

Depolymerization of Polyester Fibers with Dimethyl Carbonate-Aided Methanolysis

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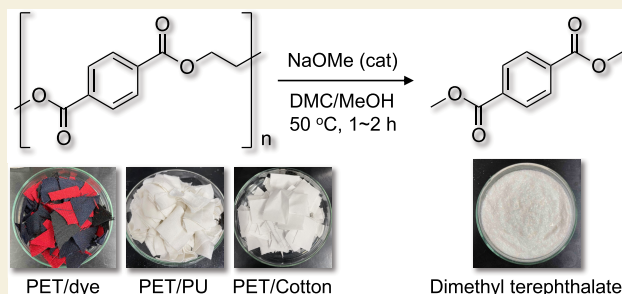
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ABSTRACT: Polyester fibers, comprising mostly poly(ethylene terephthalate) with high crystalline content, represent the most commonly produced plastic for ubiquitous textiles, and approximately 60 million tons are manufactured annually worldwide. Considering the social issues of mismanaged waste produced from used textile products, there is an urgent demand for sustainable waste polyester fiber recycling methods. We developed a low-temperature, rapid, and efficient depolymerization method for recycling polyester fibers. By utilizing methanolysis with dimethyl carbonate as a trapping agent for ethylene glycol, depolymerization of polyester fibers from textile products proceeded at 50 °C for 2 h, affording dimethyl terephthalate (DMT) in a >90% yield. This strategy allowed us to depolymerize even practical polyester textiles blended with other fibers to selectively isolate DMT in high yields. This method was also applicable for colored polyester textiles, and analytically pure DMT was isolated via depolymerization and decolorization processes.

KEYWORDS: polyester, catalysis, chemical recycling/upcycling, plastic waste, textiles



Dimethyl Carbonate-Aided Methanolysis for polyester textiles

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INTRODUCTION

Plastic materials are indispensable in daily life, but most of them are consumed as single-use products, leading to serious environmental pollution around the world.^{1–3} Polyester fibers, comprising mostly poly(ethylene terephthalate) (PET), are an abundant plastic utilized for ubiquitous textile products, and ca. 60 million tons are produced for fabric items annually worldwide (ca. 30 million tons for beverage bottles and films).^{4,5} A recent survey revealed that 73% of used textiles are currently incinerated or disposed of in landfills and oceans.⁶ The amount of recyclable polyester waste in the world is estimated to be 42 million tons per year.^{5,7} Efficient strategies for end-of-life treatment of wasted polyester fibers in a low-energy process are urgently needed to realize a circular economy.^{4,8–12} However, the material recycling method via a simple melting and remolding process is ineffective because most polyester fibers are blended with other materials and/or colored with dyes.⁴ Therefore, chemical recycling, where virgin plastic equivalents can be infinitely reproduced via depolymerization and repolymerization, is a promising approach to recycling a wide range of polyester fibers. Unlike PET resins utilized for beverage bottles and films, however, polyester fibers possess a relatively high crystalline component, and thus their depolymerization under mild conditions is normally unfeasible, particularly below glass transition temperature (ca. 70 °C).¹³ Indeed, polyester fibers can be efficiently depolymerized when

heating at high temperatures in an alcoholic solvent (ethylene glycol [EG], MeOH, etc.) with a catalyst (Scheme 1(a), glycolysis),^{14–17} or utilizing an equimolar base,¹⁸ or heating in acetic acid.¹⁹ Another problem with depolymerizing practical polyester fibers is the presence of impurities (e.g., dyes, other fibers). Under harsh reaction conditions, these impurities induce competing side reactions that retard the depolymerization of PET. Moreover, contamination with byproducts derived from the impurities leads to an energy-consuming process requiring multistep monomer purification.^{19,20}

