Electronic Supplementary Material (ESI) for RSC Sustainability.

Recycling Post-consumer PLA into Acrylic Acid or Lactide using Phosphonium Ionic Liquids

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Experimental section

Materials

All chemicals were used as received: poly(lactic acid) (Natureworks®), tetrabutylphosphonium bromide (Sigma-Aldrich, 98%), tetrahydrothiophene-1,1-dioxide or sulfolane (Sigma, 99%), Ar (Air Liquide, α1), H_2SO_4 (Merck, 98%), HBr (Sigma-Aldrich, 48% in water), DL-lactic acid (Sigma-Aldrich, 90%), DL-lactide (Thermo Fischer, 99%), acrylic acid (Acros Organics, 99.5%, stabilized), 2-bromopropionic acid (Sigma-Aldrich, 99%), 3-bromopropionic acid (Sigma-Aldrich, 97%), HBr (Acros Organics, 33% in acetic acid), tetrabutylphosphonium chloride (IoLiTec, >95%), tetraethylphosphonium bromide (TCI, 98%), 1-bromohexadecane (Sigma-Aldrich, 97%), 1-bromopropane (J&K Scientific, 98%), $ZnBr_2$ (Thermo Fischer, 98%), $MgBr_2$ (Acros Organics, 98%), DMSO d_6 (Sigma-Aldrich, 99%), benzyl alcohol (Alfa Aesar, 99%), post-consumer PLA (plastic cutlery from the university canteen).

Catalytic reaction

All standard reactions are performed in a glass crimp cap vial (11 mL) flushed with Argon to obtain an inert atmosphere and stirred at 500 rpm for a given time and at a certain temperature. The inert atmosphere was obtained by sending an Argon flow through the headspace for 1 minute and deemed necessary as reactions under ambient, humid air showed significantly lower yield compared to Ar atmosphere. After reaction, the vial was cooled to room temperature and equimolar amount of benzyl alcohol (BZA), relative to the PLA repeating unit, was added as an external standard and stirred vigorously at room temperature for 5 minutes. Next, a 100 µL aliquot of the crude mixture was diluted in 400 µL DMSO-d_6 and measured on NMR without additional workup. If the reaction mixture solidifies at room temperature, e.g. in the absence of sulfolane cosolvent, the reaction mixture was first diluted in an excess of 0.5 mL DMSO-d_6. Subsequently, BZA was added again in an equimolar amount compared to PLA, stirred for 5 min, and 500 µL was measured. Lastly, in the case of post-consumer PLA, the reaction mixture was centrifuged for 5 min at 3000 rpm to remove the solid impurities as they disturb the NMR analysis.

Reproducibility experiments were performed during the analysis of the time profile in five-fold. Results are incorporated in Figure 1. All reactions showed high reproducibility with a standard deviation below <3% for all reported products.

Product analysis

All product yields were obtained from ^{1}H NMR analysis of the crude reaction mixture, using BZA as an external standard. NMR spectra were measured on a Bruker Advance 400 spectrometer and analyzed using Topspin 4.0.9 software. Chemical shifts were obtained through comparison with pure reference compounds or previous reports in literature (Table S1, Figure S1).[1] In this work, we did not perform any analysis on the headspace of the reaction vial. It is expected to contain ethylene, acetaldehyde and CO/CO_2 as undesired, terminal end products resulting from decarbonylation/decarboxylation reactions.[2] However, these terminal end-products are not of interest for the recycling of PLA to valuable polymer precursors.

