

Catalytic Fabric Recycling: Glycolysis of Blended PET with Carbon Dioxide and Ammonia

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Abstract

Abstract: The ubiquity of non-biodegradable polyethylene terephthalate (PET) materials has led to significant waste management challenges. Although PET plastics can be recycled, blended materials, such as PET/cotton fabrics, complicates the recycling process due to the labile glycosidic bonds in cotton. In this study, we presented a practical and scalable approach for recycling of PET and PET/cotton interwoven fabrics via catalytic glycolysis with ammonium bicarbonate (NH₄HCO₃), which decomposed to ammonia, carbon dioxide, and water. This catalytic approach outperformed conventional acid/base and metal catalysis in selectively recovering and upcycling cotton-based materials. We demonstrated the large-scale recovery of textile from blended fabrics (up to 213 grams), showcasing the advantages of traceless catalysis using ammonia and CO₂ from ammonium bicarbonate. Owing to our metal-free reaction conditions, high-purity bis(hydroxyethyl)terephthalate (BHET) was obtained which was thermally re-polymerized to PET. Through thermal analysis, kinetics, and control experiments, we show that ammonia and CO₂ are crucial for achieving optimal glycolysis via transesterification. Our method offered a traceless, environmentally friendly, and practical approach for polyester recycling and cotton recovery, representing a significant step toward sustainable, closed-loop production of plastics and textiles.

Keywords: polyethylene terephthalates, plastic, fabric, carbon dioxide, glycolysis,

Introduction

Synthetic polymers represent one of the most significant polluting agents threatening the sustainable growth of human society. The worldwide polymer production (ca. 388 million metric tons in 2019) has grown exponentially over the years.^{1,2} Among them polyethylene terephthalate (PET) stands out as one of the most commonly produced polymers, with ca. 70 million metric tons being produced every year and an expected annual growth rate exceeding 4%.^{3,4} PET-based polymers are primarily utilized in the production of beverage bottles, while approximately one-third of the produced PET is blended with cotton-based fibers and viscose to manufacture fabrics in the textile industry.^{5,6} In 2020 alone, over 109 million metric tons of textile fiber were produced, with polyester (accounting for 52% of the volume share) and cotton (representing 24% of the volume share) being the two most prevalent fiber types.⁷⁻⁹ However, less than 20% of textile waste (equivalent to 65-92 million tons) is recycled annually,¹⁰ with the remaining 80% being either landfilled or incinerated.¹¹ Therefore, recycling these composite plastic-based materials has become an urgent societal issue. Chemical recycling or upcycling of plastic waste has emerged as an attractive option to mitigate fossil fuel depletion, reduce greenhouse gas emissions, and minimize negative environmental impacts resulting from energy recovery in waste incinerators.¹²⁻¹⁶

The catalytic and enzymatic glycolysis of PET yields valuable intermediate bis(hydroxyethyl)terephthalate (BHET) (Fig. 1A and 1B),¹⁷⁻¹⁹ which can be recycled as a precursor for PET via repolymerization,²⁰⁻²⁵ and other biodegradable polymers.²⁶ Traditionally, Lewis acidic metals have served as catalysts at high reaction temperatures (160–220 °C),^{22, 27, 28} to overcome the substantial reaction barrier and enhance the solubilization of PET substrates. They often necessitate laborious purification steps to ensure high purity of BHET, minimizing the environmental risk of metal contaminations.²⁸⁻³⁰ For instance, Zn(II) (including ZnO) is a commonly used catalyst, but it exhibits significant cytotoxicity *in vitro* with a greater risk compared to cobalt, iron, copper, and manganese.³¹⁻³³ One potential solution to prevent metal contamination lies in the use of metal-free organocatalysts.³⁴⁻³⁷ Recently, the combination of a strong acid and a strong base (1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD) has been reported for PET glycolysis.^{38,39} Ionic liquids have also been explored as reaction media in PET glycolysis.⁴⁰⁻⁴² For these approaches, the price and recycling of the catalysts are still the major obstacles to practical application. Thus, there is a need for cheaper, more accessible and practical catalytic protocols to handle the mountainous PET wastes, especially the PET blended fabrics.

The challenge in chemical recycling of blended fabrics lies in the selective recovery of either fiber type, given their blended and intertwined nature.^{43, 44} Acidic media and Lewis acid catalysts can cause the degradation of cotton due to the labile glycosidic bonds present (Fig. 1E), resulting in a more challenging purification of monomers,⁴⁵ especially for terephthalic acid (TPA).⁴⁶ Basic media, such as over-stoichiometric amounts of inorganic bases, can be utilized to depolymerize PET/viscose blended fabric (filament, PET 30%) into TPA and viscose through PET hydrolysis (Fig. 1C), requiring an additional re-protonation step.^{47,48} In this process, mercerization or even degradation of cotton and cellulose-based materials is essentially unavoidable during the depolymerization reaction.⁴⁹

Recently, Zn(OAc)₂ has been investigated for the selective glycolysis of polyester/cotton blends (at a 5 g scale).⁵⁰ The scalability raises questions including the heavy metal contamination, considering 1) the additional cost associated with the use of betaine-based deep eutectic solvents, and 2) the known degradation of cotton under glycolysis conditions, such as elevated temperatures and the presence of Zn(II) catalysts.⁵¹ Thus, it is crucial to develop a mild catalytic chemical recycling method for PET/cotton blends under practical conditions, avoiding the acid- and base-mediated hydrolysis of cotton materials.^{52, 53}