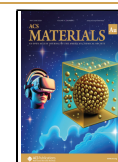
To date, an enzymatic approach^{21–25} that enables depolymerization of amorphous PET into terephthalic acid at ambient temperature (~50 °C) (Scheme 1b) has been reported, but it exhibits low activity toward polyester fibers.²⁴ Molecular catalyst approaches under mild conditions^{26–28} have also targeted amorphous PET resin, yet studies on polyester fibers are unexplored. Consequently, a feasible and practical method for depolymerizing polyester fibers, especially those with a high crystalline content, under mild conditions is a big

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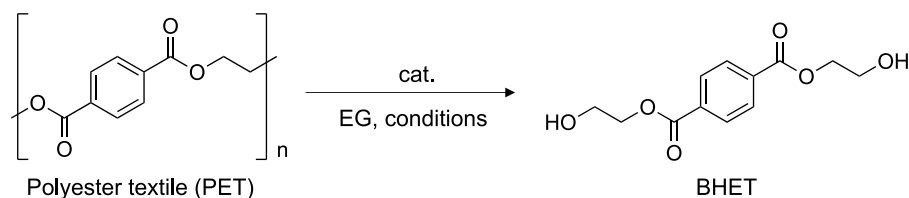
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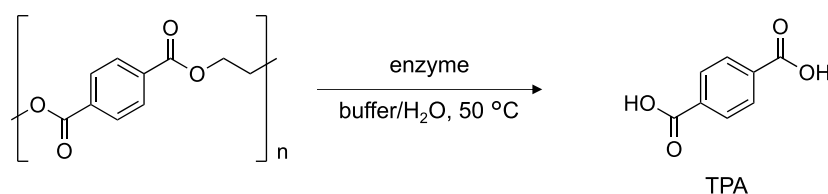


Scheme 1. Depolymerization Approaches for Polyester Textiles⁴

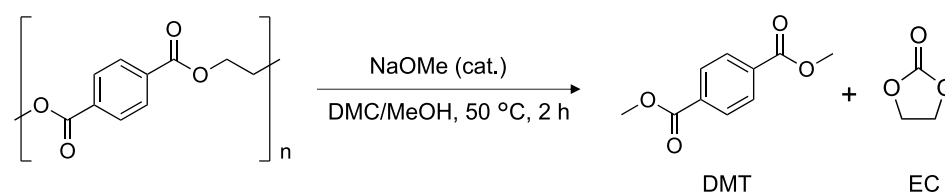
(a) Reported work : Glycolysis



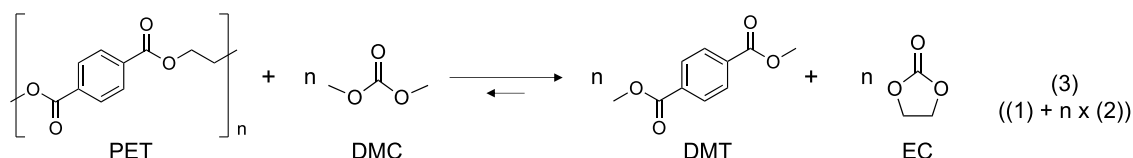
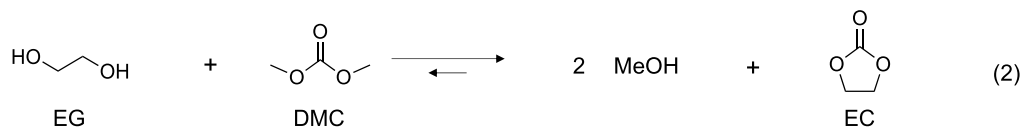
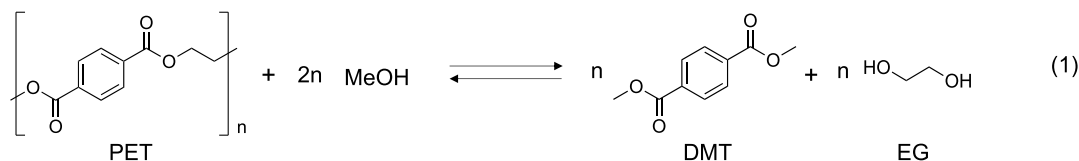
(b) Reported work : Enzymatic hydrolysis



(c) This work : Dimethyl carbonate-aided methanolysis (DCAM)



⁴EG: ethylene glycol, BHET: bishydroxyethyl terephthalate, TPA: terephthalic acid, DMC: dimethyl carbonate, DMT: dimethyl terephthalate, and EC: ethylene carbonate.