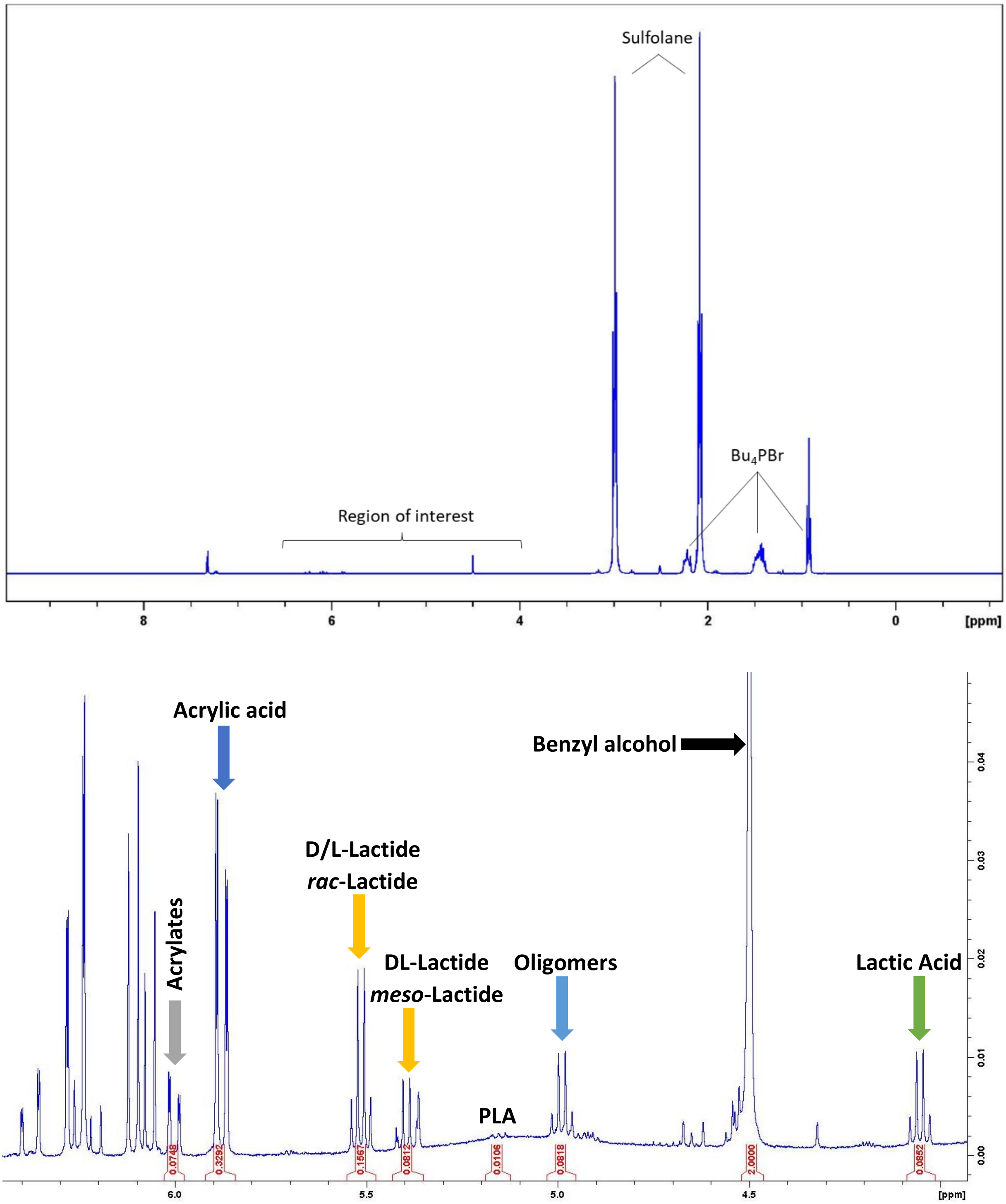


Figure S1 ^{1}H-NMR spectrum of crude reaction mixture after reaction (Table 1, entry 1), chemical shifts and corresponding products are displayed in Table S1. Top: full spectrum, Bottom: magnification of relevant region (6.4-4.0 ppm) including integration of the compounds of interest, reported in the main manuscript (Table 1, entry 1).

Table S1 Chemical shifts and corresponding products.

Chemical Shift (δ, ppm)	Corresponding Product
6.00	Acrylates
5.87	Acrylic Acid (AA)
5.51	Racemic mixture D/L lactide
5.38	Meso lactide (DL-lactide)
5.15	Unconverted PLA (Broad)
4.98	Oligomers
4.50	Benzyl alcohol (External standard)
4.05	Lactic Acid
3.62 & 1.7	3-BrPA/2-BrPA

Yields reported in this work are a result of the integration of the corresponding product peaks in comparison to the benzyl alcohol (BZA) external standard. When 2-bromopropanoic acid was tested as a cocatalyst, we took this into account for the overall yield as each 2-BrPA can result in an AA formed. For simplicity purposes, all forms of lactide were bundled in one overall lactide product yield (LAC) and reported relative to the PLA repeating unit incorporated in the lactide monomer (since lactide is a dimer consisting of 2 PLA units).

Thermogravimetric analysis (TGA)

Thermogravimetric analyses of PLA samples were carried out under air atmosphere on a NETZSCH STA 449 F3 Jupiter® thermal analyzer with a heating rate of 5°C min^{-1} over a range from 25°C-700°C. As can be observed in Figure S2, the pure PLA completely decomposes between 300-350°C. The post-consumer PLA on the other hand, while decomposing in the same temperature interval, retains approximately 30% of its original mass up until 700°C. It is hypothesized that the additives used for additional thermal stability, are in fact mineral fillers used as PLA hardeners.

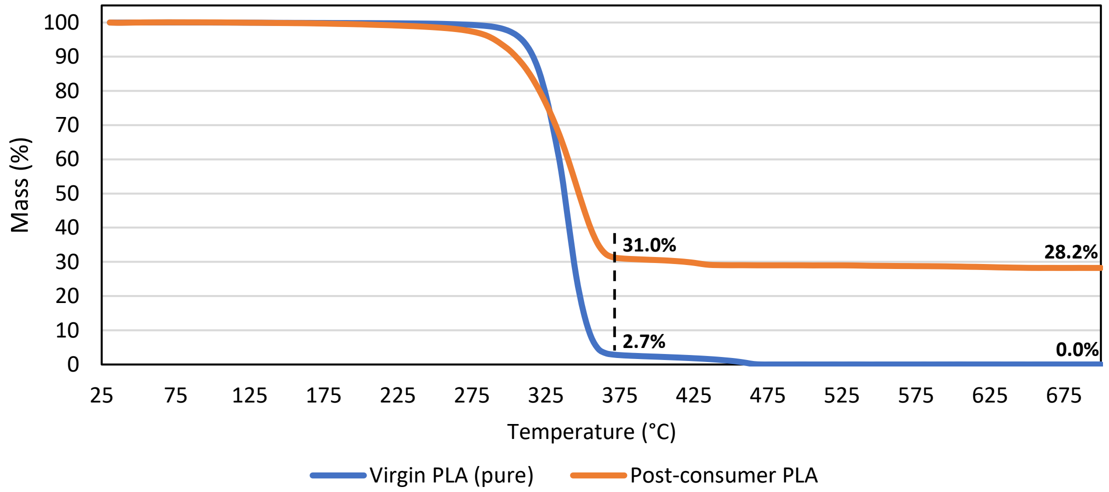


Figure S2 TGA for pure (virgin) PLA and post-consumer PLA cutlery. Mass percentages of pure PLA (blue) and waste PLA (orange) are expressed in function of temperature. The temperature was increased at a constant rate of 5°C/min.

