propylene and ethylene were found, which are typical degradation products of PHB.[19] Most likely, these products are formed from decarboxylation of crotonates, which is known to be the dominant degradation pathway for CA.[38] Control experiments with MC as substrate in methanol (Figure 5) also showed mass losses, especially at higher temperatures, which is in confirmation with the hypothesis of decarboxylation products.

To investigate the hypothesis of decarboxylation of MC causing mass loss in the conversion of PHB, MC was exposed to the same experimental conditions as PHB. At 25°C, MC is stable and a full recovery is observed (Figure 5). When the temperature is increased to 50°C, less than 10% of the initial mass is lost. This amount slowly increases with increasing temperature to 30% at 275°C. These values are slightly higher than the reported literature values, where roughly 30% MC is decomposed without the presence of methanol at 480°C after 40 min.[44] In comparison to the mass loss of PHB, the mass loss of MC is slightly lower (28% for PHB and 15% for MC at 200°C).

It is important to notice that CA and M3HB can also undergo decarboxylation and we observe mass loss to gaseous products for these compounds as well, which can explain this difference (Figures 2 and 3). A side reaction of methanol with MC to form methyl 3-methoxybutanoate *via* a Michael addition could explain the faster loss of MC in methanol than the observed literature value without the presence of methanol.[44] The catalytic Michael addition of methanol to MC has been previously observed[45] and there are indications that at 125–175°C, CA can form a dimer *via* a Michael addition.[46] However, this side reaction is excluded since this product was not detected by HPLC.

In order to determine the effect of reaction time on the conversion of PHB in methanol, *via* CA to MC, a series of experiments were performed at 200°C and 8 bar. Figure 6 shows that in the first 2 h, more monomeric compounds are formed from oligomeric PHB as the sum of crotonates increases.

At 8 bar, the sum of crotonates reaches a maximum of 60%, from where it slowly goes down to reach 55% after 22 h. Figure 6 also shows that CA is initially formed and is converted into MC over time. Initially there is 35% CA, which goes down to 4% after 22 h.

To study the mechanism of the conversion of PHB to MC in more detail, the reaction was run at 200°C for 6 h at several different pressures (Figure 7).

In Figure 7, the reaction at 2 bar of pressure build-up was obtained by putting the reactor under vacuum after cooling in an ethanol/liquid nitrogen bath to avoid methanol evaporation, followed by applying the reaction conditions. A trend can be observed where selectivity toward MC rises to a maximum of 60% at 18 bar before going down when pressure is further increased to 30 bar, and then drops rapidly to 20% above 30 bar. The rapid drop above 30 bar matches the vapor pressure of methanol at 200°C, which means the methanol reaches the bottom of the reactor. When methanol is present in dead volumes and refluxing at the reactor head, the reaction has a higher

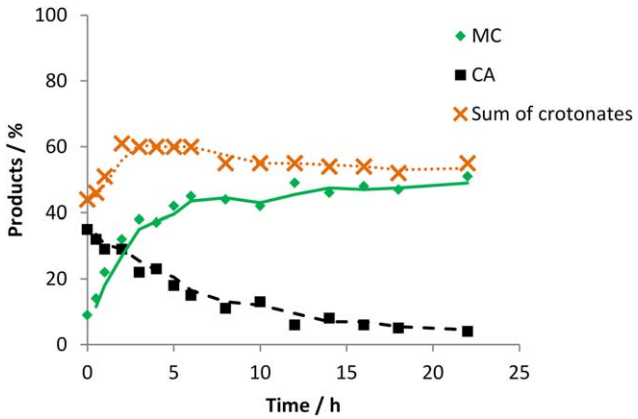


Figure 6. Reaction of PHB to MC at 200°C and 8 bar of pressure build-up performed at different reaction times. The reaction at $t = 0$ h was heated to 200°C and immediately cooled to room temperature. Average of duplicate experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

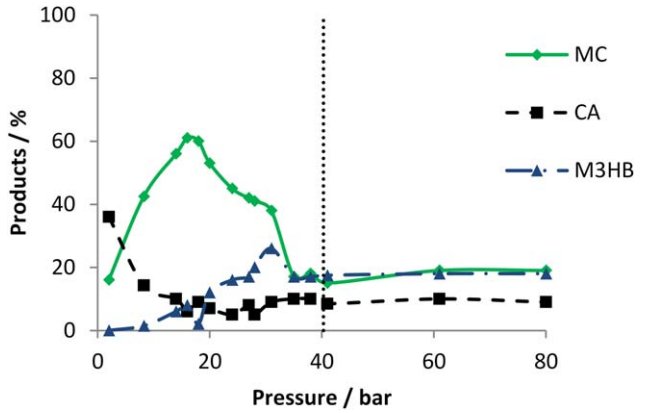


Figure 7. Selectivity toward MC at 200°C at different pressures. Reaction conditions: 0.6 g PHB, 10 mL MeOH, $t = 6$ h. Pressure indicates the pressure build-up at the reaction temperature. The dotted line represents the vapor pressure of methanol at 200°C. Average of duplicate experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

selectivity than when methanol is reaching the PHB at the bottom of the reactor in the liquid phase.