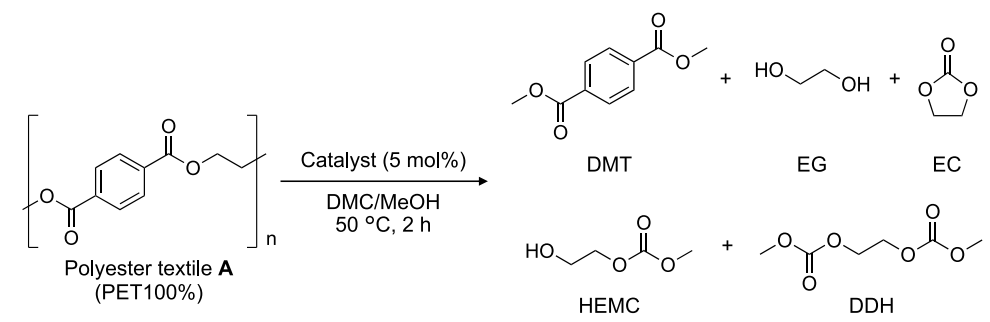
Scheme 2. Strategy of Dimethyl Carbonate-Aided Methanolysis (DCAM)⁴

⁴PET methanolysis (eq 1), an entrapment of EG by DMC producing EC and MeOH (eq 2), and an overall reaction equilibrium shifted toward the product system (eq 3).

challenge in the field of chemistry, as well as the textile industry.

In this context, we recently achieved an efficient PET depolymerization reaction, dimethyl carbonate-aided methanolysis (DCAM) (Scheme 2), in which the product (i.e., dimethyl terephthalate [DMT]) is available for PET production.²⁹ While methanolysis is a classical method for PET depolymerization,^{30–34} it is difficult to achieve high depolymerization efficiency under mild conditions due to the reaction equilibrium (Scheme 2 (eq 1)). In the DCAM method, dimethyl carbonate (DMC) is added to trap EG to

form thermodynamically stable ethylene carbonate (EC) as well as MeOH (Scheme 2 (eq 2)). By utilizing this methodology, the PET depolymerization equilibrium is shifted toward DMT, and PET resins obtained from beverage bottles are efficiently depolymerized under mild conditions, affording analytically pure DMT in up to a 94% yield. It is worth noting that DMC is produced from CO₂ and MeOH in the industrial process and is widely used as an environmentally benign organic solvent.³⁵ Herein, we investigated the application of the DCAM approach toward polyester fibers derived from polyester textiles. We first examined the optimization of the

Table 1. Optimization of Reaction Conditions for the DCAM Reaction of Polyester Textile A (PET 100%, Colorless)^a


entry	catalyst	DMC (mL)	MeOH (mL)	DMT (%)	EC (%)	EG (%)	HEMC (%)	DDH (%)
1	LiOMe	1.5	0.2	83	70	3	2	5
2	NaOMe	1.5	0.2	95	86	2	1	5
3	KOMe	1.5	0.2	95	93	1	<1	2
4 ^b	NaOMe	1.5	0.2	93	92	<1	<1	3
5 ^b	KOMe	1.5	0.2	85	77	2	<1	3
6	TBD	1.5	0.2	21	18	1	2	<1
7	None	1.5	0.2	0	0	0	0	0
8	NaOMe	0	1.5	4	1	1	0	0
9	NaOMe	0 ^c	0.2	17	0	28	0	0
10	NaOMe	1.0	0.13	98	67	4	18	11
11	NaOMe	0.5	0.065	93	60	3	20	12

