

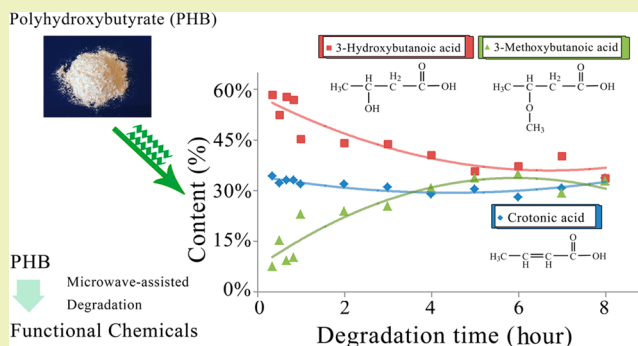
# Microwave-Assisted Reaction in Green Solvents Recycles PHB to Functional Chemicals

Xi Yang, Karin Odelius, and Minna Hakkarainen\*

Department of Fibre and Polymer Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

**ABSTRACT:** An efficient microwave-assisted process for chemical recycling of poly(3-hydroxybutyrate) (PHB) in green solvents was demonstrated. Previously, PHB has been thermally recycled to crotonic acid and unsaturated oligomers. Our aim was to utilize green solvents (water, methanol, and ethanol) under alkaline conditions to achieve fast hydrolysis and monomeric or oligomeric degradation products with carboxyl and hydroxyl or methoxy or ethoxy end groups. Preliminary screening confirmed that the most efficient degradation process was obtained in alkaline methanol. In addition, sample amount, sodium hydroxide concentration, and degradation time all influenced the degradation process and final degree of degradation. Comparison with pure thermal degradation clearly demonstrated the effectiveness of the microwave-assisted process as the time and temperature needed for complete degradation was significantly reduced. Several characterization techniques were utilized for mapping the degradation processes and resulting degradation products. After optimization of the process, complete degradation of PHB to monomeric degradation products (3-hydroxybutanoic acid, 3-methoxybutanoic acid, and crotonic acid) was reached after only 20 min of microwave heating at 110 °C. Functional chemicals for synthesis or modification of biopolymers are thus obtainable from microwave-assisted degradation of PHB in green solvents. This offers new possibilities for retaining the material value of PHB via chemical recycling.

**KEYWORDS:** Poly(3-hydroxybutyrate), Microwave, Recycling, Hydrolysis, Polyester



## INTRODUCTION

Recycling plastic waste is of critical importance for a sustainable society as it generates new resources for material production and reduces environmental pollution.<sup>1</sup> Chemical recycling of polymers aims at production of fuels, new functional chemicals, and materials or reproduction of the original polymer through depolymerization followed by repolymerization to a product corresponding to the original material. Biodegradable polymers can be biologically recycled, but still, an effective low energy recycling to new chemicals would be a more environmentally and economically benign solution. Polyhydroxyalkanoates (PHA)s are biobased and biodegradable polyesters produced in nature as a carbon and energy storage materials in various microorganisms generally under conditions of limited nutritional elements and excess carbon sources.<sup>2–5</sup> PHAs with four to six carbon atoms have similar properties to commodity thermoplastics.<sup>6</sup> The most common PHA is poly(3-hydroxybutyrate) (PHB), first isolated and characterized in 1925.<sup>7,8</sup> Previously, PHAs have been chemically recycled through thermal degradation or pyrolysis to crotonic acid (CA) and well-defined oligomers with one unsaturated and one carboxylic acid chain end<sup>9–11</sup> and cyclic oligomers.<sup>11</sup> The degradation temperatures generally ranged from 170 to 300 °C. As an example, highly selective transformation of PHB to crotonic