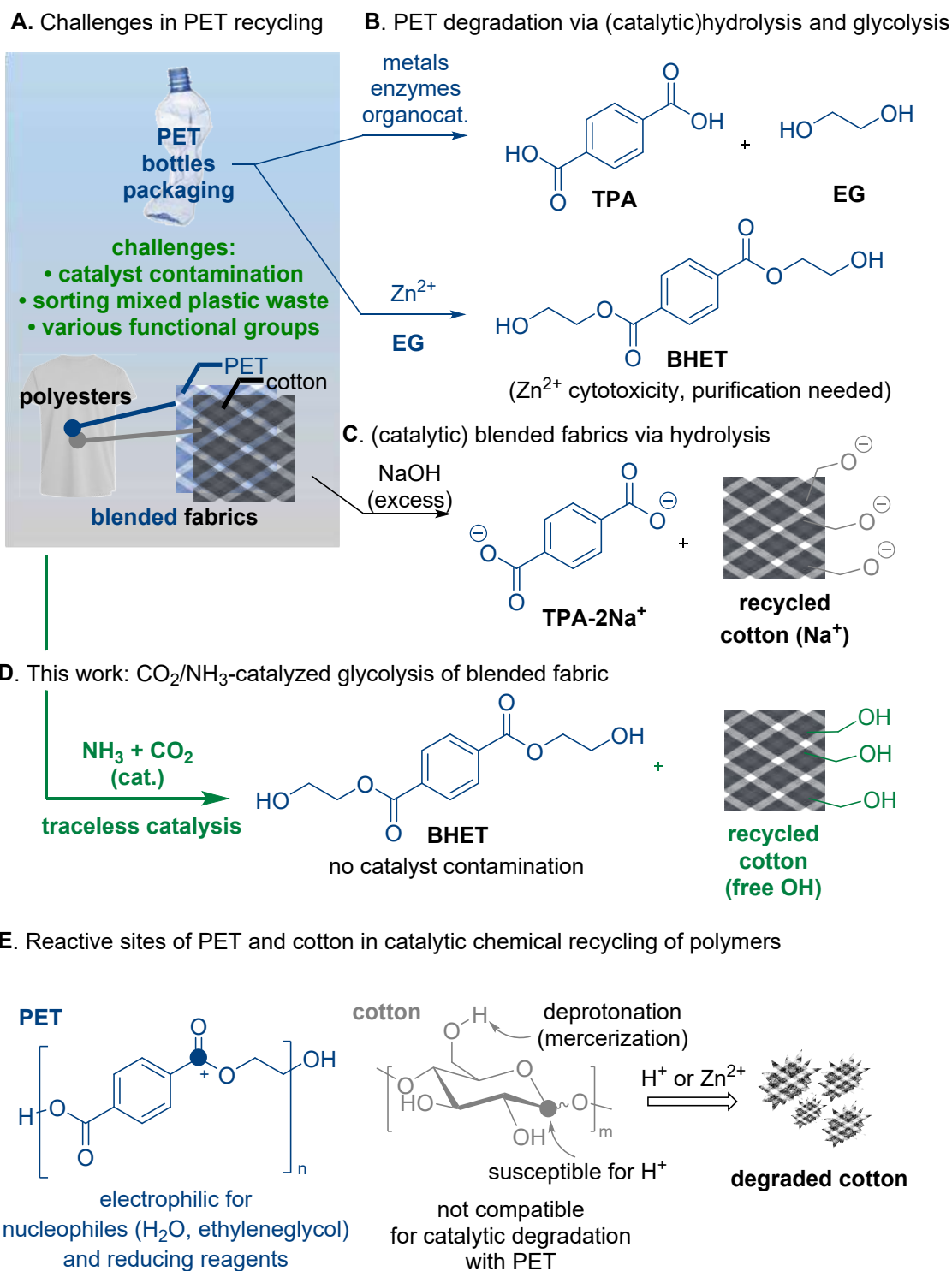


Fig. 1. Comparison of approaches to PET and blended fabrics chemical recycling. A) Challenges in chemical recycling of PET and blended fabric, B) catalytic hydrolysis to access terephthalic acid (TPA) and ethylene glycol (EG), C) NaOH-promoted hydrolysis of PET/cotton blended fabrics D) ammonia and CO₂-catalyzed glycolysis of PET to BHET, and recovery of cotton from PET/blended fabrics. E) Chemical structures of PET and cotton and cellulose-based materials and their multiple reactive sites.

We have previously demonstrated the successful utilization of CO₂ in catalysis and (bio)polymer degradation. Specifically, CO₂ can accelerate chemical recycling of Nylon-6,6 through a CO₂-catalyzed transamidation reaction and amide bond activation.⁵⁴ Upon

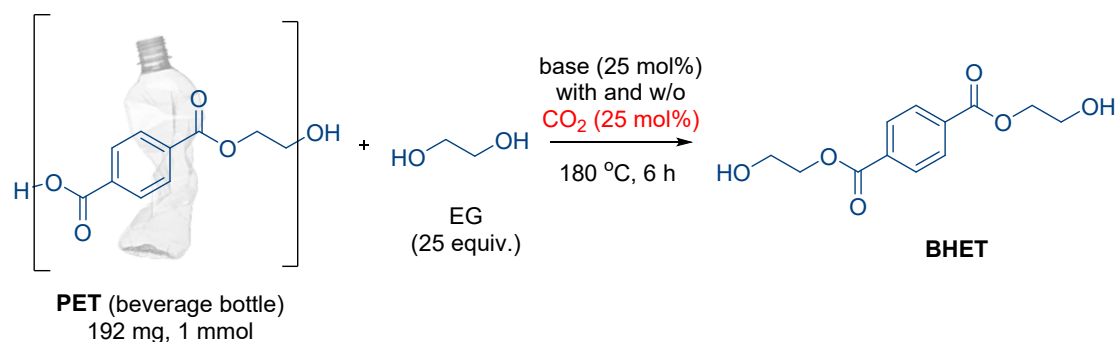
completion of the reaction, CO₂ can be easily removed without leaving any residue, resulting in a purification-free process. Building on these findings, our objective was to develop a practical, efficient, and scalable method for recycling PET using catalytic glycolysis with a traceless catalyst—CO₂, thereby streamlining the green chemical recycling process.

Herein, we showcase catalytic chemical recycling of blended materials,⁵⁵ addressing the challenges associated with glycolysis of PET in the presence of cotton-based materials. These materials present several unresolved challenges, particularly the need for selective glycolysis of PET while preserving the cotton fabrics in the blends (Fig. 1A and 1E). Sustainable recovery methods for cotton are crucial due to its significant carbon footprint, high water usage, and labor issues during production. Consequently, there is a growing interest in environmentally responsible alternatives for cotton or chemical recycling methods for polyester-blended fabrics (Fig. 1D). In this study, we demonstrated a traceless and selective catalytic transesterification of PET/cotton blended fabrics using NH₄HCO₃ as an inexpensive and easy-to-handle pre-catalyst (up to 25 mol%). This pre-catalyst decomposed into CO₂, basic ammonia, and water at temperatures above 36°C.^{56,57} Our reaction operated under practical, mild conditions (pH ca. 7–8) and effectively produced high-purity BHET while recovering cotton fabrics without significant mercerization or hydrolysis. This approach paves the way for large-scale chemical recycling and upcycling of blended composites and PET-containing waste.

