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Letter

Reactive Crystallization via Metal−Organic-Framework Formation Enables Separation of Terephthalic Acid from Textile Impurities

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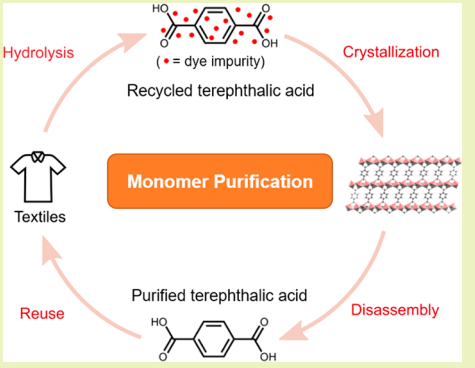
ABSTRACT: Polyethylene terephthalate (PET) fibers are among the largest plastics in production. Used commonly in textiles, PET fibers are often blended with non-PET components such as cotton, dyes, and additives. As these non-PET components generate impurities during depolymerization, extracting a high-purity terephthalic acid (TPA) monomer from the chemical recycling of textiles is challenging. Here, we demonstrate the extraction of high-quality TPA from the impure crude digestion mixtures containing depolymerized PET fibers and non-PET components. Our approach uses reactive crystallization to turn TPA into a metal−organic framework (MOF). As TPA is the only component in the mixture capable of forming an extended, crystalline structure, TPA monomers are separated from impurities as MOF crystallizes. We demonstrate this concept on recycled TPA (rTPA) extracted from a polyester−cotton blend textile through alkaline hydrolysis, where the impure rTPA was used as an organic linker to prepare MOF MIL-53(Ga). This MOF crystallization removed the trapped impurities. After MOF disassembly, colorless TPA, reminiscent of a virgin-grade monomer, was obtained (yield: 78%). These results demonstrate self-assembly-induced crystallization as a new strategy to selectively recover monomers from complex mixtures.



KEYWORDS: *recycling, monomer recovery, purification, circular, depolymerization, polycotton*

INTRODUCTION

Polyethylene terephthalate (PET) materials are major contributors to global plastic waste, making up 40% of discarded plastics.[1,2] Recycling has the potential to alleviate this concern and to reduce the greenhouse gas emission associated with the plastics production.[3−5] However, existing approaches such as mechanical recycling require chemically clean starting materials. Thus, while PET bottles can be mechanically recycled through a series of cleaning steps, blended PET products such as textiles, which contain dyes and other additives, are not suitable for mechanical recycling.[6] Chemical recycling, which uses reagents to depolymerize PET into monomers, can depolymerize blended plastics;[7] however, separating the desired monomer from impurities is not straightforward.[8,9] Considering that the textile industry is responsible for over 60% of the global PET production,[10] devising a strategy to separate impurities from recycled textile monomers is a key step toward reducing global plastic waste.[6,11]

Polyester and cotton make up the largest share of synthetic and natural fibers used in textile manufacturing today, respectively.[12] Palme et al. reported that alkaline hydrolysis can chemically recycle the PET fibers in polycotton to form terephthalic acid (TPA) and ethylene glycol (EG) monomers while leaving the cotton intact.[24] Cosimbescu et al. similarly found that alkaline hydrolysis can depolymerize colored PET bottles; however, the impurities present in the starting material remain in the recycled TPA (rTPA) even after the purification step.[8] These impurities are a significant concern, because they can affect the quality, appearance, and safety of recycled products. Driven by the requirement of high-grade monomers for safety and appearance,[13] new strategies are needed to recover high-purity TPA from complex mixtures resulting from the digestion of fabrics.

Current methods for purifying TPA are energy and reagent intensive. The most common approach is to take advantage of the temperature-dependent solubility of TPA in various solvents. In water, TPA has limited solubility.[14] Thus, the water-based method requires a hydrothermal reactor with a large water−monomer ratio, where the condition must be precisely tuned to avoid damaging TPA[15] and minimizing impurity trapping during cooling.[16] Alternatively, one can take advantage of the increased solubility of TPA in organic solvents such as N,N-dimethylacetamide,[17] where the increased solubility allows more precise control during

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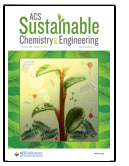

crystallization. The drawback of this approach is the need for a solvent recovery system as the crystallization cycle increases the impurity concentration in the organic phase. Another possibility is to add excess methanol during depolymerization (methanolysis) to form dimethyl terephthalate (DMT), which has a lower melting point than TPA.[18] This approach enables DMT purification via crystallization; however, it requires methanol purification and recycling.