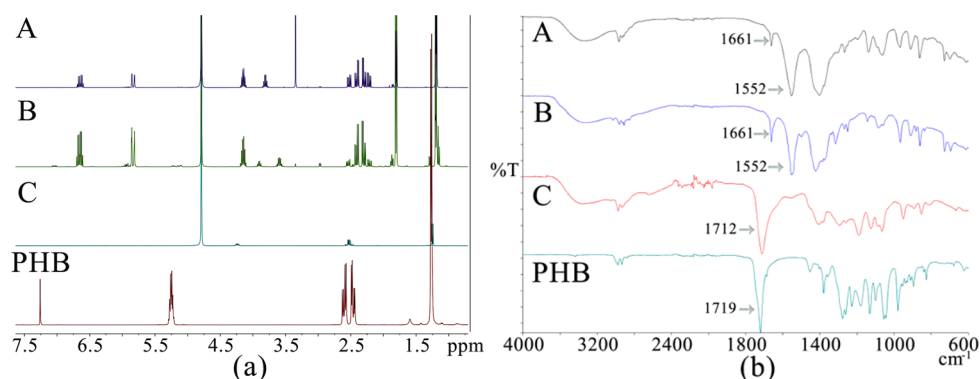
acid was achieved by catalytic thermal degradation at 240–280 °C in the presence of MgO or Mg(OH)<sub>2</sub>.<sup>12</sup> 3-Hydroxybutanoic acid, the potential monomer for synthesis of new PHB through a chemical route, is not formed during thermal degradation; however, it can be produced through enzymatic hydrolysis of PHB.<sup>13</sup>

The application of microwave energy is superior in comparison with conventional heating on accelerating chemical processes leading to rapid transformations, high yields, and milder reaction conditions. Microwave-assisted reactions in several studies were utilized for chemical recycling of polymers<sup>14,15</sup> and biomass.<sup>16–18</sup> Recently, it was also shown that microwave irradiation is an efficient approach for high yield production of PHB oligomers through the thermal degradation route resulting in oligomers with unsaturated chain ends and varying molecular weights.<sup>19</sup> The temperature range studied for the microwave-assisted thermal degradation was 180–220 °C, and the degradation rate was about 100 times faster than during conventional thermal heating at the same temperature.

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**Figure 1.** (a) <sup>1</sup>H NMR spectra of PHB degraded in (A) methanol, (B) ethanol, and (C) water, and original PHB spectra. (b) IR spectra for corresponding samples.

Previous studies on chemical recycling of PHB mainly concentrated on thermal recycling to crotonic acid and unsaturated oligomers.<sup>9,19–21</sup> Even though thermal pyrolysis can successfully degrade PHB to unsaturated monomers and oligomers, efficient low-temperature recycling of PHB to monomers that can be repolymerized to the corresponding degradable materials would be of high interest. We aimed to utilize microwave-assisted reaction in green solvents water, methanol, and ethanol under alkaline conditions to achieve fast low-temperature hydrolysis of PHB to functional monomers with carboxyl and hydroxyl or methoxy or ethoxy end groups instead of the unsaturated end groups. These monomers could then be directly exploited for synthesis of new PHB or PHB oligomers.

## EXPERIMENTAL SECTION

**Materials.** PHB powder (Tianan Biologic Materials Co. Ltd.), 99% LC-MS grade methanol (VWR), 96% ethanol (VWR), LC-MS grade water (Merck) 97+% sodium hydroxide pellets (Aldrich), and 2,5-dihydroxybenzoic acid (DHB) (Fluka) were used as received.

**Microwave-Assisted PHB Degradation.** PHB degradation was induced by a microwave solvent extraction system, model MES-1000, purchased from CEM Corporation. The MES-1000 is furniture with an alternating turntable drive system rotating 360° with 12 sample vessel holders. It delivers selectable power up to 950 W at a frequency of 2450 MHz at full power. There is a pressure and temperature control system equipped with MES-1000 to monitor and control pressure conditions inside the sample vessels. Originally, three solvents were tested as degradation medium: water, methanol, and ethanol. In addition to degradation in pure solvents, the effect of NaOH addition was evaluated as it is known that alkaline conditions catalyze the hydrolysis of PHB.<sup>20</sup> The original trials showed rapid hydrolysis in alkaline methanol, and a more thorough method optimization was performed with alkaline methanol as a solvent. A series of experiments were performed to optimize PHB degradation conditions in the alkaline methanol by varying the solvent/polymer ratios, NaOH concentration (0.01–1.0% w/w), time (20 min to 8 h), and temperature (fixed to 110 °C after initial trials). After degradation, most of the solutions contained suspended solid particles, while under some conditions almost clear solutions were obtained. The solutions, after degradation, were collected and concentrated using a rotary evaporator. The white solid products were subsequently placed in a vacuum oven at room temperature overnight or until a constant weight of the solid products was reached. The final collected solid products were thereafter analyzed using various characterization methods.

**Thermal Degradation.** To compare microwave-assisted PHB degradation with pure thermal degradation, PHB powder was heated for 4 h at 190 °C in a nitrogen atmosphere or under vacuum.