Results and Discussion

First we attempted to study CO₂ mediated glycolysis with PET bottle substrate, without any prior chemical or thermal pre-treatment. An application of CO₂ in transesterification at high pressures (147 bar of CO₂, at 100–110 °C; 5 h) has been reported by Otsuji et al., which employed ethyl formate, HCO₂Et, and *n*-octanol, rendered up to a 27% yield of a transesterification product.⁵⁸ Building on this work, we hypothesized that the addition of a base could enhance general base catalysis, while a catalytic quantity of electrophilic (Lewis acidic) CO₂ would provide cooperative general acid catalysis under thermal conditions.

An examination of various organic and inorganic bases revealed that the conversion of PET to BHET is related to the *pK_a* values of the base catalysts. The maximum conversion was achieved when employing weak bases (*pK_a* ≈ 6, Fig. 2A) in the presence of 25 mol% of CO₂. Stronger bases displayed no significant improvement with or without CO₂. Interestingly, weak bases like ammonia and pyridine demonstrated exceptional performance, exhibiting enhanced PET degradation to BHET in the presence of CO₂ (Fig. 2B). These results suggest that the glycolysis reaction mechanism follows a general base catalysis, highlighting the crucial role of catalytic CO₂ in reactions involving weak bases, especially ammonia—generated from NH₄HCO₃ through thermal decomposition.



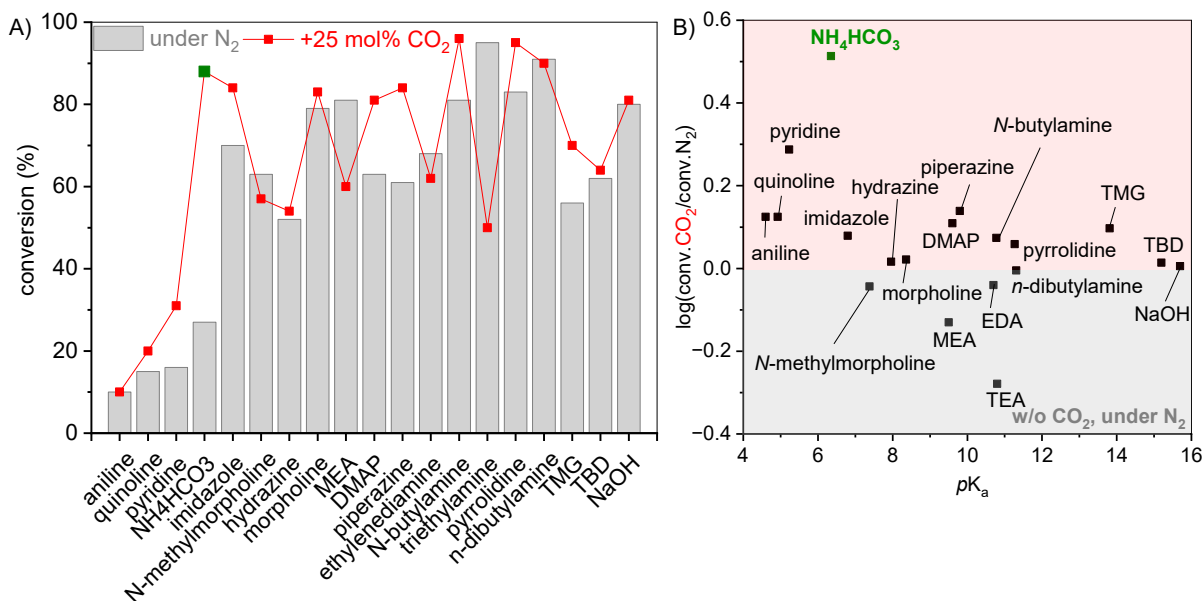


Fig. 2. A) Conversion of PET to BHET with various bases in catalytic glycolysis with additional 25 mol% of CO_2 (red squares, for NH_3 , NH_4HCO_3 was used, green square) and with only bases under N_2 atmosphere (gray bars). B) Illustration of positive CO_2 effect in glycolysis. Abbreviations: ethylene glycol (EG), dimethylaminopyridine (DMAP), ethylenediamine (EDA), monoethanolamine (MEA), triethylamine (TEA), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,1,3,3-tetramethylguanidine (TMG).

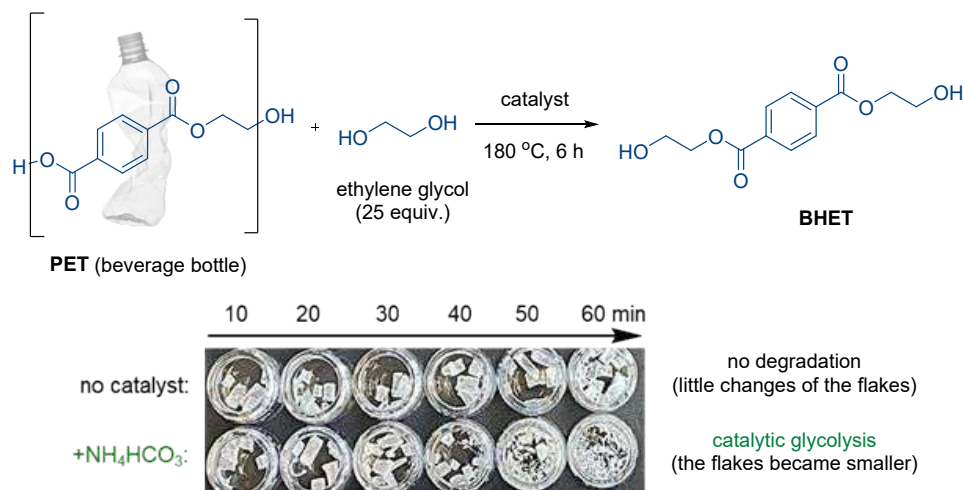
Through further optimization, we successfully established practical reaction conditions, even in scales ranging from 0.2 to 50 grams, that consistently produced high-purity BHET without the need for complex purification steps, (Table 1). Under an N_2 atmosphere and in the absence of catalysts, no background glycolysis was observed (Entry 2; see pictures of time-dependent PET flakes degradation with and without a catalyst). The utilization of CO_2 alone, whether in catalytic amounts (15-30 mol%) or as a reaction atmosphere (1 atm), had no discernible effect on the reaction, even with extended reaction times (up to 24 hours at 150-200 $^\circ\text{C}$; Entry 1).