Up to 18 bar, more MC is formed with increasing pressure, while formation of CA slowly decreases. This indicates that esterification of CA is the rate-determining step (RDS) and that this step speeds up with increasing pressure. At 18 bar, a sudden change in the trend is observed, where the formation of MC declines with increasing pressure, which implies that the esterification is now sufficiently fast to overtake the thermolysis, which makes the thermolysis step the RDS above 18 bar. The thermolysis slows down with increasing pressure, resulting in a lower selectivity toward MC with further increasing pressure. At higher pressures, the methanol is forced lower into the reactor and therefore more reactions between methanol and PHB takes place increasing the M3HB formation. This effect can be explained by the reaction pathway, where the transesterification of PHB to M3HB competes with the productive conversion of PHB to CA (Scheme 2).

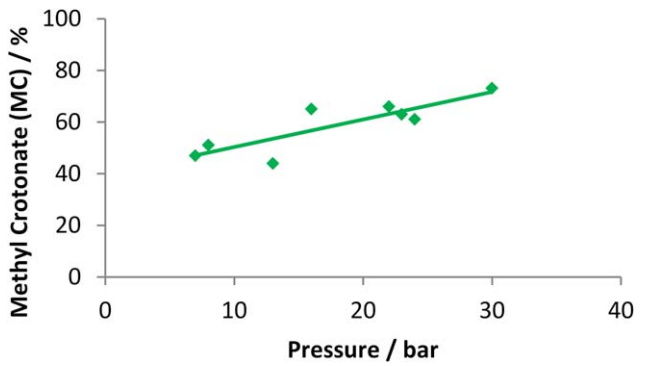


Figure 8. Conversion of CA to MC at various pressures. Reaction time = 6 h, temperature = 200°C. Pressure indicates the pressure build-up at the reaction temperature. Average of duplicate experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

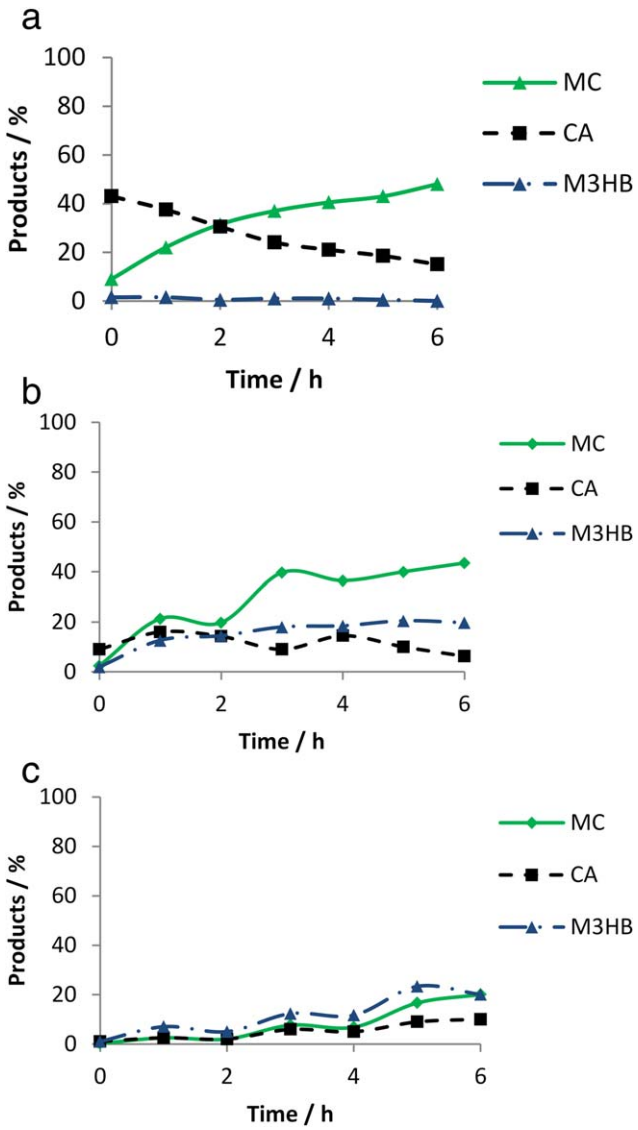


Figure 9. Conversion of PHB to MC at 200°C, various reaction times, and pressure build-up of (a) 8 bar, (b) 26 bar, and (c) 55 bar. Average of duplicate experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To verify the hypothesis that rate-determining steps depend on pressure applied during the reaction, CA was used as substrate and subjected to the same conditions (Figure 8).