**Characterization.** Weight loss was measured for each specific degradation time. The clear supernatant solutions were kept for later

analysis, and the remaining solid samples were filtered and washed with methanol four consecutive times to remove NaOH and were then dried in a vacuum oven to a constant weight.

Fourier transform infrared spectrometry (FTIR) of neat PHB powder was performed on a PerkinElmer Spectrum 2000 FTIR with an attenuated total reflectance (ATR) crystal accessory (Golden Gate). All spectra were scanned at 2 cm<sup>-1</sup> resolution in the 4000–600 cm<sup>-1</sup> interval. The structure of neat PHB powder and thermally degraded PHB were analyzed by a Bruker Avance iii HD 400 NMR instrument. <sup>1</sup>H NMR was determined at 400 MHz and <sup>13</sup>C NMR at 100 MHz. The number-average molecular weight ( $M_n$ ) and dispersity index ( $\bar{D}$ ) of neat PHB and thermally degraded PHB were evaluated with a Verotech PL-GPC 50 Plus Size exclusion chromatography (SEC) system equipped with a PL-RI detector and two PLgel 5 μm MIXED-D (300 × 7.5 mm) columns from Varian. The mobile phase was chloroform, and polystyrene standards were used for calibration. Matrix-assisted laser desorption ionization-mass spectrometry (MALDI-MS) was used to analyze the molecular weight of thermally degraded PHB. The Voyager DE-STR time-of-flight mass spectrometer with a 337 nm nitrogen laser source was used with positive ion mode and in reflector mode. The acceleration voltage was 25 kV, and the reflector voltage was 26.3 kV.

Degradation products from microwave-assisted reaction were analyzed by NMR, FTIR, and electrospray ionization-mass spectrometry (ESI-MS). A Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA, U.S.A.) was used in positive mode. The ion source was operating at 5 kV. The capillary heater was set to 175 °C. The flow rate of the syringe pump was 5 μL/min. Nitrogen was used as the nebulizing gas. The damping gas and collision gas in the mass analyzer was helium.

## RESULTS AND DISCUSSION

PHB was microwave heated in green solvents: water, methanol, and ethanol. Alkaline conditions were utilized to additionally accelerate the hydrolysis rate aiming at effective high yield chemical recycling of PHB to functional monomers or oligomers. It was not possible to conventionally heat the selected solvents to temperatures reached during microwave heating. Although not scientifically comparable, to obtain an idea of degradation times during conventional heating and to show the difference in obtained degradation products, thermal degradation of PHB under vacuum and nitrogen atmospheres was performed. The resulting degradation products were carefully identified and characterized by ESI-MS, MALDI-MS, NMR, and FTIR.

**Solvent Selection for Microwave-Assisted Degradation.** To select the best solvent for the degradation reaction, PHB was microwave heated in water, methanol, or ethanol keeping the reaction time and sodium hydroxide concentration

constant. Due to differences in boiling points and resulting pressure in the microwave vials, the maximum possible heating temperatures were 110 °C for methanol, 140 °C for ethanol, and 150 °C for water. It took 1 min to heat methanol and ethanol to these maximum temperatures, while it took 20 min for water to reach 150 °C. Higher temperature usually accelerates the degradation rate, and at the same time, short RAMP time is vital both for obtaining a short total reaction time and for comparing the degradation rates under different conditions.

The trends for the degradation products formed after microwave heating in methanol and ethanol were similar but distinctly different from the degradation products formed in water (Figure 1A–C). All the  $^1\text{H}$  NMR spectra of the soluble degradation products have very clear and distinct peaks, which indicates that a limited number of degradation products with low molecular weight were formed. The products obtained after degradation in all three solvents showed shifted peaks compared to neat PHB, which demonstrates that degradation has taken place. The main degradation products identified after microwave heating in alkaline methanol were crotonic acid, 3-hydroxybutanoic acid, and 3-methoxybutanoic acid. The latter product is a secondary product formed due to the reaction of 3-hydroxybutanoic acid with alkaline methanol. The formation of monomeric products is in agreement with the mechanism shown for conventional alkaline hydrolysis of PHB in water proceeding through sequential degradation of PHB from the chain ends resulting in monomeric degradation products.<sup>22</sup> Crotonic acid and 3-hydroxybutanoic acid were also formed when ethanol was used as a solvent. In addition, ethanol reacted with 3-hydroxybutanoic acid forming 3-ethoxybutanoic acid. This is shown by the additional peak in the  $^1\text{H}$  NMR observed between 3.5 and 4.0 ppm. The peak at 3.3 ppm assigned to the  $-\text{O}-\text{CH}_3$  protons was absent after degradation in ethanol. After degradation in water, the main degradation product was 3-hydroxybutanoic acid and its oligomers. No crotonic acid was detected, which could be due to a much lower degree of degradation.