The optimal strategy for recovering TPA from digested textiles would be to crystallize the monomers from water at the purification temperature to avoid trapping impurities upon cooling. To achieve this goal, we were inspired by the synthesis of metal−organic frameworks (MOFs), where TPA is a common building block.[19] MOFs are crystalline, porous, and insoluble coordination polymers consisting of inorganic clusters coordinated by organic linkers. Previously, TPA derived from PET waste has been used to prepare MOFs, including UiO-66(Zr) (UiO = Universitetet i Oslo),[20] MIL-53(Al) (MIL = Matériaux de l'Institut Lavoisier), and MIL-47(V).[21] In some cases, PET waste can be used directly to prepare MOFs, including Cr-MOF,[22] MIL-47(V), MIL-53(Cr), MIL-53(Al), MIL-53(Ga), and MIL-101(Cr).[23] Out of all the components present in the mixture after digesting textiles, only TPA possesses the requisite rigidity and symmetry to self-assemble into a high-quality MOF and precipitate from solution. As such, we hypothesized that self-assembly into a MOF represents a potential strategy to separate TPA from textile impurities such as dyes. Simple chemical digestion of the MOF using acid would return pure TPA and the recovered metal salt. Herein, we demonstrate that recycled TPA from blended PET waste can be reversibly self-assembled into MIL-53(Ga) and that the resulting MOF can be disassembled to yield TPA free from impurities. Furthermore, we show that the metal salt can be circularly recycled for further crystallization (Figure 1).

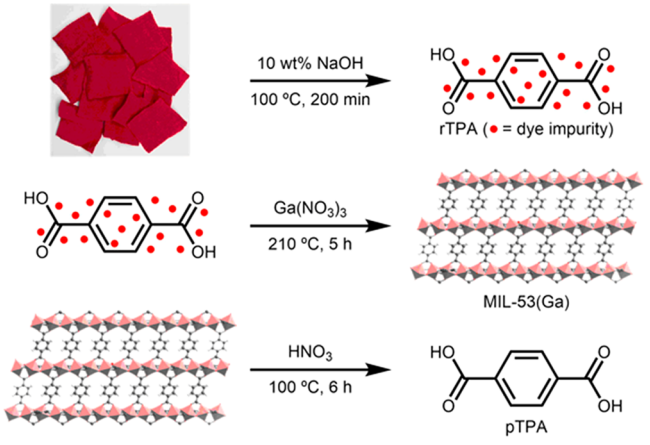

Figure 1. A schematic of the steps taken to recover terephthalic acid from waste textiles. rTPA and pTPA stand for recycled TPA and purified TPA, respectively.

RESULTS AND DISCUSSION

We initially examined the suitability of reactive crystallization for purifying TPA using red polycotton (65/35 polyester/cotton blend) fabric as a model system. The alkaline hydrolysis procedure (Figure 2) is adapted from Palme et al.[24] Powder X-ray diffraction (PXRD) confirms the formation of rTPA from a red polycotton fabric after alkaline hydrolysis (Figure 2a). All observed PXRD peaks are in good agreement with the TPA crystal structure.[25] Analysis with nuclear magnetic resonance (NMR) (Figure S4) and Fourier-transform infrared spectroscopy (FTIR) (Figure S3) also confirmed the formation of TPA upon hydrolysis. However, the rTPA still contained significant amounts of fabric dye, even after extended washing with water. The leftover impurity was visually recognizable through the color of the TPA and its solution in DMSO (Figure 2b), even though the impurities present were below the detection limit of NMR spectroscopy, thermogravimetric analysis (TGA), and FTIR (Figures S2−S4). This finding demonstrates that hydrolysis of textiles to yield TPA does not facilitate its separation from textile impurities such as dyes.

