Sustainable, highly selective and metal free thermal depolymerization of poly-(3-hydroxybutyrate) to bio-crotonic acid in recoverable ionic liquids

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Highlights

- Highly selective and metal free synthesis
- Industrially important bio-crotonic acid
- Mild reaction conditions and high yield
- High accuracy of the kinetic model when the catalyst deactivation parameter (kd) was applied

1. Introduction

Valorization of renewable and biodegradable biopolymers to value added chemicals and green fuels is currently considered as an important research topic aiming at reducing the dependency on fossil derived feedstocks as well as their negative consequences on the environment. In this report, we are introducing an ionic liquid (IL) mediated, sustainable, and green synthesis of crotonic acid (CA) from poly-(3-hydroxybutyrate, PHB), a biopolymer derived from microbial fermentation. Imidazolium cation comprising ILs were used in the synthesis, where influence of various reaction parameters such as reaction temperature, types of ILs as well as the amount of polymer, water, and IL in the reaction mixture were examined. The conversion of PHB to CA in IL took place by a base catalyzed depolymerization with formation of crotonyl terminated polymeric entities as intermediates, a mechanism that was confirmed by NMR analysis of the reaction mixtures sampled when the reactions were carried out at various temperatures. The rate of CA formation via the IL mediated base catalyzed depolymerization increased with increasing temperature in the tested interval, and 97 % yield of CA was obtained after 90 min at 140°C. The [EMIM][AcO] IL applied as solvent and catalyst is capable of completely depolymerizing PHB to CA in 5 h at 120°C up to a polymer loading of 40 wt. %.

2. Methods

Reagents and chemicals. Poly-(3-hydroxybutyrate) was purchased in powder form as PHI 003 from NaturPlast (Ifs, France) and used without further processing. All chemicals were used without additional purification.

NMR analysis. The progress of the depolymerization of PHB and formation of CA in the reaction mixtures under varying reaction parameters were monitored by ^{1}H and ^{13}C NMR.

Differential scanning calorimetric analysis (DSC) of [EMIM][AcO] IL and crotonic acid mixtures. A Mettler DSC 821e differential scanning calorimeter (Mettler Toledo, Columbus, OH, USA) was used to investigate the enthalpy changes associated with thermal transition of the mixtures.

Kinetic study of the synthesis of CA from poly-(3-hydroxybutyrate) in ILs. A kinetic study of the conversion of PHB to CA in IL media was also carried out. Prior to this study, a calibration curve to calculate the amount of CA was established by ^{1}H NMR in $CDCl_3$ with methanol as internal standard. Kinetic models for the synthesis of CA from PHB, with and without catalysts deactivation parameter, were developed using the modelling and optimization software ModEst®, where the kinetic parameters such as reaction rate constants (k), activation energy (Ea) and deactivation parameter (kd) were estimated by non-linear regression using the Simplex and Levenberg−Marquardt methods. This software solves the system of ordinary differential equations forming the batch reactor model with the backward difference method. The mass balances for the starting material (PHB as moles of monomer units) and

the product (CA) in a batch reactor are defined by the following differential equations, where m_{cat}, c, and α are the catalyst mass, concentration, and catalyst activity, respectively, while t is time.

$$\frac{dc_A}{dt} = -k\, c_A\, m_{cat}\, \alpha \ldots\ldots\ldots (1)$$

$$\frac{dc_B}{dt} = k\, c_B m_{cat}\, \alpha \ldots\ldots\ldots\ldots (2)$$

$$\alpha = e^{-k_d t} \ldots\ldots \qquad \ldots (3)$$

The rate constants were presumed to obey the Arrhenius law where the modified Arrhenius equation 3 was used to suppress the correlation between the pre-exponential factor and the activation energy,

$$k = Ae^{-\left(\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_{mean}}\right)\right)} \ldots\ldots (4)$$

Here *k, A, Ea, R, T*, and T_{mean} represent the reaction rate constant, the frequency factor at the mean temperature (105 °C), activation energy of the reaction, the universal gas constant, the temperature, and the mean temperature of the experiments, -respectively. Additionally, a statistical analysis was conducted using the Monte Carlo Markov Chain (MCMC) method. In this method, the samples are drawn randomly to approximate the probability distribution of parameters. The MCMC method is usually designed on the basis of a Bayesian approach and incorporated in the optimization software ModEst®.

3. Results and discussion

Synthesis of CA through depolymerization of poly-(3-hydroxy butyric acid) in ILs. The synthesis of CA was carried out in ionic liquid media by thermal depolymerization of commercially available PHB, where the influence of key reaction parameters such as the IL type, reaction temperature and time, polymer:IL ratio, and addition of water were studied. The 1H NMR spectra reveal that the amount of PHB in the reaction mixture gradually decreased with time and was completely reacted after 5 h under the applied conditions.

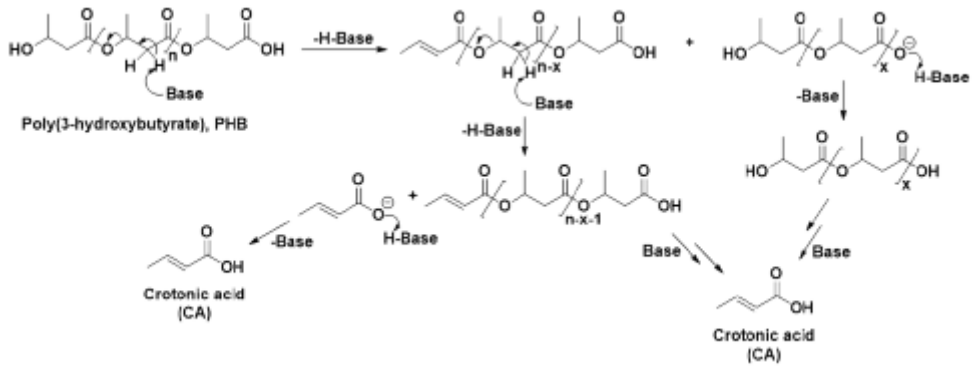

Figure 1. Schematic representation of the base catalyzed conversion of poly(3-hydroxybutyrate) to crotonic acid.

4. Conclusions

The applied kinetic model demonstrated high degree of explanation after introducing the catalysts deactivation parameter. Basic ILs with imidazolium cations and acetate anions have for the first time been used for efficient and highly selective depolymerization of PHB to CA under mild conditions, converting 20 wt.% PHB in IL to CA with 97 % yield in 90 min at 140°C.

References

[1] P. Jablonski, D. Nikjoo, J. Wärnå, K. Irgum, J. Mikkola and S. G. Khokarale, Green Chem., 2022, 24, 4130-4139, DOI:10.1039/D2GC00621A

Keywords
poly-(3-hydroxybutyrate, PHB), [EMIM][AcO] IL, crotonic acid