^aConditions: PET textile (100 mg), catalyst (5 mol % based on the PET alternating unit), DMC (1.5 mL), MeOH (0.2 mL), 50 °C, and 2 h. Yields were determined by gas chromatography using biphenyl as a standard and based on the molar amount of the PET alternating unit (MW: 192.17 g/mol). Averages of more than two runs are shown. ^b1 h. ^cToluene (1.5 mL) was added instead of DMC. Abbreviations are as follows: DMC: dimethyl carbonate, DMT: dimethyl terephthalate, EC: ethylene carbonate, EG: ethylene glycol, HEMC: 2-hydroxyethyl methyl carbonate, DDH: dimethyl 2,5-dioxahexanedioate, and TBD: triazabicyclodecene.

Table 2. DCAM Reactions of Various Engineered Polyester Textiles (A, B, C, and D)

sample no.	polyester textile	component	scale (g)	NaOMe loading	recovered textile	DMT yield
1	lab coat for the analytical experiment (A)	PET 100%	10	0.16 g (5 mol %)		9.5 g (94%)
2 ^a	functional undershirt (B)	PET 88% PU ^b 12%	10	0.16 g (6 mol %)	0.98 g (PU) ^b	7.2 g (80%)
3	lab coat for the chemical experiment (C)	PET 65% cotton 35%	10	0.30 g (15 mol %)	3.1 g (cotton)	6.2 g (94%)
4	apron (black, red, blue) (D)	PET 100% + disperse dyes	50	0.80 g (5 mol %)		39 g (78%)

^aReaction time: 1 h. ^bPolyurethane.

DCAM conditions by using polyester textiles (PET 100%). Upon optimized conditions, we further explored the depolymerization of PET/polyurethane (PU) blend, PET/cotton blend, and colored polyester textiles and elaborated on the state of DMT as well as the state of recovered textiles.

RESULTS AND DISCUSSION

We initiated our study with polyester textiles obtained from a colorless lab coat (polyester textile A, PET 100%), which was cut as ca. 10 mm × 10 mm square size and used for depolymerization as is. The molecular weight (Mw) of the PET content in the textile was 3.1×10^4 g/mol based on gel permeation chromatography (GPC) analysis (Figure S1). The crystallinity was determined to be 40% by differential scanning calorimetry (DSC) (Experimental Section and Figure S2), and the value is higher than that of amorphous PET chips (ca. 10%).^{36,37} An initial experiment with optimized conditions for depolymerization of PET powder²⁹ (LiOMe catalyst (5 mol %) in DMC/MeOH (v/v 7.5:1), 28 °C, 5 h) resulted in a low yield of DMT (13%). We therefore investigated suitable reaction conditions for the PET fiber. When the reaction temperature was set to 50 °C with a LiOMe catalyst, the DMT yield increased to 83%, and EC was obtained as a major EG

fragment-derived product together with a small amount of EG and opened-form carbonates (2-hydroxyethyl methyl carbonate [HEMC], dimethyl 2,5-dioxahexanedioate [DDH];³⁸ Table 1, entry 1). NaOMe and KOMe exhibited higher catalytic activity in comparison to LiOMe (entries 2 and 3). High product yields (93% for DMT and 92% for EC) were also achieved with an even shorter reaction time (1 h) when NaOMe was used as the catalyst (entry 4). Interestingly, the EC yield was increased to 92%, indicating that a ring-opening reaction of EC occurred at a late stage of the reaction. In contrast, using KOMe as the catalyst led to a slight decrease in the DMT yield at a reaction time of 1 h (entry 5). A metal-free catalyst, triazabicyclodecene,³⁹ also exhibited catalytic activity, but the efficiency was significantly lower than that of alkaline methoxides (entry 6). The reaction without a catalyst produced no monomers at all (entry 7). The reactions without DMC resulted in low yields of DMT and EC (entries 8 and 9, respectively), supporting the vital role of DMC as a trapping agent. Reducing the amount of the reaction media, DMC and MeOH, led to a decrease in the EC yields and an increase in the yields of EG, HEMC, and DDH (entries 10 and 11). Nevertheless, high DMT yields were maintained, and no partially depolymerized products (e.g., BHET, mono(2-hydroxyethyl)methyl terephthalate, and oligomers) were