In accordance, the water-soluble degradation products formed after microwave heating in methanol and ethanol had very similar FTIR spectral trends, and the FTIR spectra were distinctly different from the spectra of the original PHB. The ester carbonyl band at  $1719\text{ cm}^{-1}$  was the strongest absorbance band for original PHB, but after degradation in alkaline methanol or ethanol, the carbonyl absorbance shifted to  $1552\text{ cm}^{-1}$ . This shows that the acid products are present as sodium salts. Meanwhile, a new band at  $1661\text{ cm}^{-1}$  indicated that  $\text{C}=\text{C}$  bonds were formed. The FTIR spectrum of the product mixture after degradation in water showed much smaller changes compared to the FTIR spectra of neat PHB. The FTIR spectra also supported the NMR results showing that no crotonic acid was formed during microwave heating in water. Altogether the fastest degradation, and in the lowest temperature, was achieved in alkaline methanol. This reaction also resulted in a limited number of water-soluble degradation products. Somewhat higher temperature was required for degradation in alkaline ethanol, and degradation in alkaline water showed much low efficiency and long RAMP times.

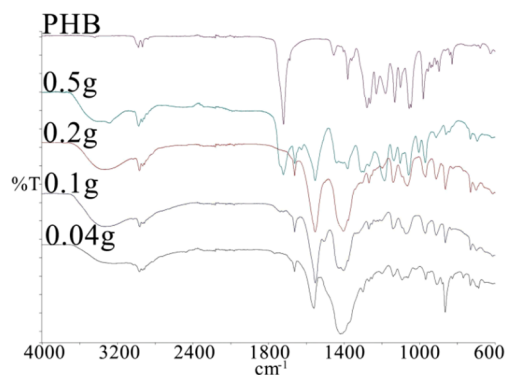
To evaluate the effect of alkaline conditions, PHB was microwave heated in pure methanol for 1 h. During this time, PHB powder swelled forming a pudding-like product (Figure 2), but the degree of degradation was low. Similarly, after 1 h degradation in pure water, the weight loss was less than 3%.



**Figure 2.** Solid product remaining after 1 h of microwave heating in pure methanol.

The degradation in alkaline methanol with 0.5% w/w NaOH, on the other hand, resulted in almost complete degradation to water-soluble products and clear transparent solutions within 20 min. The main focus was therefore placed on optimization of PHB degradation in alkaline methanol. Concerning the mechanism of degradation, the identified degradation products together with the very limited degradation in pure methanol strongly indicate that the main degradation mechanism was alkaline hydrolysis between ester and hydroxyl groups. For example, the glycolysis reaction between ester and methanol groups did not take place.

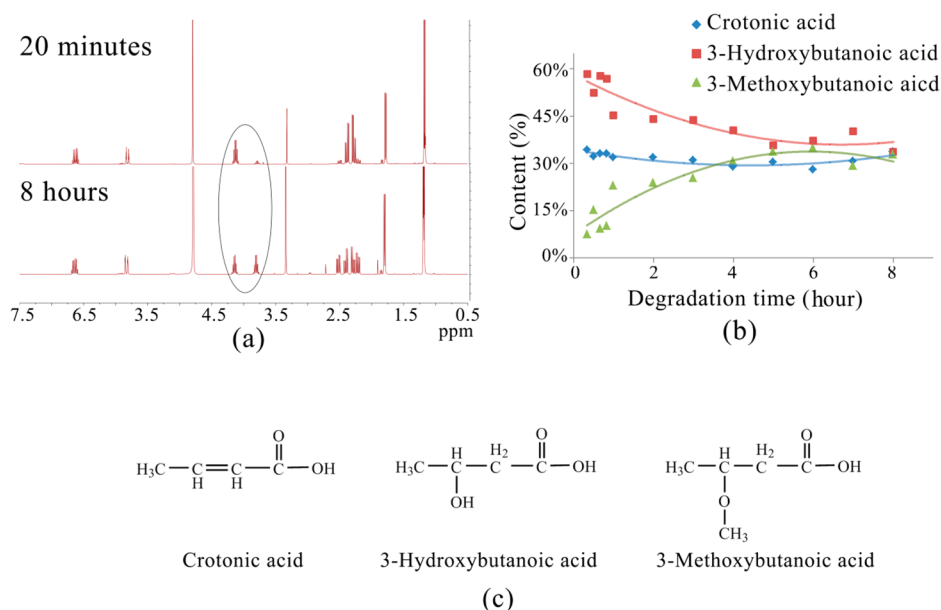
**Effect of PHB and NaOH Concentrations.** The process was also optimized with respect to the amount of PHB and NaOH. The influence of the original sample amounts on the degradation process in 0.5% w/w alkaline methanol solution is illustrated in the FTIR spectra (Figure 3). The figure shows