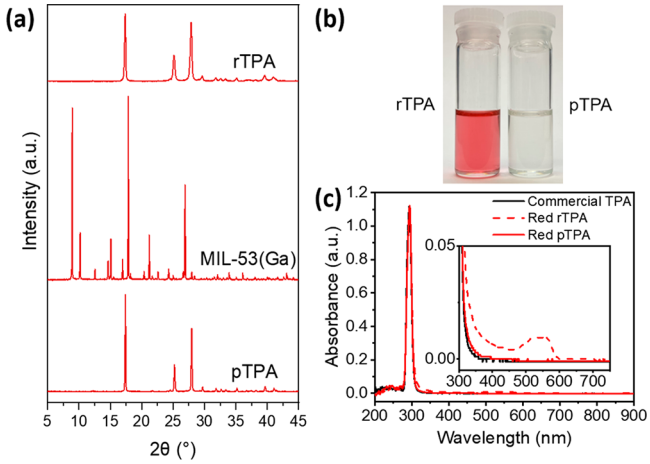

Figure 2. (a) Powder X-ray diffraction of recycled TPA (rTPA) from red polycotton, MIL-53(Ga) MOF synthesized from rTPA (MIL-53 (Ga)), and purified TPA from MOF disassembly (pTPA). (b) Photos and (c) UV−vis spectra of rTPA and pTPA in DMSO.

In order to synthesize MIL-53(Ga) from rTPA, a mixture of rTPA, $Ga(NO_3)_3 \cdot xH_2O$, and water was heated in an autoclave at 210 °C for 5 h.[26] The PXRD pattern of the prepared MIL-53(Ga) (Figure 2a) matches well with that reported in the literature,[26] confirming that impure rTPA can serve as the organic linker in a metal organic framework synthesis. The particle sizes were on the order of 10−100 μm, as confirmed by scanning electron microscope (SEM) images (Figure S5). The MOF products were needle-like crystallites that were pale green in color, and the resulting effluent was bright yellow. The MOF solution was centrifuged to separate the crystals from the yellow solution. The MOF was then rinsed with DMF and acetone to wash off any last remnants of impurities.

Last, we subject the MIL-53(Ga) crystals to 2 equivalents of boiling HNO_3 to digest the MOF, yielding purified TPA (pTPA), which precipitated as a solid in a solution of $Ga(NO_3)_3$. Figure 2a shows the PXRD of pTPA obtained after the MIL-53 (Ga) disassembly. The peak positions match well the TPA crystal structure and have narrower full width at half-maximum (fwhm) values than rTPA, indicating the formed crystallites are larger.

The comparison between rTPA and pTPA dissolved in DMSO reveals that rTPA contains a residual red color that is absent in pTPA (Figure 2b). The red tint of the rTPA solution indicates the presence of dyes and other impurities from the red fabrics, while the pTPA solution is clear and colorless, indicating no dye impurities. Given that the impurity was recognizable through the color of the solution but not

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detectable by NMR, TGA, or FTIR, we assessed the relative purities of the two TPA samples using UV−vis spectroscopy in DMSO (Figure 2c.) Comparing the absorbance spectra of rTPA and pTPA to commercial TPA, all three have a characteristic peak at 300 nm, indicative of TPA. Commercial TPA has no absorbance peaks other than the characteristic TPA feature at 300 nm. In contrast, rTPA has absorbance peaks that extend as far as 600 nm. We assign these peaks to the impurities in rTPA, most likely dyes and colorants. These higher-wavelength absorbance peaks disappear in pTPA, which possesses an absorbance spectrum closely matching that of the commercial TPA. pTPA was further tested for Ga impurities using X-ray photoelectron spectroscopy (XPS). The results of this test showed Ga impurities of less than 0.1 atomic percent (referenced against carbon and oxygen, Figure S8). This observation suggests that pTPA has a purity close to the commercial TPA monomers, validating our hypothesis that reactive crystallization via MIL-53(Ga) assembly-disassembly rejects textile impurities.

We applied the reactive crystallization approach to polycotton dyed with different colors (blue: Figure 3a, b, green: Figure 3c, d). The photographs of rTPA dissolved in DMSO from the blue and green fabrics showed a tinted solution, indicating the presence of impurities, similar to the red polycotton sample. We quantified this phenomenon using UV−vis spectroscopy. Figure 3b and d compares the spectra of rTPA, pTPA, and commercial TPA, where pTPA went through the same methodology as red polycottons. The results showed the same outcome: pTPA showed only the 300 nm peak that is characteristic of TPA, and no other absorbance features. This finding indicates that the TPA purification process works irrespective of the color of the starting textile.