With this observation, we swiftly conducted comparative studies to evaluate our glycolysis method against existing PET depolymerization techniques. Zn-based Lewis acidic catalysts, such as $\text{Zn}(\text{OAc})_2$ and ZnCl_2 , have been widely used in industrial glycolysis of PET and have demonstrated satisfactory conversion of PET to BHET—44% and 75%, respectively (entries 3 and 4).^{27, 59} However, an elemental analysis of the isolated BHET from these experiments with Zn^{2+} revealed varying degrees of metal impurities after hot filtration and crystallization of BHET (see Table S9), likely due to residual zinc ions. These impurities might hinder their application in the repolymerization of BHET to PET.²⁸

Under our optimized glycolysis conditions, the use of NH_4HCO_3 as a catalyst allowed us to conduct a larger scale reaction (260 mmol, 50 grams of waste PET bottle substrate). This catalytic system achieved quantitative conversion of PET, yielding BHET with an isolated yield of 64% in a single crystallization step without any by-products (Table 1; Entry 5).⁶⁰ This result represents, to the best of our knowledge, the first demonstration of the synergistic effect of catalytic CO_2 and an amine in glycolysis. Solely using ammonia as a catalyst without CO_2 (aqueous ammonia and an NH_3 solution in methanol, Table S1, Entry 22) was not effective, yielding inferior results compared to the NH_4HCO_3 catalyst, highlighting the importance of CO_2 . The use of ammonium carbonate $(\text{NH}_3)_2\text{CO}_3$, a reagent commonly employed in the Bucherer-Berg reaction, yielded comparable results to the ammonium bicarbonate catalyst

(87% yield of BHET, Table S1, Entry 18). In contrast, inorganic bases led to the contamination of BHET with the hydrolysis product, terephthalic acid (TPA), as summarized in Table S1.⁶²

Table 1. PET bottle chemical recycling.^a



entry	PET (g)	catalyst (mol%)	conversion (%)	yield of BHET (%)
1 ^b	0.2 g	CO ₂ (15-30 mol% or 1 atm)	not detected	0%
2	0.2 g	N ₂	n.a.	0%
3	2 g	Zn(OAc) ₂ (25 mol%)	44%	40%
4	2 g	ZnCl ₂ (25 mol%)	75%	52%
5	50 g	NH ₄ HCO ₃ (25 mol%)	88%	64% (32 g)

^aReaction conditions: PET bottle substrate (0.2–50 g); a catalyst and ethylene glycol were added with a magnetic stirring bar, and the vial was heated for 6 h; Conversion (%) = $(W_{\text{oligomers+BHET}}/W_{\text{PET bottles}}) \times 100$, yield of BHET (%) = $(W_{\text{BHET}}/W_{\text{PET bottles}}) \times 100$, W = weight. The reaction mixture was diluted with water to precipitate oligomers and BHET, which was crystallized to determine the yield of isolated BHET. ^bReaction time extended to 24 h.

With our optimized conditions for PET glycolysis, we aimed to depolymerize PET in the presence of cellulose, as in blended fabrics, to separate BHET and recycled cellulose (Fig. 3). Under acidic conditions, cotton and cellulose-based materials are prone to decompose via hydrolysis, as demonstrated in Fig. 3A. The catalytic reaction with Zn(II) catalyst resulted in complete decomposition of the cotton fabric within 2 hours, with all visible cotton threads disintegrating after 3 hours of reaction time. FT-IR (Fourier-transform infrared spectroscopy) showed full conversion of ester functional groups on PET fabric (Fig. 3B, see full spectra in Fig. S18) while the cotton fabric remained intact even after prolonged reaction times under catalytic conditions with NH₄HCO₃, (18 hrs). Solid-state ¹³C NMR spectra were evident to confirm the effective catalytic glycolysis of PET in the presence of cotton materials (Fig. 3C). The spectra clearly showed the full conversion of PET and preservation of the recycled cotton (green), with no presence of aromatic and sp²-carbons from PET starting material (black).⁶³

The quality of the recovered viscose was further assessed using powder X-Ray diffraction (PXRD, Fig. 3D). The peaks centered at angles $2\theta = 12.5, 20$ and 22 correspond to the crystalline structure of cellulose II. Notably, the PXRD pattern of the recovered cotton (green) using NH₄HCO₃ exhibited mild crystallization as reported in the literature under basic

conditions with NaOH (gray),⁴⁹ while the use of ZnCl₂ catalyst (black) significantly increased the crystallinity of viscose after 6 hours.

Based on optical microscopy of the recovered materials (20-80 fold magnification, Fig. 3E. also see Figs S20-21), it was evident that glycolysis reactions of blended fabrics with Zn-based catalysts resulted in complete degradation, with all fabric threads being degraded within 3 hours of reaction time. In contrast, NH₄HCO₃ effectively converted PET to BHET while preserving the integrity of the textile thread. Additionally, the analysis using dynamic light scattering (DLS) (Fig. S24) and thermogravimetric analysis (Fig. S25) confirmed the same conclusion, further validating the quality of the recovered viscose materials under our depolymerization reaction conditions compared to those obtained using ZnCl₂ and NaOH.