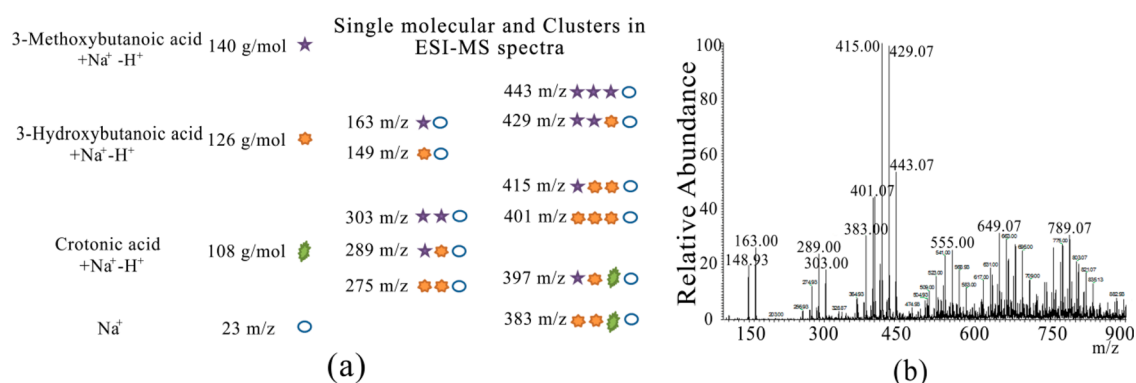
**Figure 3.** FTIR spectra of PHB degradation products as a function of original PHB sample mass.

that in 20 mL of 0.5% w/w alkaline methanol solution degradation of up to 0.2 g of PHB follows a similar pattern. However, when a higher amount of PHB was added, the degradation rate of PHB decreased. The intensity of the ester carbonyl band at  $1719\text{ cm}^{-1}$  originating from the solid PHB residue increased with a higher original PHB amount, indicating less complete degradation when the sample amount increased. The water-soluble hydrolysis products were in the form of sodium salts, and the carbonyl band originating from these compounds was shifted to  $1552\text{ cm}^{-1}$ .

It has been reported that hydroxyl ions can lower the energy barrier of ester bond breakage.<sup>22</sup> Theoretically, the higher the concentration of hydroxyl ions the faster the degradation observed. The effect of different NaOH concentrations on the microwave-assisted degradation of PHB was, therefore, also evaluated. The higher the NaOH concentration in methanol is, within the NaOH solubility range, the faster the degradation rate of PHB is. When the same amount of PHB and the same



**Figure 4.** (a) <sup>1</sup>H NMR spectra of PHB degraded in 0.5% w/w alkaline methanol solution and microwave heating for 20 min and 8 h. (b) Ratio of different main degradation products according to <sup>1</sup>H NMR. (c) Chemical structures of the main degradation products.