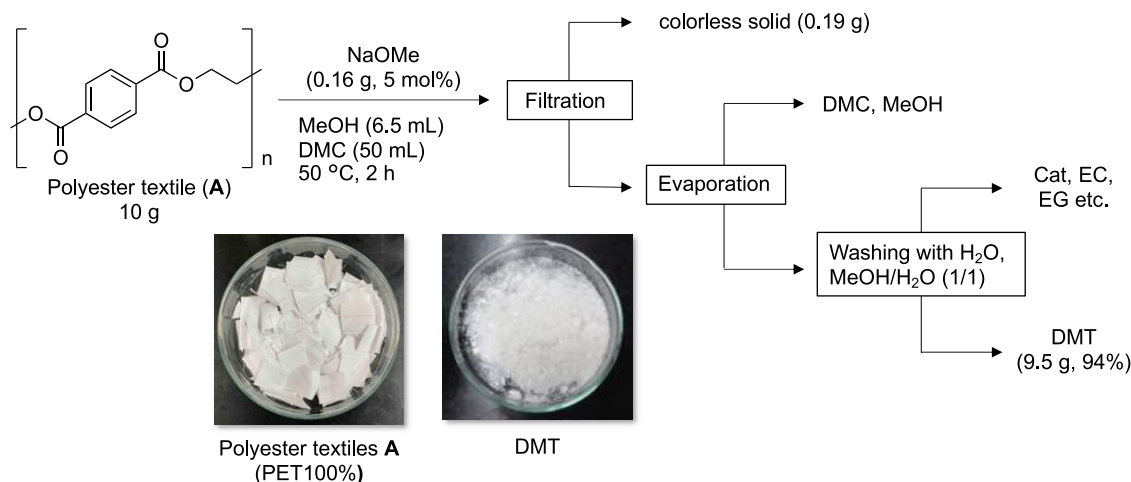


Figure 1. Depolymerization of polyester textiles (PET 100%) (A) by the DCAM approach.