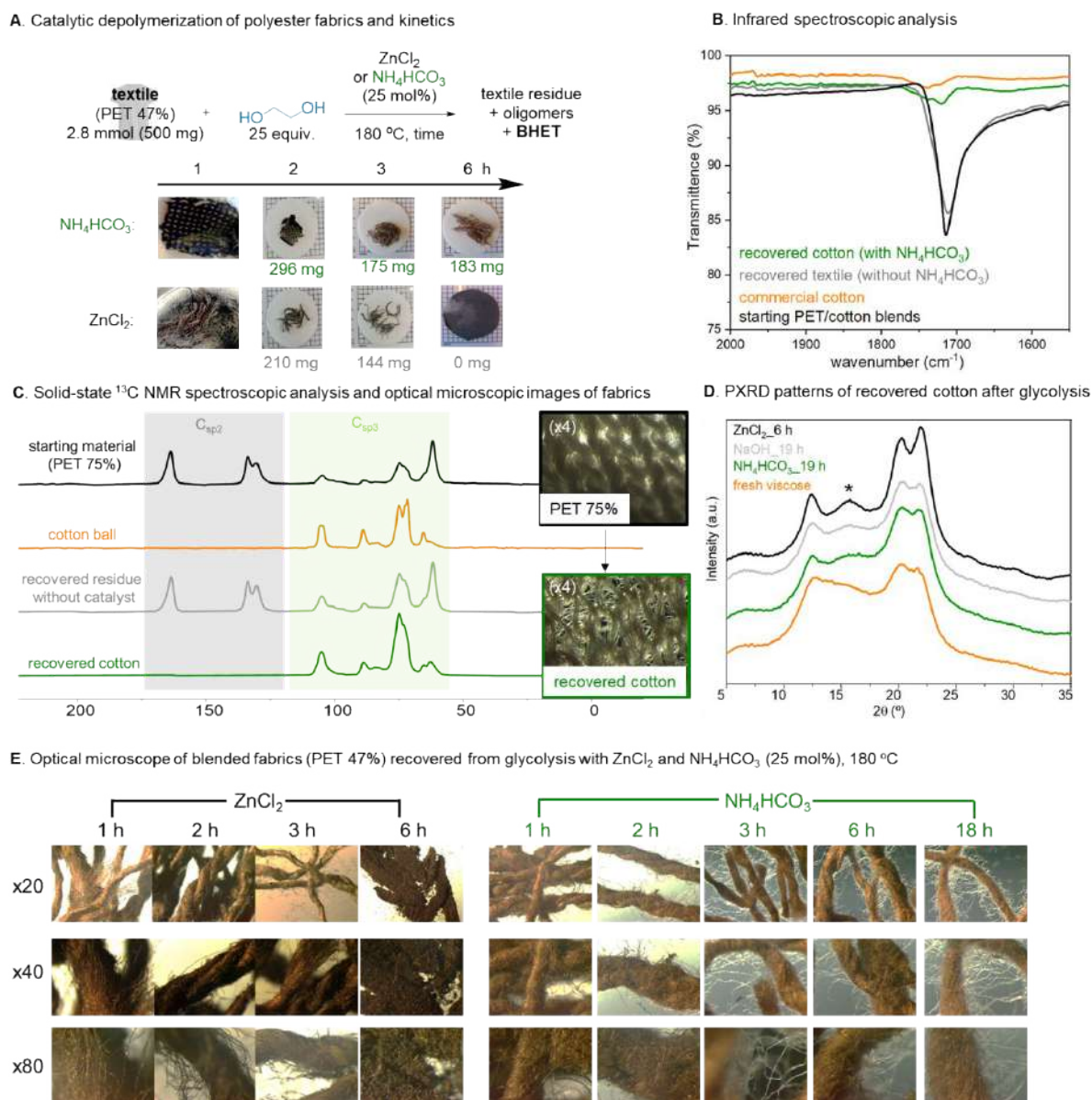


Fig. 3. Catalytic depolymerization of blended textiles, and characterization of recovered textile. A) catalytic glycolysis of blended fabric and gravimetric analysis of textile residue, B) FT-IR analysis of the recovered cotton from the reaction with NH₄HCO₃ (green), without catalysts (gray), commercial cotton (orange), and starting material (black), C) Solid-state ¹³C NMR spectra and D) PXRD (powder X-Ray diffraction) patterns (smoothed) of the substrate (orange, viscose) and recovered viscose from glycolysis conditions with ZnCl₂-(black, 6 h),

NaOH-(gray, 19 h), and NH_4HCO_3 -catalyst (green, 19 h), and E) Optical images of the recovered cotton over time, starting from the blended fabrics (47% PET+53% cotton), with ZnCl_2 and NH_4HCO_3 as catalysts.

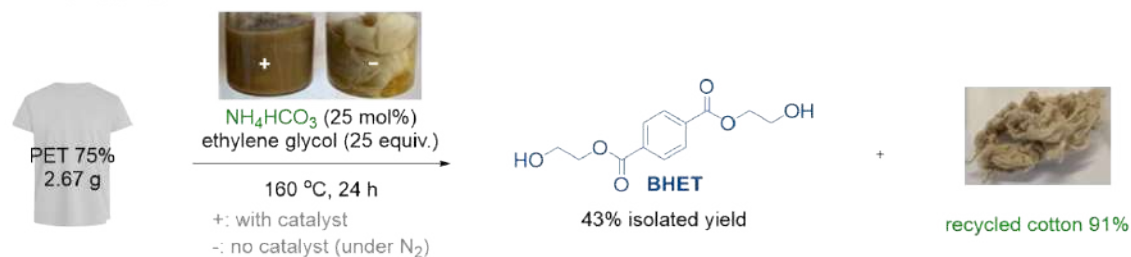
Considering the diverse range of blended fabric waste to be recycled, including various PET:cotton blending ratios, unidentifiable dyes,⁶⁴ additives, and impurities, we subjected different commercial textile materials to our catalytic glycolysis without any pre-treatment. Reactions performed without the catalyst were visibly slower, with textile starting materials still remained in the reaction vessels even after 24 hours of reaction time. In contrast, catalytic glycolysis with NH_4HCO_3 enabled clean conversion of the starting materials to the desired BHET, even in large-scale reactions without pressure build-up (Fig. 4A and 4B). For instance, end-of-life sofa covers consisting of PET/cotton blended fabrics (213 g) yielded 62% and 94% for BHET and cotton, respectively, without requiring substrate pre-treatment.

Furthermore, we evaluated the tolerability of our NH_4HCO_3 -catalyzed glycolysis method on different blended fabrics (47–100% PET with cotton, viscose, and lyocell). To our delight, reasonable yields of BHET and quantitative yields for recovered cotton and other fabrics were achieved through a straightforward separation process (Fig. 4B). The purity of BHET obtained from our catalysis was confirmed by PXRD and high-performance liquid chromatography (HPLC), with no indication of metal impurities or oligomers (Figs. S26-27).

The quality of the isolated BHET was further supported by catalyst-free thermal re-polymerization to PET (rPET), as analyzed by FT-IR, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) (Figs. S28-29), and elemental analysis (Table S10). Thermal gravimetric analysis (Fig. S19) and elemental analysis (Table S5) were also conducted on the residual cellulose and solid materials from the glycolysis process to corroborate these results. Although the low whiteness of the obtained BEHT can deteriorate the quality of rPET, a new sublimation method can effectively improve the whiteness.⁶⁴

To demonstrate the feasibility and robustness of our methodology, we mixed several types of polymers (PVC, PP, PE, polyamide, PU, PS, ABS, POM, NBR, and SEBS) and even included human hair, simulating realistic plastic waste from a waste collection point (Fig 4C). Under our standard reaction conditions, selective glycolysis of PET was achieved, with a 23% isolated yield of BHET after a single recrystallization step, and 75% yield of recovered cotton. The other plastic materials were recovered with some deformation but without any signs of chemical depolymerization. The formation of the pre-catalyst NH_4HCO_3 during the reaction was confirmed, and the catalyst was easily recovered through simple sublimation.