**Figure 5.** (a) ESI-MS identification of the different degradation products. (b) ESI-MS spectrum showing the degradation products after 4 h of microwave-assisted degradation under optimized conditions.

degradation time were used, there were white insoluble particles left after degradation in 0.01% w/w and 0.1% w/w NaOH after 4 h. When the NaOH concentration was raised to 0.5% w/w, more than 98% of the PHB was degraded to water-soluble products after 20 min. It is quite difficult to remove NaOH from the degradation products, and the remaining NaOH will influence the further usage of the degradation products and characterization using base-sensitive characterization methods. On the basis of this and the fact that PHB was almost totally degraded in 20 min under these conditions, 0.5% w/w NaOH in methanol was chosen for further experiments. The effect of NaOH concentration on degradation product composition was not studied, but earlier studies have shown that while NaOH concentration greatly influences the hydrolysis rate, it does not significantly influence the product composition.<sup>22</sup>

**Time Effect on Microwave-Assisted Degradation.** The degradation trials showed that effective hydrolysis was achieved when 0.1 g of PHB powder was degraded at 110 °C in 10 mL methanol with 0.5% w/w NaOH. After performing microwave degradation for different times under these conditions, methanol was evaporated, and the degradation products were

obtained as white solid powder. The degradation products were dissolved in water and analyzed by <sup>13</sup>C NMR and <sup>1</sup>H NMR (Figure 4). The main degradation products identified were crotonic acid, 3-hydroxybutanoic acid, and 3-methoxybutanoic acid (Figure 4c). <sup>1</sup>H NMR spectra indicate the formation of the same chemical structures after different degradation times, but the composition of the product mixture changed with time. The presence of peaks at around 6.64 and 5.85 ppm correspond to the protons in carbon–carbon double bonds and shows that the product mixture contains degradation products with unsaturated carbons. <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra also significantly differed from the original PHB spectrum. In the <sup>1</sup>H NMR spectra, the relative intensity of peaks at 4.15 and 3.82 ppm changed as a function of degradation time from 20 min to 8 h. The peaks around 4.15 ppm representing the protons in 3-hydroxybutanoic acid decreased, while the peaks around 3.82 ppm corresponding to the protons in 3-methoxybutanoic acid increased. Long degradation time, thus, meant increasing amounts of 3-methoxybutanoic acid formed by the reaction between methanol and 3-hydroxybutanoic acid. The amount of crotonic acid did not change significantly with time. The trend is shown in Figure 4b. The relatively constant ratio between

crotonic acid and the other monomeric products (3-hydroxybutanoic acid and its further reaction product 3-methoxybutanoic acid) indicates that crotonic acid and 3-hydroxybutanoic acid are formed from the PHB backbone as a result of two competing reactions (dehydration and hydrolysis), and crotonic acid is not formed from 3-hydroxybutanoic acid as a result of dehydration. This is in agreement with what was reported earlier during conventional alkaline hydrolysis of PHB in water.<sup>22</sup>

The weight of the solid fraction after microwave-induced degradation was almost independent of degradation time. Already, after 20 min of degradation, the PHB powder experienced a weight loss of no less than 98%, and the weight loss remained between 98% and 100%.

To confirm and identify the degradation products formed, ESI-MS analysis was performed on all the degradation product mixtures after different degradation times. In accordance with NMR results, ESI-MS confirmed that crotonic acid, 3-hydroxybutanoic acid, and 3-methoxybutanoic acid were formed during microwave-assisted degradation in alkaline methanol irrespective of degradation time (Figure 5). Several clusters consisting of two or three monomeric degradation products also appeared in the ESI-MS spectra. Similar cluster formation has been observed during previous ESI-MS studies.<sup>23</sup>

**Thermal Degradation.** For comparison, PHB was thermally degraded under vacuum and in an inert atmosphere at 190 °C. During thermal degradation, the original fine white powder turned to a brown solid with a slight smell. A large molecular weight reduction was observed as compared to the original value, but in both cases, a nonwater-soluble residue remained after 4 h of degradation (Table 1). Thermal

**Table 1. Molecular Weight and Dispersity Index after Thermal Degradation as Measured by SEC**

sample	temperature	duration	conditions	$M_n$	$\bar{D}$
original PHB powder	—	—	—	326,100	1.8
thermal degradation under nitrogen	190	4 h	nitrogen	38,200	1.5
thermal degradation under vacuum	190	4 h	vacuum	6300	2.3

degradation under vacuum proceeded at a higher rate as compared to the degradation under nitrogen. Even though the

degradation temperature was much higher, the degradation rate was still significantly lower than during the microwave-assisted alkaline hydrolysis, clearly demonstrating the effectiveness of the developed microwave process.