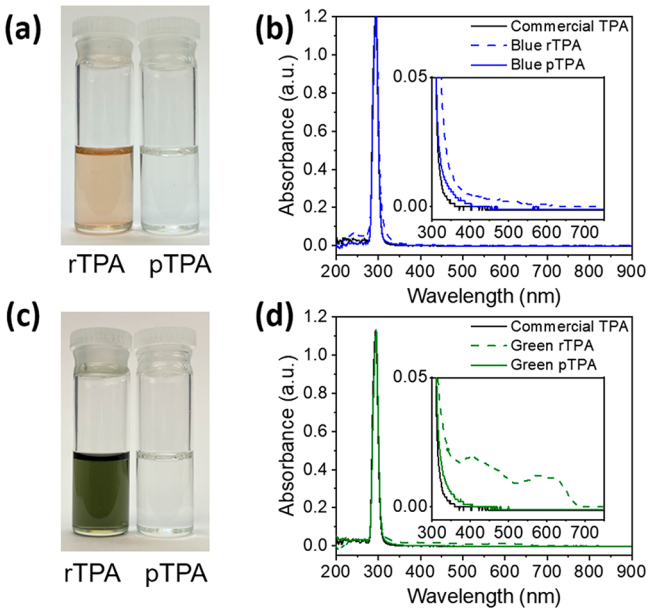

Figure 3. (a) Photos and (b) UV−vis spectra of rTPA obtained from blue polycotton and the corresponding pTPA in DMSO. (c) Photos and (d) UV−vis spectra of rTPA obtained from green polycotton and the corresponding pTPA dissolved in DMSO.

We note that the reported procedure can be applied without using organic solvent. In this work, MIL-53(Ga) after its synthesis from rTPA was washed using DMF and acetone to remove the excess TPA to improve the quality of the PXRD data. Similarly, when the MIL-53(Ga) MOF was dissembled in nitric acid, water can be used as a solvent to recover the Ga in place of methanol, which was used to help with the sample drying. We show that when organic solvents are not used, pTPA can still be produced from the reactive crystallization using the MIL-53(Ga) structure (Figure S6). Because no organic solvents were used in the washing step, the MIL-53(Ga) PXRD, however, contains additional peaks due to the presence of excess TPA inside the solid. Nonetheless, the obtained MOF can still be disassembled to form pTPA, as shown by UV−vis.

Finally, we demonstrate that both nitric acid and gallium nitrate can be recovered from the MOF synthesis and disassembly. The effluent from the MOF hydrothermal synthesis was distilled to recover nitric acid. The Ga nitrate was recovered from the effluent after the MOF disassembly by boiling off the excess liquid. This recovered Ga nitrate can then be used in the subsequent reactive MOF crystallization (Figure S7). The lower intensities of the PXRD peaks suggest that the crystallization could be interfered by the impurities in the recovered Ga nitrate powder. Nevertheless, the MOF could be still decomposed to form pTPA, illustrating that the presented reactive crystallization strategies can be circular. While not shown here, nitric acid should be recoverable after the MIL-53(Ga) formation, which combines TPA with Ga nitrate to form MIL-53(Ga) and nitric acid solution. This step requires distillation similar to methanolysis. The advantage of our approach is that it is fully aqueous.

CONCLUSION

We report the purification of recycled TPA from waste polyester textiles through reactive crystallization. Our approach enables the selective crystallization of TPA from a complex digestion mixture from alkaline hydrolysis. Our methodology starts by assembling TPA into an insoluble MIL-53(Ga) MOF intermediate, which we subsequently disassemble in nitric acid to extract the purified monomer. Colorimetric analysis using DMSO as a solvent demonstrated that purified TPA produced a clear, colorless solution. This observation contrasts with the colored tint of prepurified TPA solutions, which contain leftover dyes from depolymerization. This result confirmed the removal of impurities, e.g., dyes and colorants. The outcome of the process also produced Ga nitrate and nitric acid that can be reused in the additional cycle of reactive crystallization. This work demonstrates an aqueous method for purifying TPA from impurities and contributes a technique for purifying recycled waste textiles to enable circular polyesters. The advantage of this process is that it does not require organic solvents, making it possible to extract virgin-grade TPA from polyester textiles in an environmentally friendly manner. We note that in theory this strategy should be amenable to the recovery of other monomers capable of reversibly forming insoluble, extended networks, which we will explore in future work.