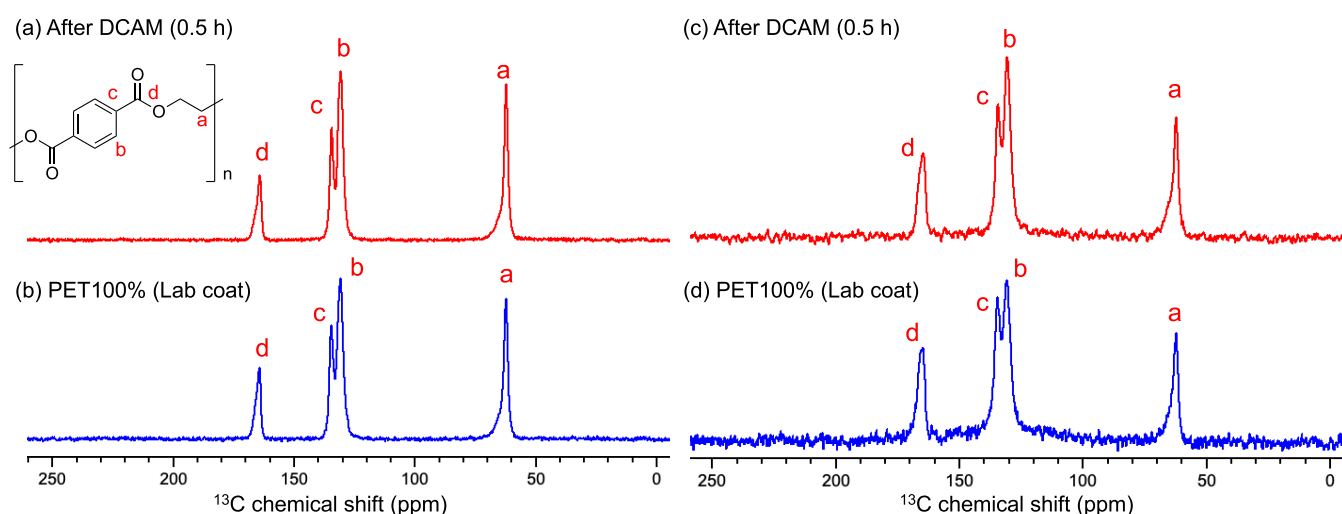


Figure 2. Solid-state ¹³C NMR of the polyester textile (A) and the residual textile after the DCAM reaction for 0.5 h with ¹H–¹³C cross-polarization (a, b) and ¹³C direct observation with ¹H dipolar decoupling (c, d).

observed. A smaller solvent volume is likely preferable on a practical scale, and we thus determined the ratio of 0.5 mL of DMC/0.065 mL of MeOH/0.1 g of PET (entry 11) as the optimal condition for further experiments.

The results of 10 g scale DCAM reactions using various engineered textiles are listed in Table 2. Colorless polyester textiles A (10 g, PET 100%) were depolymerized by immersing them in a solution of DMC (50 mL) and MeOH (6.5 mL) using NaOMe as a catalyst (5 mol %; Table 2 entry 1, Figure 1). The textiles fully disappeared when they were heated at 50 °C for 2 h. After filtration at 50 °C using additional DMC to rinse the insoluble solids, the filtrate was concentrated under reduced pressure to remove the DMC and MeOH. The residue was washed with H₂O and H₂O/MeOH (1:1), affording DMT in a crystalline form (9.5 g, 94%) (Figures S5–S7). H₂O washings comprised mainly EC together with other byproducts stemming from EG. Insoluble solids separated from the first filtration were analyzed by a solid-state ¹³C CPMAS NMR as well as a solution-state ¹H NMR in a D₂O solvent, which revealed that the solid was mainly sodium monomethylterephthalate (Figures S3 and S4). This compound was possibly formed by the hydrolysis of DMT with

NaOH, which was generated from NaOMe and residual water. No unreacted PET was observed in the spectra (Figure S3).

To gain insights into the reaction mechanism, we conducted a DCAM reaction of the polyester textile (A) with a shortened reaction time under the same conditions as for Figure 1 and analyzed the residual unreacted PET. The unreacted textiles (2.1 g) were recovered after 0.5 h, where DMT was obtained in a 67% yield (6.8 g). GPC of the recovered textiles displayed a similar profile as that of the starting material (Figure S1), indicating that PET polymer chains were depolymerized and fragmented on the liquid–solid interface.²⁵ DSC analysis of the recovered textiles also showed a pattern similar to that of the starting material with a peak at 253 °C (Figure S2). The crystallinity of the recovered textiles was almost the same as that of the starting material (recovered textiles: 39%, starting material: 40%). Moreover, a solid-state ¹³C cross-polarization/magic-angle spinning (CPMAS) NMR spectrum of recovered textiles was mostly identical to that of the starting material (Figure 2a,b), exhibiting four signals centered at 62 ppm (a), 130 ppm (b), 134 ppm (c), and 164 ppm (d). The crystallinity determined from an integral ratio of the amorphous/crystalline EG unit (signal a; 60–70 ppm)⁴⁰ in ¹³C direct observation with ¹H dipolar decoupling (Figure 2c,d), which allows a