Powder X-ray diffraction (PXRD)

The chemical composition of the 30 wt% filler found in the post-consumer PLA during the TGA measurements was determined using powder X-ray diffraction (PXRD). PXRD were recorded on a Malvern PANalytical Empyrean diffractometer equipped with a PIXcel 3D 1x1 detector. The powder samples were put onto a 96-well plate and patterns were recorded at room temperature in transmission geometry within a 1.3°-45° 2θ-range with a step size of 0.013° and analyzed via PANalytical Data Viewer software and MS Excel (Figure S3). For the PLA, a characteristic peak at 16.5° is observed, corresponding to literature (110/200)[3,4], which is absent in the PLA filler after the polymer is extracted with chloroform.[3] The post-consumer PLA shows additional peaks in the diffractogram, which are attributed to the filler as they remain present in the solid impurities after extraction and centrifugation. The observed diffraction pattern is in good correspondence with those of talc mineral, $Mg_3Si_4O_{10}(OH)_2$, with characteristic peaks at 9.5° (001), 19.4° (002) and 28.7° (003)[4,5], elucidating the inert nature of these fillers in the PLA depolymerization reaction.

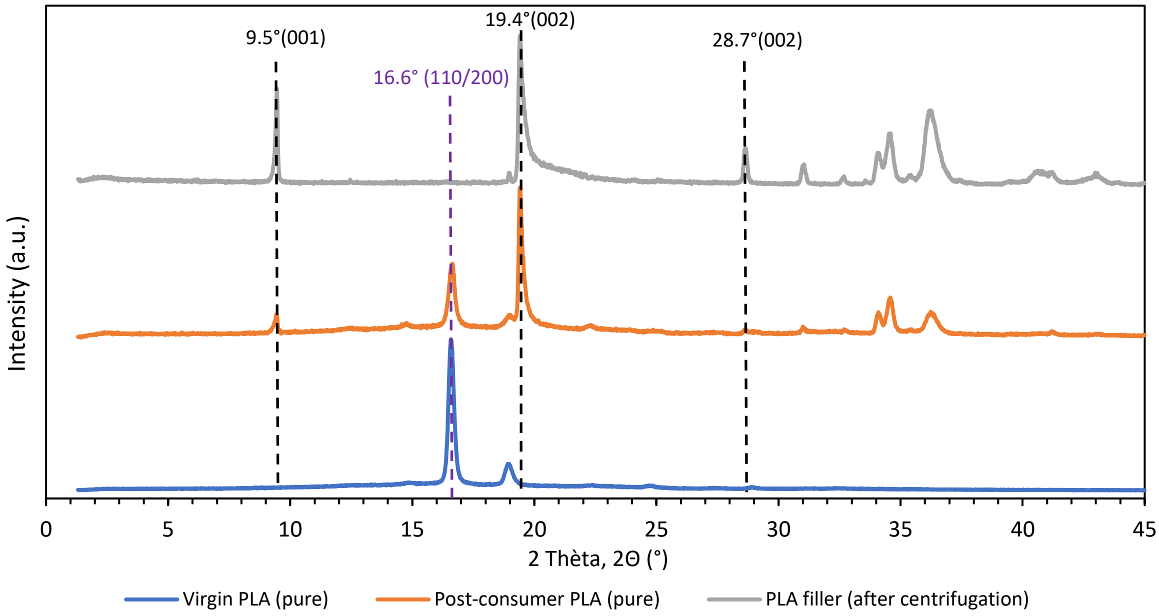
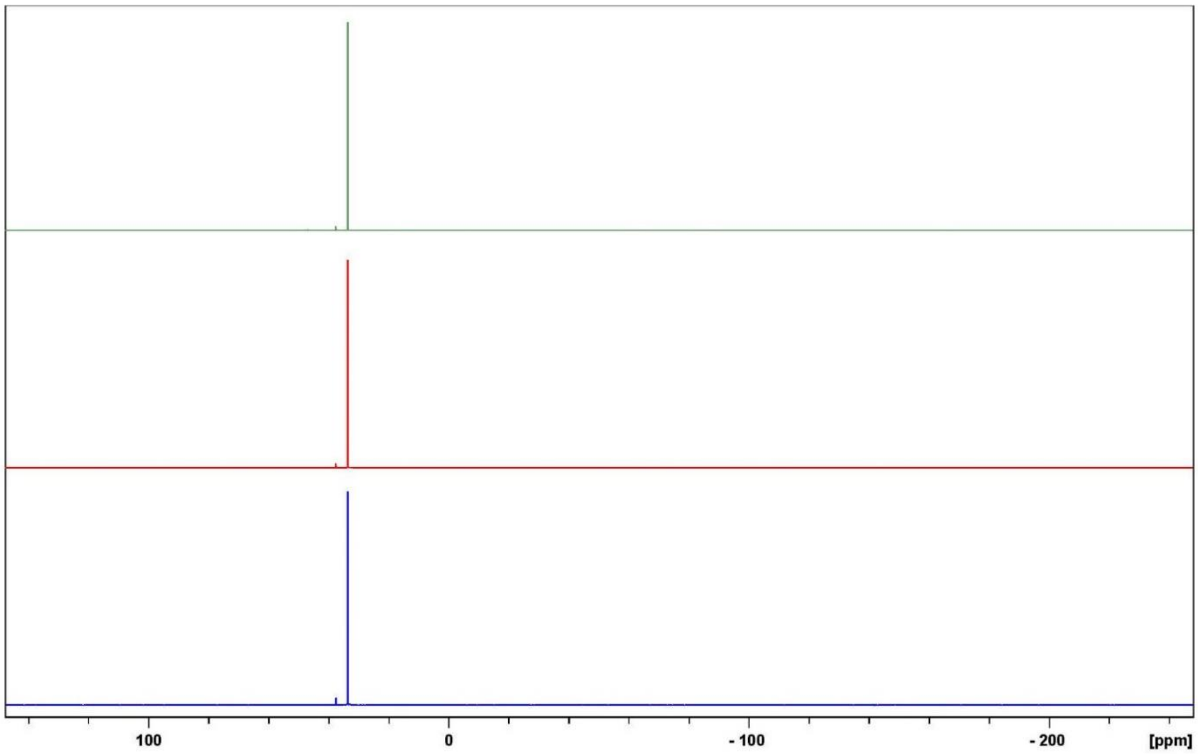