In Figure 8, there is a clear trend where a higher pressure leads to more esterification product formed, with 50% conversion of CA to MC at 8 bar and 70% at 30 bar. This is in agreement with the hypothesis of switching RDS.

To further prove our hypothesis, conversion of PHB to MC was performed at 200°C with three set pressures of 8, 26, and 55 bar and stopped at different times, where $t = 0$ h stands for a reaction that was heated up and immediately cooled down. The results of these experiments are presented in Figure 9(a–c).

In Figure 9(a) with 8 bar of pressure build-up, a fast thermolysis to CA and a slow esterification to MC are observed. This

leads to an immediate formation of a large amount of CA (43%), while only 9% of PHB is subsequently converted to MC. Over time, the CA is converted into MC, resulting in 48% MC and 15% CA after 6 h.

In Figure 9(b) with 26 bar of pressure build-up, the thermolysis step slows down and initial formation of CA was lower than the initial CA formation observed at 8 bar (9% versus 35%) and only 3% was already converted into MC at $t = 0$ h. The esterification step, however, speeds up and after 6 h, only 6% CA remains against 15% at 8 bar. The slower thermolysis gives rise to a competing transesterification pathway forming 20% M3HB after 6 h, limiting the formation of total crotonates to 50% at 26 bar compared to 63% at 8 bar.

In Figure 9(c), with 55 bar of pressure build-up and methanol reaching the bottom of the reactor, thermolysis is slowed down sufficiently for the competing transesterification reaction to become the predominant pathway, resulting in 20% M3HB formation after 6 h. This lowers the formation of CA and MC at 55 bars to a total of 30% crotonates formed.

From Figures 7–9(a–c), it can be concluded that the thermolysis step favors low pressures and when the methanol reaches the PHB in the bottom part of the reactor, transesterification takes place, which competes with the thermolysis. This makes the esterification step the RDS at pressures below 18 bar and the thermolysis step the RDS at pressures above 18 bar. The switching RDS creates an optimum pressure for MC production from PHB at 18 bar. Moreover, at higher pressures, a transesterification pathway competes with the slowed down thermolysis step, resulting in the formation of more M3HB and less crotonates.

Where transesterification reactions applied to biomass generally use catalysts, either homogeneous or heterogeneous, we show that PHB can undergo transesterification in methanol without the use of a catalyst. Moreover, when catalyst-free transesterifications are performed, supercritical conditions or use of co-solvents are often applied.[47] When PHB undergoes pyrolysis to CA, similar conversions of 63% CA are reached compared to 60% MC in our system. With pyrolysis, however, higher temperatures are needed (310°C compared to 200°C) and the obtained product has to undergo an addition esterification to obtain MC. In our system, there is no need for harsh conditions or additional compounds. Using methanol to convert PHB to MC instead of CA does not only prevent the use of $Mg(OH)_2$[23] or concentrated H_2SO_4[21] but also gives direct access to MC, which makes an additional esterification step obsolete. Methanol used for the conversion of PHB to MC can also be obtained from biobased sources, for example, from syngas obtained from straw.[9] This results in a fully biobased conversion of PHB to chemicals, where no fossil-based compounds or catalysts are required.

CONCLUSION

We showed that polyhydroxybutyrate (PHB) can be directly converted into methyl crotonate (MC) at elevated temperatures in methanol without the use of an additional catalyst and below supercritical conditions. Using a temperature profile over the reactor, a system was created with methanol refluxing in the reactor head, creating optimal conditions for the conversion of PHB to MC. At 200°C, 18 bar, and 6 h, PHB was fully converted with a 70% selectivity toward crotonates. Based on our mechanistic study, we propose that the reaction follows a thermolysis pathway to CA, followed by a catalyst free esterification to form MC. The rate-determining step (RDS) is dependent on the reaction pressure and changes at 18 bar. Below 18 bar, esterification of CA to MC is the RDS, while above 18 bar, the thermal conversion of PHB to CA is the RDS. The direct production of MC, a suitable substrate for a further metathesis reaction generating propylene and methyl acrylate, makes it possible to obtain fully biobased monomers for the plastics industry from PHB, circumventing processing and quality issues that PHB currently faces when used as a material. Large-scale reactions, as well as downstream processing, are currently investigated in our laboratory.

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