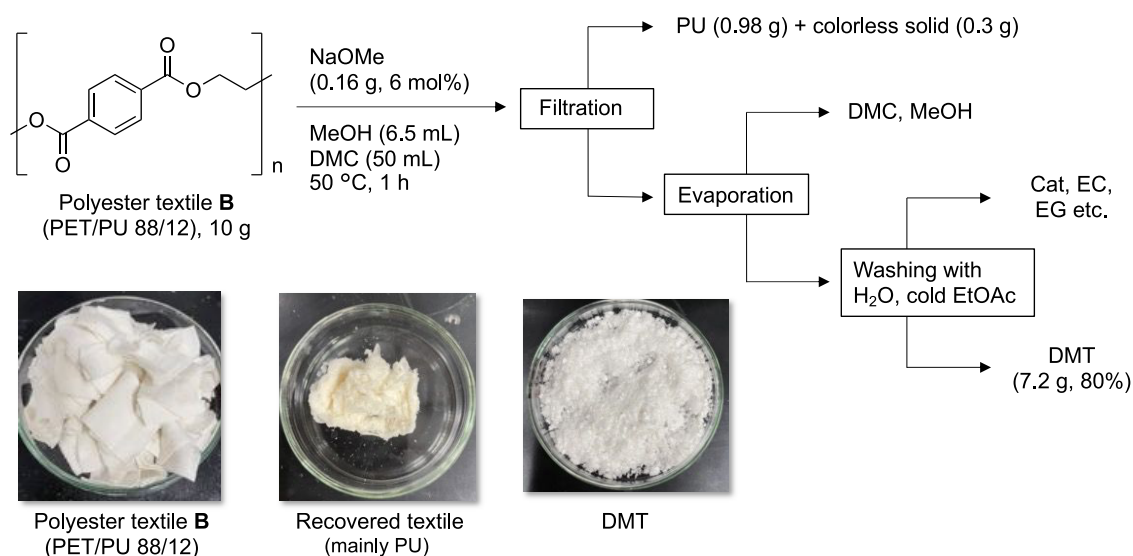


Figure 3. Depolymerization of polyester textiles B (PET/PU 88/12) by the DCAM approach.