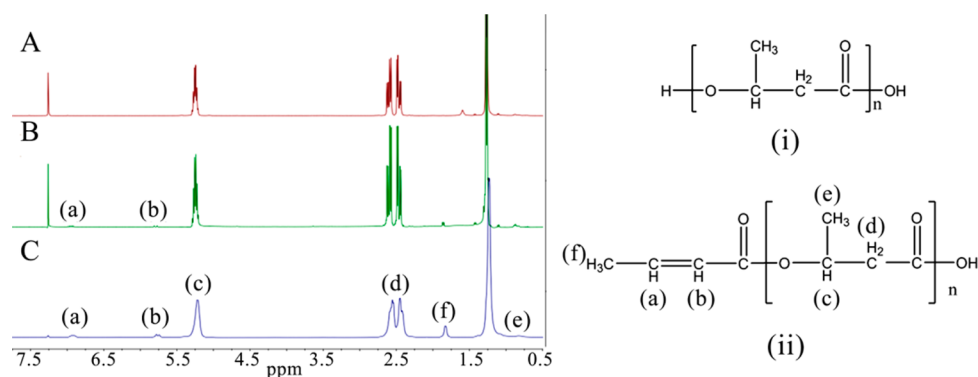
Thermal degradation products were identified by <sup>1</sup>H NMR and MALDI-MS. Oligomers with a crotonate end groups were obtained after the thermal degradation process. Figure 6 shows the <sup>1</sup>H NMR spectra of the original PHB and the residues after 4 h of thermal degradation in nitrogen and vacuum. Multiple and broad peaks were observed. Peaks around 6.92 (a) and 5.78 (b) ppm correspond to the protons (a and b) of the unsaturated end groups. After 4 h of thermal degradation under vacuum, a big doublet around 1.83 ppm corresponding to the methyl group (f) on the unsaturated carbon was observed. It shows that larger amount of oligomers with crotonate end groups were formed during degradation under vacuum compared to degradation in nitrogen. The general structure of the oligomers with crotonate end groups is shown in Figure 6 (ii).

MALDI-MS spectra of PHB degraded thermally in vacuum showed similar structural information as NMR. The wide range of oligomers with crotonate end groups corresponding to 10–54 repeating units and  $m/z$   $172 + 86n + K^+$  were observed, which is in relatively good agreement with the SEC results shown in Table 1. Even with the faster thermal degradation under vacuum, it took 4 h to degrade PHB powder to a  $M_n$  of about 6000 g/mol. This can be compared to microwave-assisted degradation, where only 20 min at lower degradation temperature was needed to degrade PHB to small water-soluble molecules.

There were no significant differences in the thermal properties of the thermally degraded and neat PHB. The melting and crystallization peaks moved to lower temperatures indicating that the molecular weight had decreased. Two melting peaks at lower temperature were found for vacuum-degraded PHB, which had much higher  $\bar{D}$  and smaller  $M_n$  than the PHB degraded in nitrogen.

## CONCLUSIONS

An efficient process for chemical recycling of PHB to functional monomers through microwave-assisted degradation in green solvents was developed and demonstrated. Alkaline conditions significantly promoted the degradation rate of PHB, and the degradation rate further increased with higher NaOH concentration. After only 20 min of microwave-assisted degradation in 0.5% w/w alkaline methanol, almost 100%



**Figure 6.** Chemical structures of (i) PHB and (ii) low molecular weight oligomers with crotonate end groups. <sup>1</sup>H NMR spectra of original PHB (A) and PHB after 4 h of thermal degradation in nitrogen gas (B) and under vacuum (C).

degradation of PHB to water-soluble monomeric degradation products (3-hydroxybutanoic acid, 3-methoxybutanoic acid and crotonic acid) was achieved. The same degradation products were identified irrespective of the microwaving time. However, during prolonged microwave heating, the amount of 3-methoxybutanoic acid increased and the amount of 3-hydroxybutanoic acid decreased due to reaction of 3-hydroxybutanoic acid with alkaline methanol. The amount of crotonic acid remained constant with heating time, indicating formation through dehydration and hydrolysis of PHB chain ends and not through dehydration of 3-hydroxybutanoic acid. Microwave-assisted degradation in green solvents proceeded at a significantly higher rate and at lower temperature compared to pure thermal degradation of PHB. Microwave-assisted hydrolysis in green solvents is a promising technique for keeping the material value of PHB via chemical recycling to functional chemicals.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: minna@kth.se. Tel.: +46-8-7908271.

### Notes

The authors declare no competing financial interest.

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