EXPERIMENTS

Reagents and Chemicals. Gallium(III) nitrate hydrate ($Ga(NO_3)_3{\cdot}xH_2O$, Beantown Chemical, 99.9%), terephthalic acid (BDC, Sigma-Aldrich, 98%), sodium hydroxide (NaOH, Macron Fine Chemicals), polyester/cotton shirts (Port & Company, 65% polyester 35% cotton), acetone (Sigma-Aldrich, 99.9%), methanol (Sigma-Aldrich, 99.8%), sulfuric acid (Honeywell, 95.0%−98.0%), and nitric acid (LabChem, 50% v/v) were used as received. All water used was deionized (MilliporeSigma, Direct-Q 5UV-R).

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Depolymerization of PET Textile Wastes. The polyester cotton fabric was depolymerized following an alkaline hydrolysis procedure from Palme et al.[24] NaOH (20 g) and deionized water (480 g) were combined in a 500 mL round-bottomed flask to prepare a 10 wt % NaOH alkaline hydrolysis solution. Here, 5 g of either red, green, or blue 65/35 polyester/cotton fabric was cut into 1 in. × 1 in. pieces and put into the reaction flask. The solution was heated to 100 °C and stirred for 200 min. The round-bottomed flask was cooled to room temperature. The mixture was filtered via vacuum filtration using a glass microfiber filter. To the liquid phase, sulfuric acid was added to precipitate TPA from solution. The mixture was filtered, and the resulting solid was rinsed with deionized water (100 mL) to yield rTPA. Prior to PXRD, rTPA was dried at 150 °C overnight. The yield of rTPA was 85%.

Synthesis of MIL-53(Ga). MIL-53(Ga) was hydrothermally synthesized under autogenous pressure from a mixture of Ga nitrate (0.525 g), recycled terephthalic acid (rTPA, 0.38 g), and deionized water (10 g) (procedure adapted from Volkringer et al.[26]). The reactants were mixed in a 100 mL Teflon-lined autoclave, which was heated at 210 °C for 5 h. The reaction mixture was allowed to cool to room temperature and filtered via centrifuge. The resulting solid was rinsed with 40 mL of N,N-dimethylformamide (DMF) to remove excess TPA and 10 mL acetone to help the product dry more quickly.

Disassembly of MIL-53(Ga). MIL-53(Ga) was disassembled to purified TPA by stirring the MOF with 2 mol equivalents of concentrated nitric acid. The mixture was stirred at 100 °C for 6 h in a lidded glass vial with a vent needle. After cooling the mixture to room temperature, the mixture was centrifuged three times with 10 mL water per run to remove remaining nitric acid and once with 10 mL methanol to help dry the product more quickly. The product was then dried and prepared for characterization. The yield of pTPA was 78%.

Characterization. The Bruker D8 Advance ECO powder diffractometer with a 1 kW Cu Kα source was used to collect PXRD in the range of $2\theta = 3°-50°$ at a scanning rate of 0.02° s^{-1}. All samples were dried overnight prior to analysis by PXRD. UV−vis spectra were recorded on Shimadzu UV-2600i UV−vis spectrophotometer in the range of 200−900 nm. Blank DMSO was used as a background for all UV−vis experiments. UV−vis samples were run at 1 mM concentration in DMSO. Here, 0.1 mmol of each TPA sample was added to 10 mL DMSO and then diluted to 1 mM. The thermogravimetric decomposition profiles were collected on a TA Instruments TGA Q5000 under an atmosphere of N_2 and with a ramp rate of 3 °C/min. FTIR spectra were collected on a Bruker Tensor II IR spectrometer equipped with a diamond attenuated total reflectance (ATR) attachment. SEM images were collected on a Zeiss Gemini 500 scanning electron microscope. The samples were carbon sputtered prior to imaging. XPS samples were analyzed using a Scienta Omicron ESCA-2SR spectrometer with operating pressure of ca. 10^{-9} Torr. Monochromatic Al Kα X-rays (1486.6 eV) with photoelectrons were collected from a 1.1 mm diameter analysis spot. Photoelectrons were collected at a 90° emission angle with a source to analyzer angle of 54.7°. A hemispherical analyzer determined electron kinetic energy, using a pass energy of 200 eV for wide/survey scans and 50 eV for high resolution scans. A flood gun was used for charge neutralization of nonconductive samples.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c05496.

Additional XRD, TGA, NMR, FTIR, SEM, and XPS characterizations (PDF)

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Notes

The authors declare no competing financial interest.

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