Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

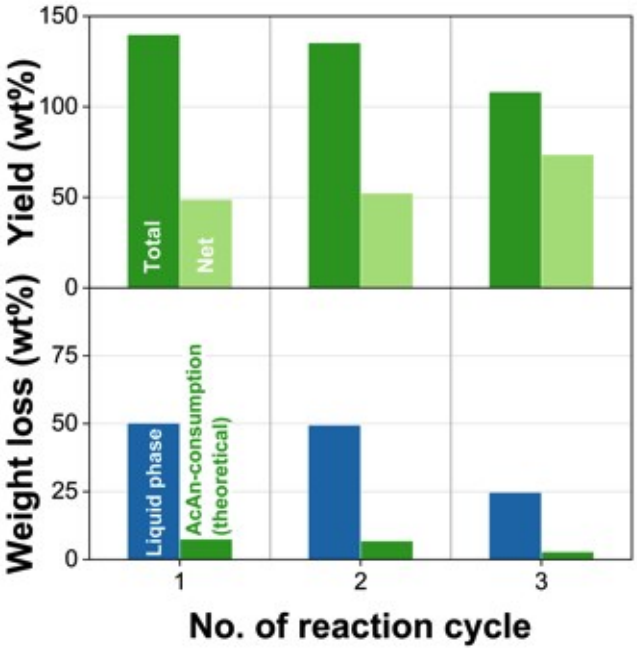

Fig. S1 Recyclability of the liquid phase in terms of product yields and the amount of liquid phase lost in subsequent reaction cycles.

Overall yields achieved in the recycling experiments (**Fig. S1**, above) are relatively low, similarly to the ones achieved using fresh raw materials, as presented in **Fig. 2c** in the main text of the paper. Although total yields typically exceed 100 wt%, this includes the molar mass increase of the polymer due to acetylation. Net yields are in the range of 50-70 wt%, i.e. 30-50 wt% of starch is lost in the process. At the same time, approximately 50 wt% of the liquid phase is lost between each subsequent reaction cycle applied in the recycling experiments (**Fig. S1**, below), far exceeding the amount of acetic anhydride consumed in the reaction; this is to be expected in a laboratory scale process and could be highly improved by optimizing transportation and separation steps in a larger scale operation.

Table S1 Commercial starch grades and their compositions.

Starch type	Abbreviation	Product name	Amylose-content (wt%)
Waxy	W	CG 04201	0
Native	N	CG 03401	25
High-amylose 1	A1	AG 03001	55
High-amylose 2	A2	AG 03003	70

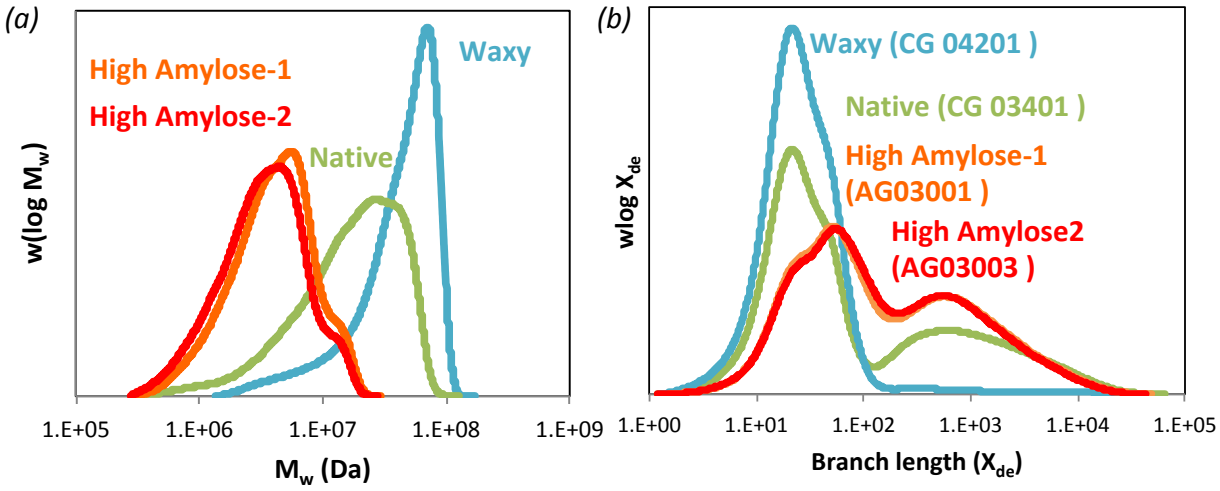

Fig. S2 Macromolecular characteristics of commercial starches by SEC-MALLS: **a)** Molar mass distribution of the intact macromolecules; **b)** Branch chain-length distribution after enzymatic destarching.

Table S2 Molar mass of esterified native corn starches.

Reagent	Mn (g/mol)	Mw (g/mol)	Polydispersity
Acetic acid	1.749E4	2.090E4	1.19
Propionic acid	1.453E4	1.719E4	1.18
Butyric acid	5.875E4	1.331E5	2.27
Valeric acid	4.226E4	1.142E5	2.70
Hexanoic acid	4.601E4	5.437E4	1.18
Acetic anhydride	1.933E5	8.814E5	4.56
Propionic anhydride	1.849E6	3.129E6	1.69
Butyric anhydride	3.813E6	5.771E6	1.51

Risks and hazards associated with the use of the acid and anhydride reagents

Organic anhydride reagents. Acetic anhydride is flammable and needs to be kept away from heat, hot surfaces, sparks, open flames and other ignition sources. The reagent is harmful if swallowed and causes severe skin burns and eye damage. It can be fatal if inhaled. Propionic anhydride and butyric anhydride may cause severe skin burns and eye damage. All reactions carried out with organic anhydrides were performed in the fume hood with conventional personal protective equipment.

Carboxylic acid reagents. Acetic acid and propionic acid are flammable and they need to be kept away from heat, hot surfaces, sparks, open flames and other ignition sources. Both reagents cause severe skin burns and eye damage. Propionic acid may cause respiratory irritation. Butyric acid causes severe skin burns and eye damage and it is harmful if swallowed. Pentanoic acid causes severe skin burns and eye damage, and it is harmful to aquatic life with long lasting effects. Its release to the environment must be avoided. Hexanoic acid is harmful if swallowed and toxic in contact with skin. It causes severe skin burns and eye damage. All reactions carried out with carboxylic acids were performed in the fume hood with conventional personal protective equipment.

None of the reagents contain components classified as persistent, bioaccumulative and toxic (PBT), or as very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.