Figure S3 Powder XRD diffractogram for virgin PLA and post-consumer PLA cutlery. Virgin PLA (blue), post-consumer PLA pure (orange) and filler present after extraction of the PLA with $CHCl_3$ and centrifugation (grey). Characteristic peaks of both PLA and Talc are assigned corresponding to the literature.[3–5]

Ionic liquid stability tests based on ^{31}P NMR

^{31}P inverse gated NMR measurements were performed on a Bruker Advance 400 MHz spectrometer. Samples were diluted in DMSO-d_6 and NMR spectra were analyzed using Topspin 4.0.9 software. The ^{31}P NMR spectra of the reaction matrix both in the presence and absence of acid cocatalyst are compared with the virgin Bu_4PBr ionic liquid as obtained from Sigma Aldrich (Figure S4). For all three samples only significant peak was observed, corresponding to the thermally stable Bu_4PBr.[2]



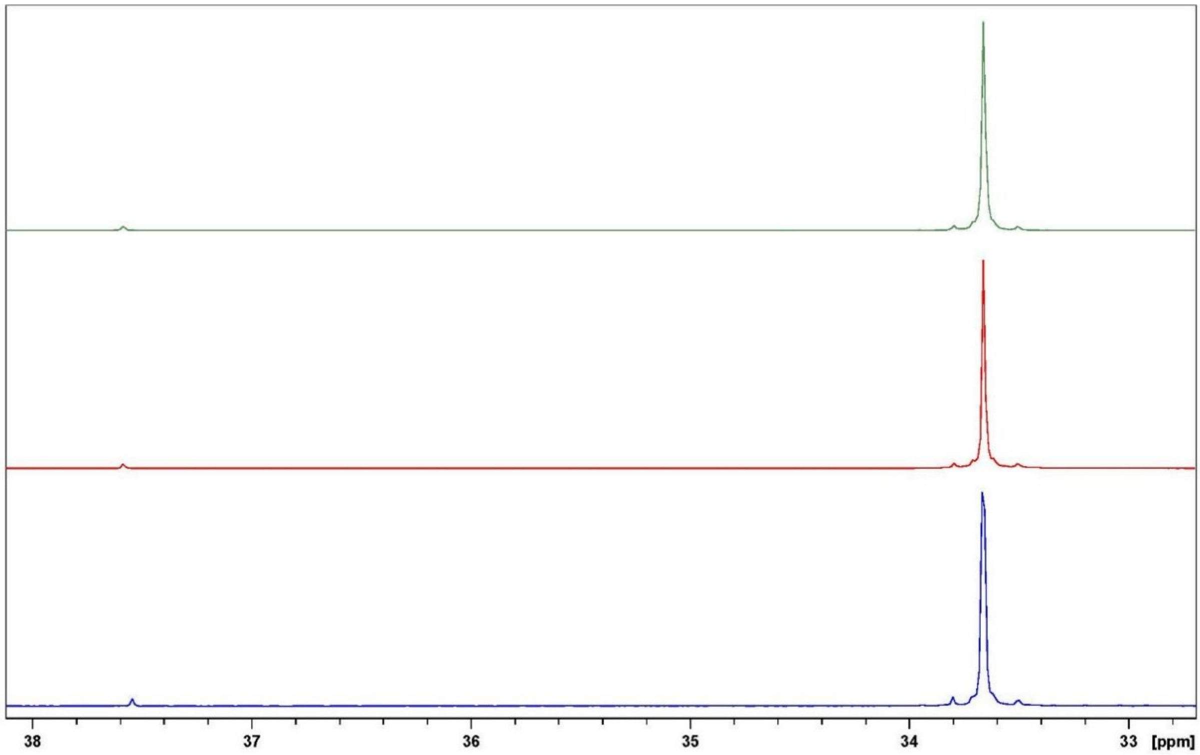


Figure S4 inverse gated ^{31}P NMR spectra of Bu_4PBr before reaction (Blue) and after 4h in the presence (Red) and absence (Green) of acid cocatalyst. Top: full spectrum, Bottom: magnification of relevant region (38-33 ppm). Reaction conditions: 0.5 mmol of PLA , 1.5 mmol Bu_4PBr, 2.5 mL sulfolane, 4h, 200°C, Ar flushed.

Product Isolation via vacuum distillation (analyzed by ^1H NMR).

Acrylic acid was obtained in high purity *via* continuous vacuum distillation (Figure S5) on a 5 gram scale PLA depolymerization reaction. Prior to the reaction, all reagents: PLA, Bu_4PBr and acid cocatalyst (2-BrPA, 5 mol%) were loaded into a 100mL flask and heated for three hours at 200°C under reduced pressure (5 mbar). The distillate was collected in a 10 mL flask, cooled on ice to allow for acrylic acid condensation. After the reaction, the setup was brought back to atmospheric pressure under argon flow to prevent spontaneous polymerization in the distillate. 1.48 gram transparent liquid was obtained, corresponding to 39% of isolated AA yield (>95% purity). The ^1H NMR spectrum was measured in DMSO-d_6 on a Bruker Advance 400 spectrometer and analyzed using Topspin 4.0.9 software.