A. Catalytic glycolysis of PET substrates from fabrics



B. Large scale glycolysis of PET fabrics and blended textiles with cotton, viscose, and lyocell

textile substrates (weight) NH_4HCO_3 (25 mol%) ethylene glycol (25 equiv.) 180 - 197 °C 18 - 24 h Isolated BHET	 PET 100% (89 g)	 PET 75% (13.3 g)	 PET 50% (80 g)	 PET 47% (213 g)
	 44% yield	 47% yield	 76% yield	 62% yield
+ recovered cotton	-	 92% yield cotton + viscose	 61% yield lyocell	 94% yield cotton

C. Catalytic glycolysis of mixture of plastics and PET, PET/cotton blended fabric

	NH_4HCO_3 (25 mol%) ethylene glycol (25 equiv.) 180 °C, 18 h	 BHET, 9.5 g (23% yield)	 Cotton, 8 g (75% from textile)	
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Fig. 4. Impact of catalysis on the selective chemical recycling of textiles. A) Catalytic glycolysis of PET containing textile (PET 75%) with and without the catalyst and the recovery of cotton. B) Large scale PET/cellulose-blended textiles for catalytic glycolysis in large scales. C) Combined mimicked plastic waste, catalytic glycolysis of PET, and isolation of BHET, cotton and other plastic waste: polyethylene (PE), polypropylene (PP), polyurethane (PU), polystyrene (PS), polyoxomethylene (POM), polyvinylchloride (PVC), polyacrylamide (PAA), acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene rubber (NBR), styrene-butadiene-styrene (SEBS), human hair (peptides).

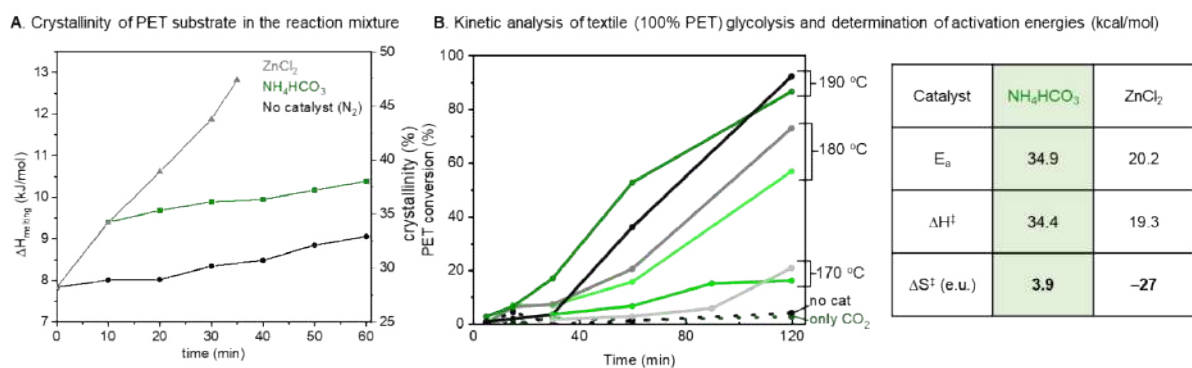


Fig. 5. A) Crystallinity of remaining PET bottle flakes from reaction mixtures under glycolysis conditions (180 °C), B) Kinetic analysis (170–190 °C) and activation barriers of the polyester fabric (PET 100%) degradation (e.u.: cal/K·mol)

To gain insight into the reaction mechanism of NH₄HCO₃-mediated PET degradation, we conducted kinetic experiments on the glycolysis of PET bottle substrates. The aim was to confirm the catalytic performance of NH₄HCO₃ compared to non-catalytic conditions by using thermal gravimetric analysis (Kessinger Model). Our analysis revealed comparable degradation kinetics with NH₄HCO₃ catalyst to that of the industrially widely used ZnCl₂ catalytic system for the depolymerization of PET under identical reaction conditions. This finding was surprising, considering that ammonia and CO₂ exhibit catalytic activities comparable to strong Lewis acidic zinc(II). Additionally, differential scanning calorimetry (DSC) analysis of the residual PET flakes collected at different reaction times indicated that the PET depolymerization with NH₄HCO₃ resulted in lower crystallinity of the PET substrates (Fig. 5A, green), while Zn-catalysis significantly increased the crystallinity of the remaining PET substrate under thermal conditions over time (Fig. 5A, gray). These observations suggest that the NH₄HCO₃-catalyzed glycolysis may have distinct mechanistic features compared to the Zn-catalyzed process, leading to differences in the crystallinity of the residual PET flakes.

Therefore, further kinetic studies were performed in terms of degradation of textile substrates (100% PET) and its conversion into BHET (Fig. 5B) at different temperatures. For the catalytic ZnCl₂, an activation barrier of 20.2 kcal/mol was obtained, which is consistent with previously reported cases.⁶⁵ In contrast, our catalyst NH₄HCO₃ exhibited a higher activation barrier (34.9 kcal/mol), as supported by our DFT (density-functional theory) calculations using methyl benzoate as a substrate (see Fig. S30). It is noteworthy that a positive activation entropy (+3.9 e.u., cal/K·mol) was calculated based on the Eyring equation for NH₄HCO₃, contrasting with the results obtained with the Zn(II) catalytic system (-27 e.u.). This positive entropy value is reasonable for addition/elimination reactions, where the addition step can be rate-determining and unfavorable negative activation entropy is commonly observed. In terms of the reaction mechanism, we postulate that NH₄HCO₃, as a thermally labile pre-catalyst, undergoes decomposition, resulting in an enthalpy loss of 8.2 kcal/mol but a significant entropic gain of 283 cal/K·mol (ΔG_{rxn} = -11.9 kcal/mol) due to the liberation of ammonia, water, and CO₂. This entropic gain likely impacts the energy profile of the transesterification reaction, lowering the ΔG[‡].

It is important to note that the decomposition of NH₄HCO₃ and the catalysis are separate events, and further mechanistic studies are required to fully understand the relationship between the entropy gain and the reduction of free energy of activation. Nevertheless, our experimental observations suggest continuous regeneration of NH₄HCO₃ via decomposition and precipitation on a reflux condenser as ammonium (bi)carbonate, which falls back into the reaction mixture. Qualitative analysis on CO₂/ammonia (Fig S21) and control experiments (Fig S21g) were conducted to confirm the fate of CO₂ and ammonia after completion of the

glycolysis. We detected higher concentrations of ammonia in the presence of CO₂, confirming our hypothesis on the role of CO₂ suppressing ammonia evaporation, in turn effectively increasing the catalyst concentration.