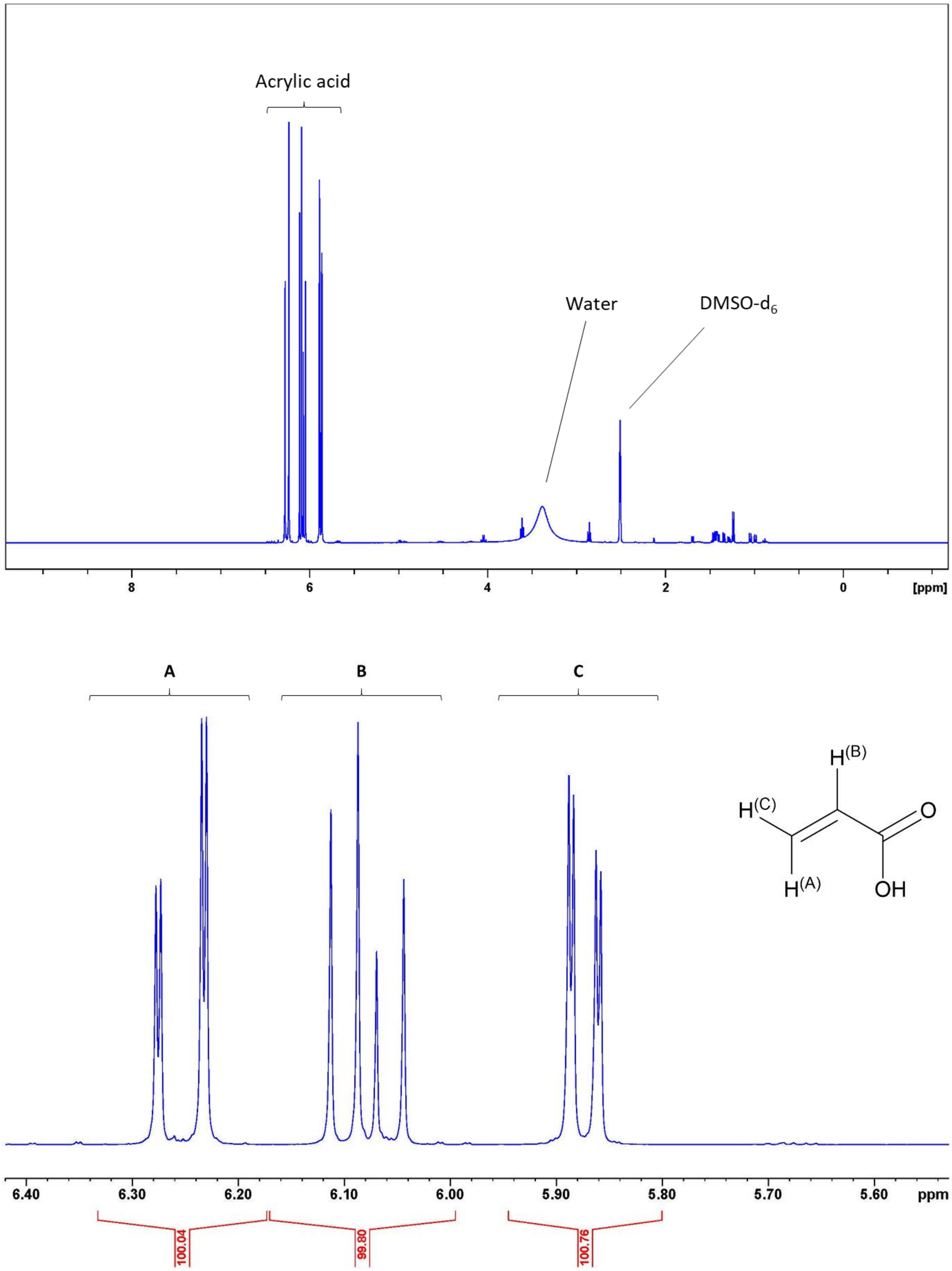


Figure S5 ^{1}H-NMR spectrum of distillate after continuous product isolation under reduced pressure. Top: full spectrum, Bottom: magnification of relevant region (6.4-5.6 ppm). Reaction conditions: 50 mmol of PLA (5 gram), 150 mmol Bu_4PBr (50 gram), 5 mol% 2-BrPA (225 µL), 3h, 200°C, continuous reduced pressure (5 mBar).

Supplementary figures

Detailed product distribution of Time Profile

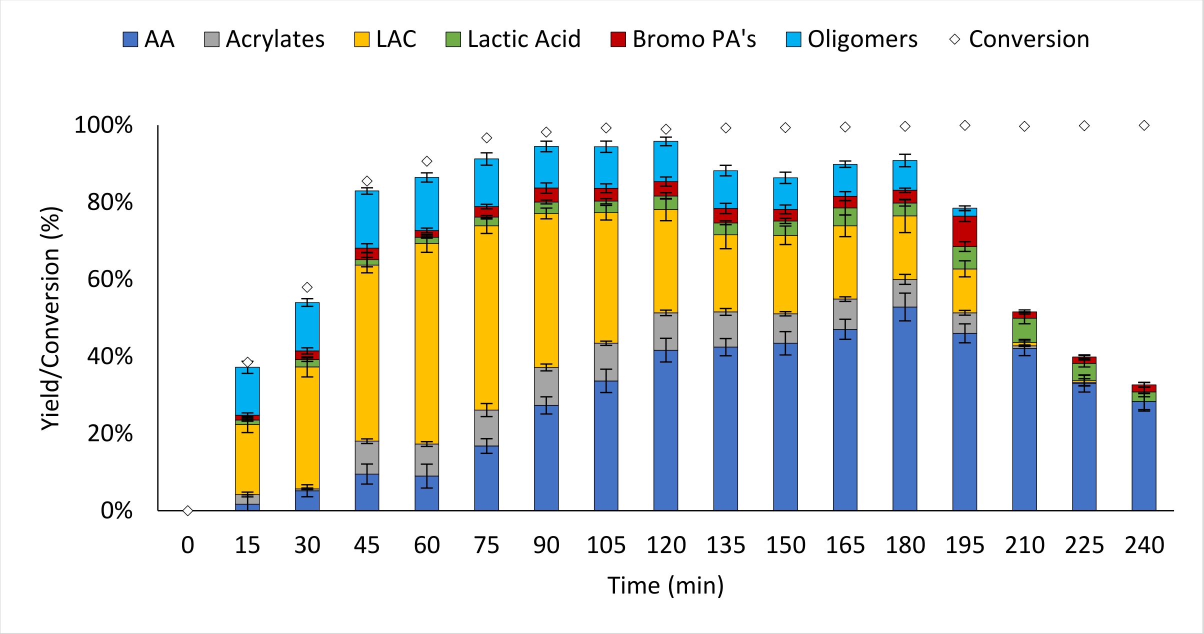


Figure S6 Detailed product distribution of Figure 1A cocatalyst (based on Table 1, entry 13). Reaction conditions: 0.5 mmol PLA, **5 mol% $C_{16}H_{33}Br$ cocatalyst**, 1.5 mmol Bu_4PBr, 2.5 mL sulfolane, 0-4h, 200°C, Ar flushed. Product yield, determined *via* ^1H NMR of the crude reaction mixture, expressed relative to monomeric unit of PLA. LAC = combined yield of lactides: L/D lactide forming a racemic mixture and DL- or meso-lactide. Bromo PA's = combined yield of 2/3-bromopropanoic acids.

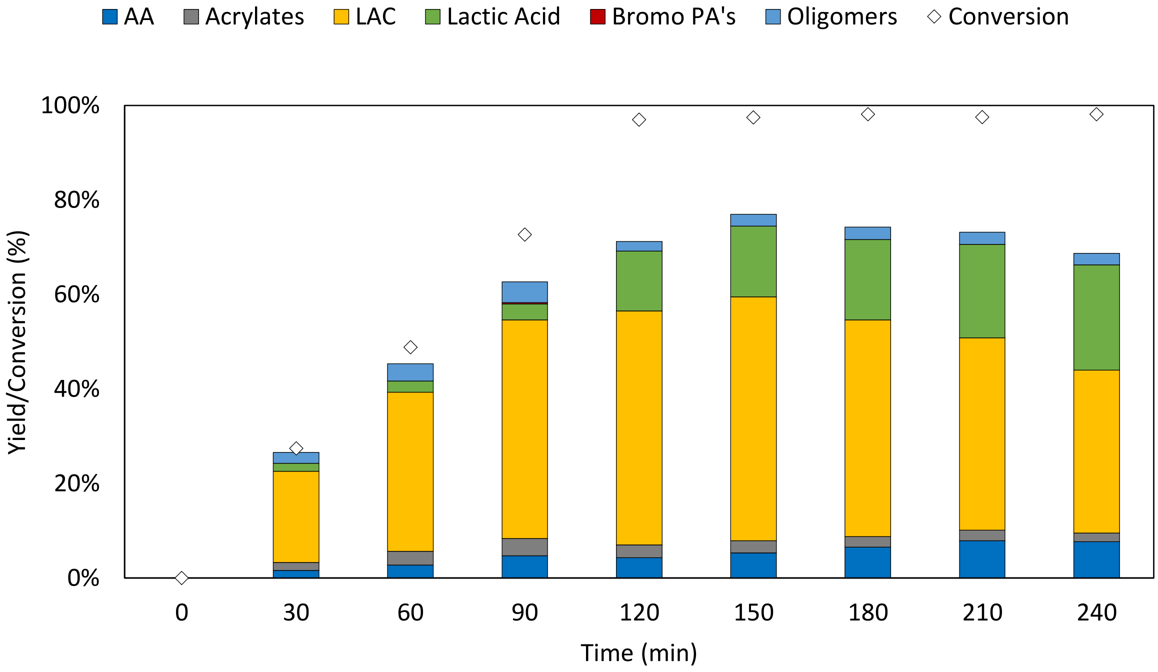


Figure S7 Detailed product distribution of Figure 1B (based on Table 1, entry 16). Reaction conditions: 0.5 mmol PLA, **no cocatalyst**, 1.5 mmol Bu_4PBr, 2.5 mL sulfolane, 0-4h, 200°C, Ar flushed. Product yield, determined *via* ^1H NMR of the crude reaction mixture, expressed relative to monomeric unit of PLA. LAC = combined yield of lactides: L/D lactide forming a racemic mixture and DL- or meso-lactide. Bromo PA's = combined yield of 2/3-bromopropanoic acids.