To further support our mechanistic hypothesis regarding CO₂ and ammonia-mediated transesterification, we conducted control experiments with PET bottle substrate and model compound **1** (Scheme 1). Trace amounts of amide by-products (**3**) were isolated as expected under standard depolymerization conditions at a low temperature of 80 °C (Scheme 1A). We found that transesterification with CO₂/ammonia was effective even at low temperatures: 57% of BHET was isolated at 80 °C, along with a mono-functionalized product (**2**, 36%). Interestingly, amide **3** (< 1%) was isolated as an aminolysis byproduct presumably originating from ammonia. It is plausible that ammonia can act as a nucleophile in the reaction mixture, with the amide intermediate subsequently being converted to BHET. To investigate this, we subjected monoamide (**3**) and diamide (**5**) to the standard conditions (Schemes 1B and 1C). Mono-transesterification predominantly produced product **4** (75% ¹H NMR yield), while the primary amide functional group remained stable and BHET was obtained as a minor product (25%). Under standard glycolysis conditions for PET, terephthalamide **5** and TPA were converted to BHET in 11% and 37% yields, respectively. Consequently, we have ruled out reaction pathways involving amides and carboxylic acid intermediates resulting from ammonia acting as a nucleophile (see also DFT calculations, Fig. S31). After eliminating a nucleophilic catalysis mechanism, we propose that ammonia and CO₂ function as general base and acid catalysts,⁶⁶⁻⁶⁸ as indicated in the experimental data (Fig. 2 and see Table S11 for DFT calculations of various reaction pathways).

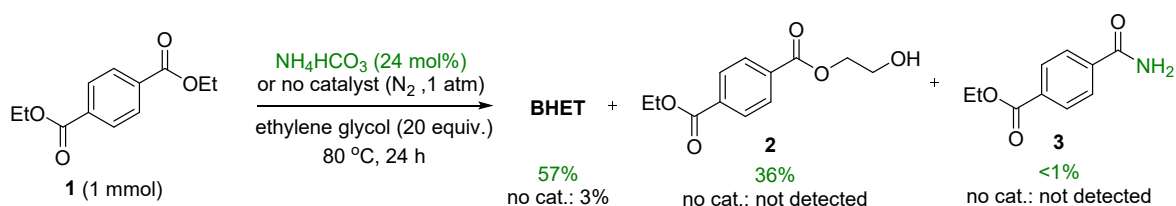
These control experiments implied that CO₂ can suppress the aminolysis of PET. To further verify this, we employed over-stoichiometric amounts of nucleophilic pyrrolidine under similar glycolysis conditions (Scheme 1D). The diamide **6** was a major product (33%) under a catalyst-free N₂ atmosphere due to the high nucleophilicity of pyrrolidine. In contrast, BHET was detected as the primary product in the presence of pyrrolidine when the reaction was carried out under ambient CO₂ conditions (1 atm). This result unambiguously confirms our hypothesis: CO₂-assisted ammonia-catalyzed transesterification takes place, with CO₂ effectively preventing aminolysis and maintaining an optimal concentration of catalytic ammonia in the solution.

Conclusion

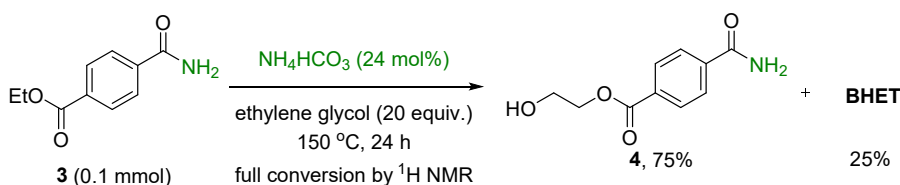
We have discovered the remarkable advantages of NH₄HCO₃-catalyzed selective depolymerization of PET, which allows for the production of high-purity BHET monomer on a large scale (213 g), while preserving the integrity of cotton and cellulose-based materials. Comprehensive structural analysis of the recycled cellulose fabrics was performed using solid-state ¹³C NMR, FT-IR, TGA, DSC, elemental analysis, and microscopy, confirming the quality of the recovered materials.

Significant contributions from CO₂ as a molecular catalyst, combined with ammonia in the general base-catalyzed PET glycolysis, were observed: 1) NH₄HCO₃, being a more user-friendly catalyst precursor due to CO₂, eliminates the use of toxic and volatile ammonia gas; 2) the presence of CO₂ effectively suppresses aminolysis reactions; 3) the avoidance of catalyst contamination in BHET simplifies repolymerization processes.⁶⁹

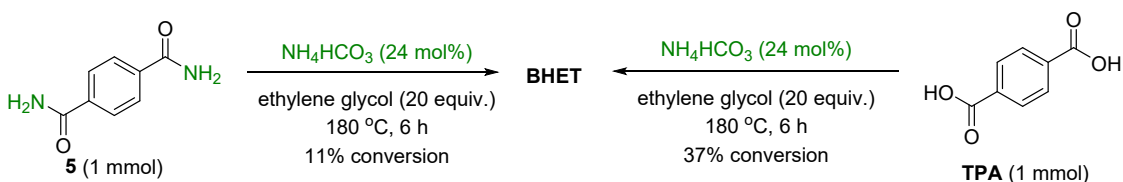
A. Glycolysis of diester **1** under mild conditions and the detection of aminolysis product



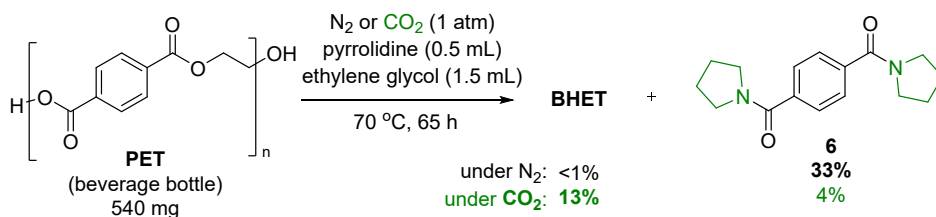
B. Esterification of monoamide **3** with ethylene glycol



C. Esterification of terephthalamide **5** or terephthalic acid (TPA) with ethylene glycol with catalytic ammonium bicarbonate



D. Selective aminolysis versus glycolysis with pyrrolidine controlled by CO_2



Scheme 1. Control experiments.