Control experiments for the proposed reaction network

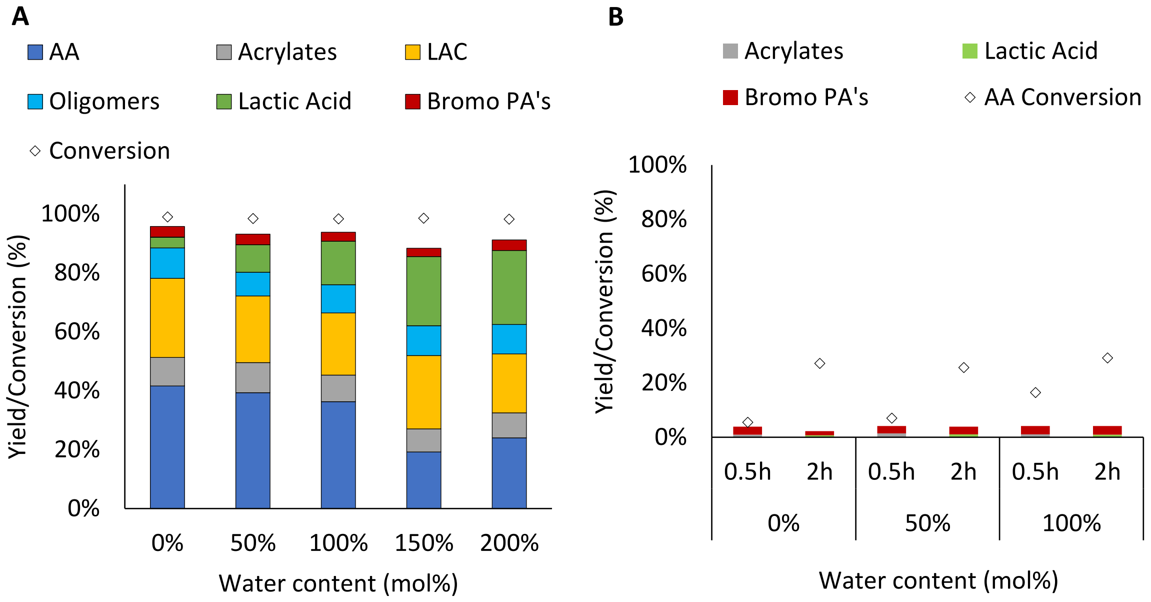


Figure S8 Impact of water on the depolymerization of PLA (A) or rehydration of AA (B). Reaction conditions: **0.5 mmol PLA (A) or AA (B)**, 5 mol% $C_{16}H_{33}Br$ cocatalyst, 1.5 mmol Bu_4PBr, 2.5 mL sulfolane, 2h, 200°C, Ar flushed. Product yield, determined *via* ^1H NMR of the crude reaction mixture, expressed relative to monomeric unit of PLA. LAC = combined yield of lactides: L/D lactide forming a racemic mixture and DL- or meso-lactide. Bromo PA's = combined yield of 2/3-bromopropanoic acids.

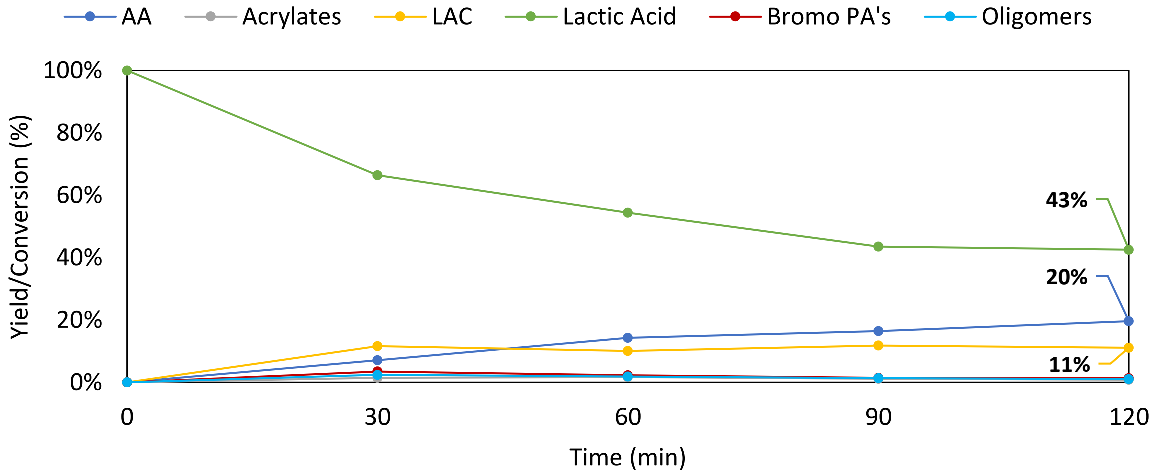


Figure S9 Lactic acid dehydration over time. Reaction conditions: **0.5 mmol Lactic acid**, 5 mol% $C_{16}H_{33}Br$ cocatalyst, 1.5 mmol Bu_4PBr, 2.5 mL Sulfolane, 2h, 200°C, Ar flushed. Product yield, determined *via* ^1H NMR of the crude reaction mixture, expressed relative to monomeric unit of PLA. LAC = combined yield of lactides: L/D lactide forming a racemic mixture and DL- or meso-lactide. Bromo PA's = combined yield of 2/3-bromopropanoic acids.

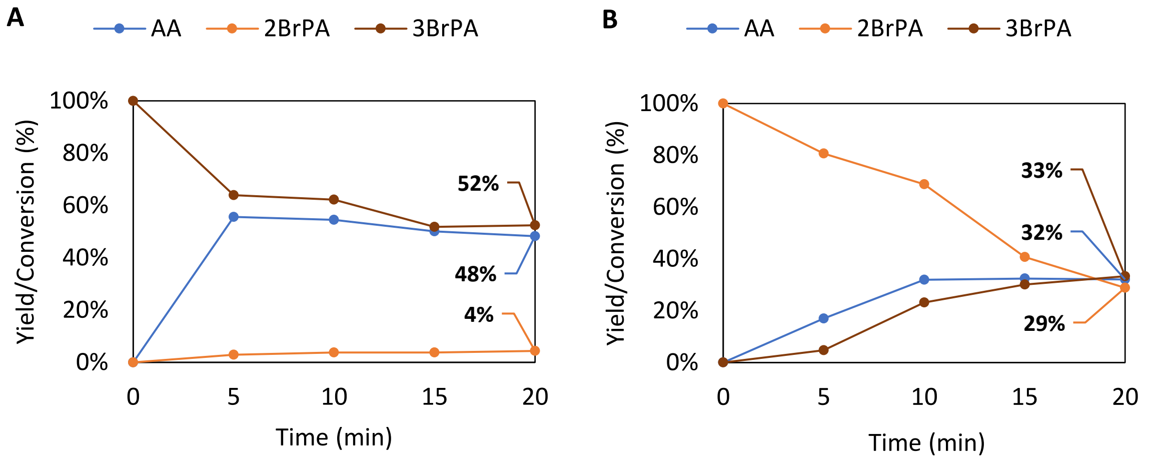


Figure S10 Dehydrobromination of Bromo-/PA's into AA. Reaction conditions: **0.5 mmol 3-BrPA (A) or 2-BrPA (B)**, 1.5 mmol Bu_4PBr, 2.5 mL Sulfolane, 2h, 200°C, Ar flushed. Product yield, determined *via* ^1H NMR of the crude reaction mixture, expressed relative to monomeric unit of PLA. LAC = combined yield of lactides: L/D lactide forming a racemic mixture and DL- or meso-lactide. Bromo PA's = combined yield of 2/3-bromopropanoic acids.

Time profiles of the gram scale experiments

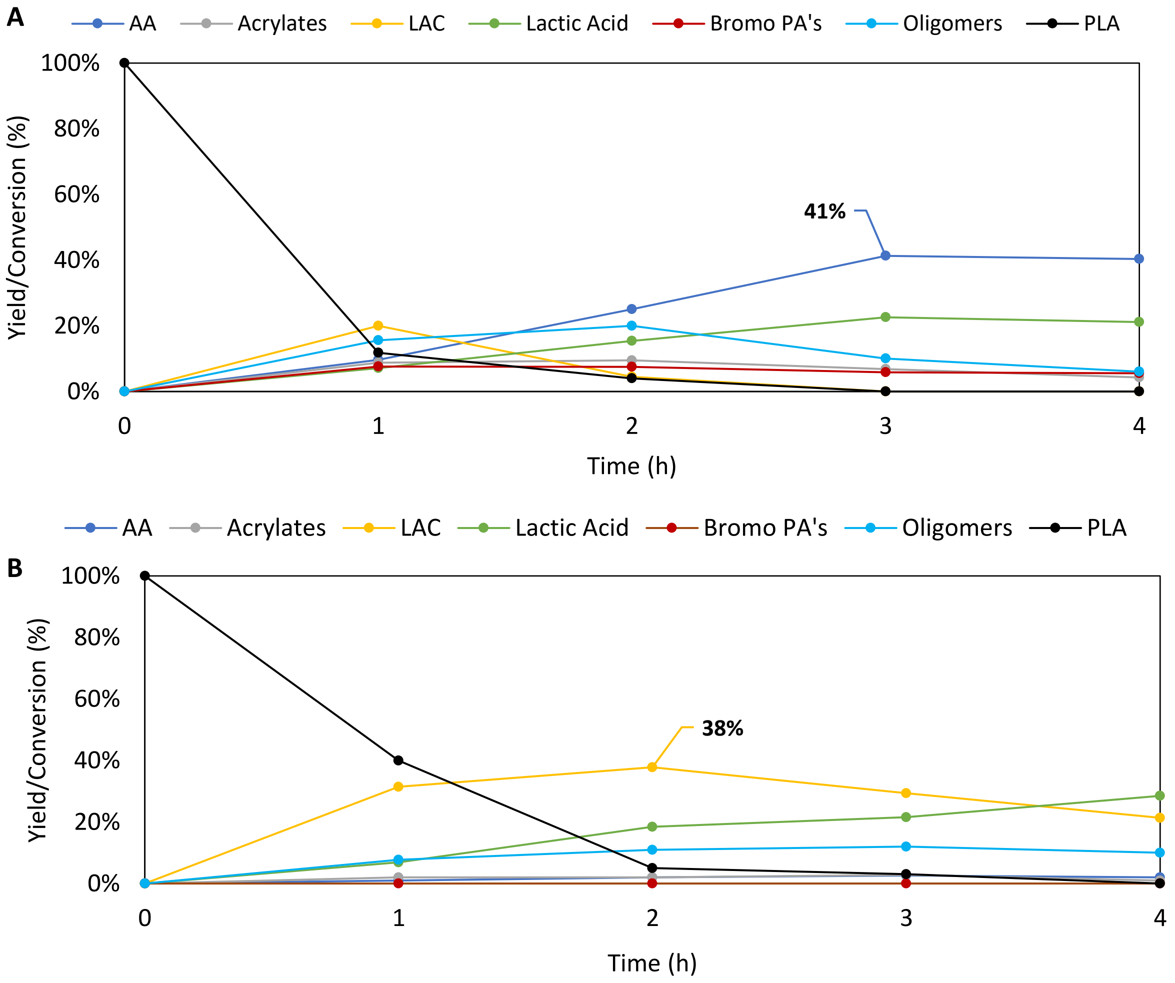


Figure S11 Time profile for post-consumer PLA depolymerization in the presence (A) or absence (B) of cocatalyst. Reaction conditions: 50 mmol post-consumer PLA (5.14 gram), **(A) 5 mol% 2-bromopropanoic acid (B) no cocatalyst**, 150 mmol Bu_4PBr, 25 mL Sulfolane, **0-4h**, 200°C, Ar flushed. Product yield, determined *via* ^1H NMR of the crude reaction mixture, expressed relative to monomeric unit of PLA. LAC = combined yield of lactides: L/D lactide forming a racemic mixture and DL- or meso-lactide. Bromo PA's = combined yield of 2/3-bromopropanoic acids.

References

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