As a result, our approach enables more environmentally friendly chemical processes, utilizing NH_4HCO_3 or other combinations of organic and inorganic bases with CO_2 . The synergistic effect of CO_2 as a catalyst will be further explored in renewable transesterification,⁷⁰ catalytic polymerization, and depolymerization of other plastics, building on the insights gained from our detailed mechanistic studies of PET depolymerization and cotton recovery. By offering a practical and sustainable solution, our method contributes to achieving closed-loop production of PET and PET blended fabrics. The utilization of recycled cellulose-based materials and cotton also addresses the challenges posed by the fast fashion industry and plastic-based textile waste.^{8, 11, 71-72}

Experimental Section

General information. All chemicals, unless stated otherwise were purchased from commercial suppliers and used without further purification. CO_2 was directly used from a CO_2 cylinder of 99.7% purity without any treatment for reactions. Solvents used were High-performance liquid chromatography (HPLC) grade. Analytical thin layer chromatography was done on Merck DC-Alufolien SiO_2 60 F254 0.2 mm thick pre-coated TLC plates. Column chromatography was performed using SiO_2 from ROCC (SI 1721, 60 Å, 40–63 μm). Liquid ^1H and ^{13}C NMR (Nuclear Magnetic Resonance) spectra were recorded with 500 MHz Ultrashield Plus 500 spectrometer and 125 MHz on a Bruker. ^1H , and ^{13}C NMR spectra were

also recorded at 500 MHz, and 126 MHz, respectively, on a Bruker Avance III spectrometer with a BBFO probe. All chemical shifts (δ) are quoted in ppm and all coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used for multiplicity for NMR resonances: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet and m = multiplet. LC-MS (Liquid Chromatography-Mass Spectroscopy). LC-MS analyses were carried out by connecting the above mentioned HPLC (High Performance Liquid Chromatography) apparatus to a Bruker MicrOTOF-QII system equipped with an ESI source with nebulizer gas at 1.2 bars, dry gas at 10 L/min, dry temperature at 200 °C, capillary at 4500 V and end plate offset at – 500 V. The ion transfer was conducted with funnel 1 and funnel RF's at 200.0 Vpp and hexapole RF at 100.0 Vpp while the quadrupole ion energy was set at 5.0 eV with a low mass cut-off at 100.00 m/z. In the collision cell, collision energy was set at 8.0 eV, collision RF at 100.0 Vpp, and a transfer time of 80.0 μ s and pre-pulse storage of 1.0 μ s were used. FT-Infrared spectra were recorded on a Bruker ALPHA-P FT-IR spectrometer with a single reflection ATR module. Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. The ethylene glycol was ordered from Sigma-Aldrich. The model compound diethyl terephthalate was ordered from TCI. Textile wastes used without any further treatment for the depolymerization reactions. Drinking bottles were collected from end users. The thermogravimetric analysis (TGA) was performed using a Discovery TGA from TA instruments (New Castle, DE, USA) under constant flow of 25 mL/min nitrogen. The samples were heated in a platinum TGA pan from room temperature to 600 °C at a heating rate of 10 °C/min. From the TGA results, the thermal decompositions and the first derivative of TGA (dTGA) temperatures of the samples were determined using Trios v5.1.1.46572 software (TA Instruments, New Castle, USA). Differential scanning calorimetry (DSC) analysis was performed using a Discovery DSC (TA Instruments, New Castle, USA). The samples of 4-5 mg were weighed in Tzero aluminum pans with a perforated lid. Analyses of the samples were conducted under nitrogen flow of 50 mL/min using a linear heating rate of 10 °C/min. The samples were heated from 30 to 300°C. The melting point temperatures (T_m) and melting enthalpy (ΔH_m) were determined using Trios v5.1.1.46572 software (TA Instruments, New Castle, USA). The purity of the isolated BHET (bis(hydroxyethyl)terephthalate) was measured with HPLC (column: Kromasil 5-AmyCoat (4.6 x 250 mm), iso-propanol/n-heptane (60/40, v/v), 0.5 mL/min, 8.9 MPa, detector A: 220 nm, detector B: 254 nm.). The X-ray powder diffraction (PXRD) patterns were recorded for 2 h using a Bruker AXS D8 powder diffractometer (Bruker, Germany) with λ CuK α = 1.5406 Å (40 kV, 40mA) covering a 2θ range from 5 to 50°. The ^{13}C solid-state NMR measurements were performed with a 600 MHz Avance III HD spectrometer ($\nu_{^{13}\text{C}}$ = 150.9 MHz) equipped with a 4 mm CP/MAS broadband probe. The reported spectra were acquired with the ^{13}C - $\{^1\text{H}\}$ CP-TOSS pulse sequence employing a ramped contact pulse of 1.5 ms (ν_{RF} = 55 kHz), an interscan delay of 5 seconds, a MAS frequency of 5 kHz and high-power SPINAL64 ^1H decoupling (ν_{RF} = 100 kHz) during acquisition. 2000 scans were acquired for each spectrum. Chemical shifts are referenced relative to TMS using the down-field signal of neat adamantane as a secondary reference (δ = 38.48 ppm). All measurements were performed at 25 °C.

Glycolysis of PET bottle flakes. A reactor equipped with a magnet was charged with bottle flakes (by mola, calculated with molar mass of the repeating unit of PET), ethylene glycol (25 equiv.) and ammonium bicarbonate (25 mol%). The reaction mixture was stirred and heated up to 150-200 °C. The conversions (In Table S1 and S2) were detected by analyzing aliquot samples by ^1H NMR spectroscopy.

Large scale glycolysis of PET/cellulose blended fabrics. To a three necked round bottom flask equipped with reflux condenser was added fabrics (47% – 50% PET, 80 – 213g), ethylene

glycol (25 equiv., referred to PET), and NH_4HCO_3 (25 mol%). Then the reaction was heated up to 187 – 195 °C for 18 – 24 h. Then hot filtration of the reaction mixture was performed. The filtrate was cooled down to room temperature and further down to 5 °C for overnight. The cotton residual was washed with water, EtOH and Et₂O respectively, and then dried overnight in open air. The BHET crystals were separated from the mother liquor by filtration as the first crop of product. Then the second crop of product was gained via crystallization with the mother liquor by adding a few crystal seeds and water (water/ethylene glycol = 1/1).

Supporting Information. The Supporting Information is available free of charge at <https://XXX>. Materials and Methods, supplementary text, Reaction optimization, characterization, kinetics, NMR spectra, TGA traces, HPLC traces, PXRD patterns, DSC analysis, FT-IR spectra, DFT calculation

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Materials and Methods, supplementary text, reaction procedures, substrate preparation, optimization, kinetics, cotton recover procedures, characterization of BEHT and cotton, spectroscopy (NMR and FT-IR), power X-ray diffraction analysis of BHET and viscose, mechanistic studies and DFT calculation.