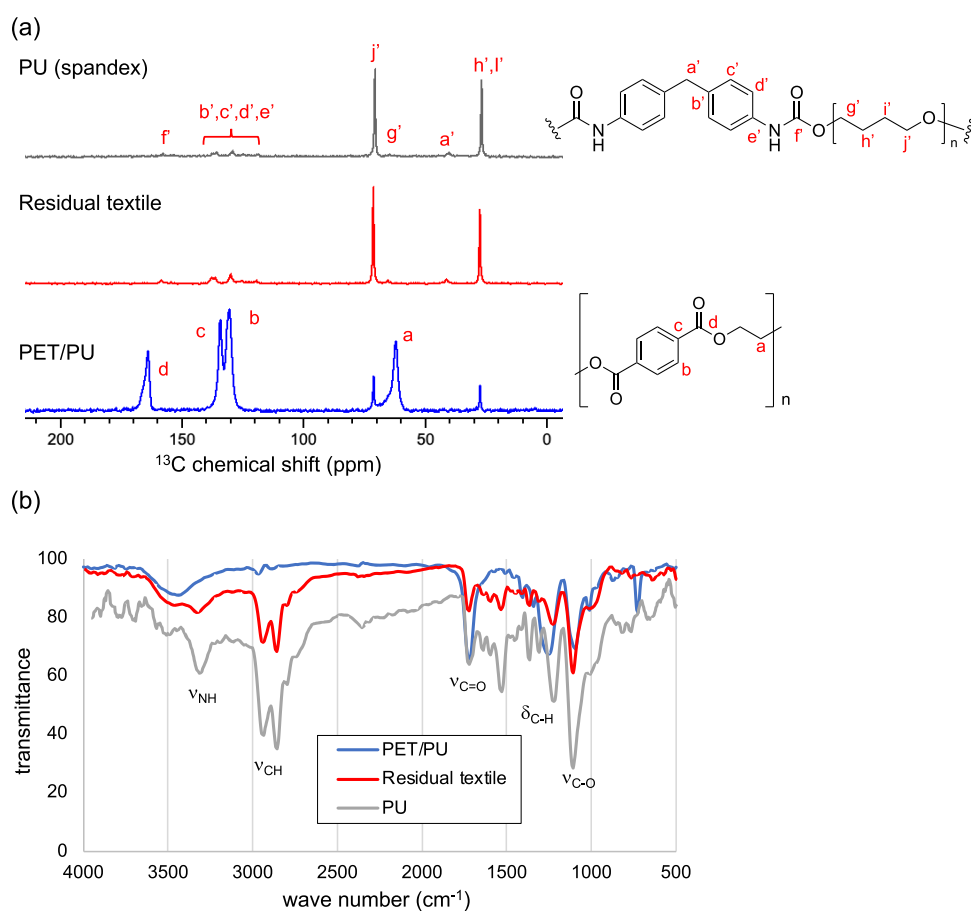


Figure 4. Solid-state ¹³C CPMAS NMR spectra (a) and FTIR spectra (b) of PET/PU (88/12) and the residual textile after the DCAM reaction.

quantitative observation of each signal, was determined to be 51% for the starting material and 54% for recovered textiles. These observations clearly indicated that both amorphous and crystalline PET domains were consumed at a similar depolymerization rate in the DCAM. This feature is a sharp contrast to low-temperature enzymatic approaches.^{23,24}

To showcase the power of the DCAM approach, polyester textiles blended with other materials were examined (Table 2,

entry 2). Polyester textiles (10 g) blended with polyurethane (PU) in an 88/12 ratio (B) obtained from a commercial colorless undershirt were successfully depolymerized under the optimized conditions, giving 7.2 g of DMT as a crystalline solid (Figure 3). Although the PU component was partially contaminated in the crude DMT, it could be removed simply by rinsing with EtOAc, affording DMT in an 80% yield (Table 2 and Figure 3). A major part of the residual solid after the

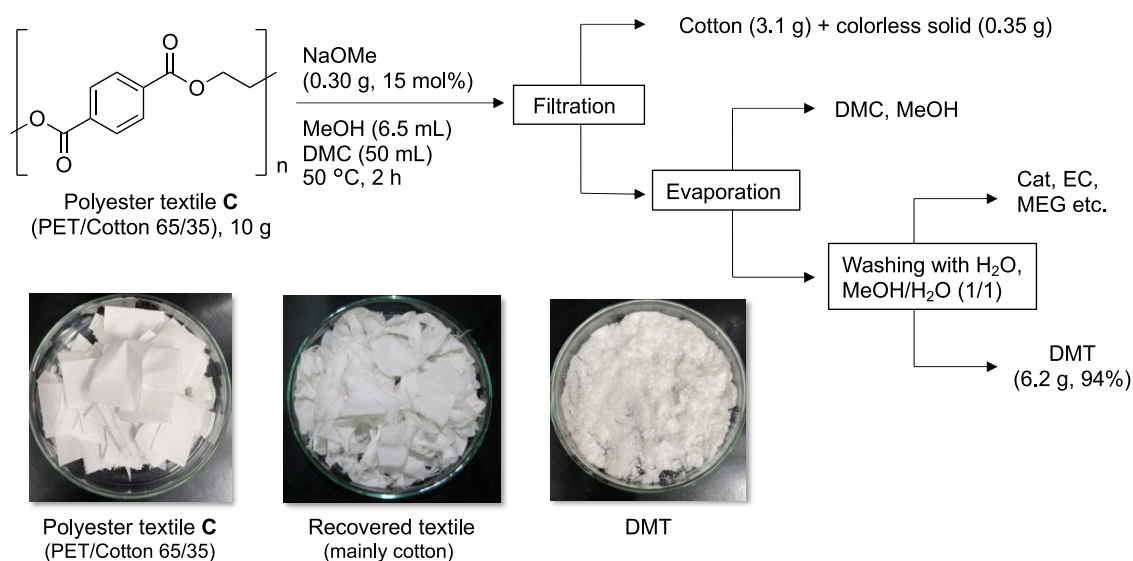


Figure 5. Depolymerization of polyester textiles C (PET/cotton 65/35) by the DCAM approach.

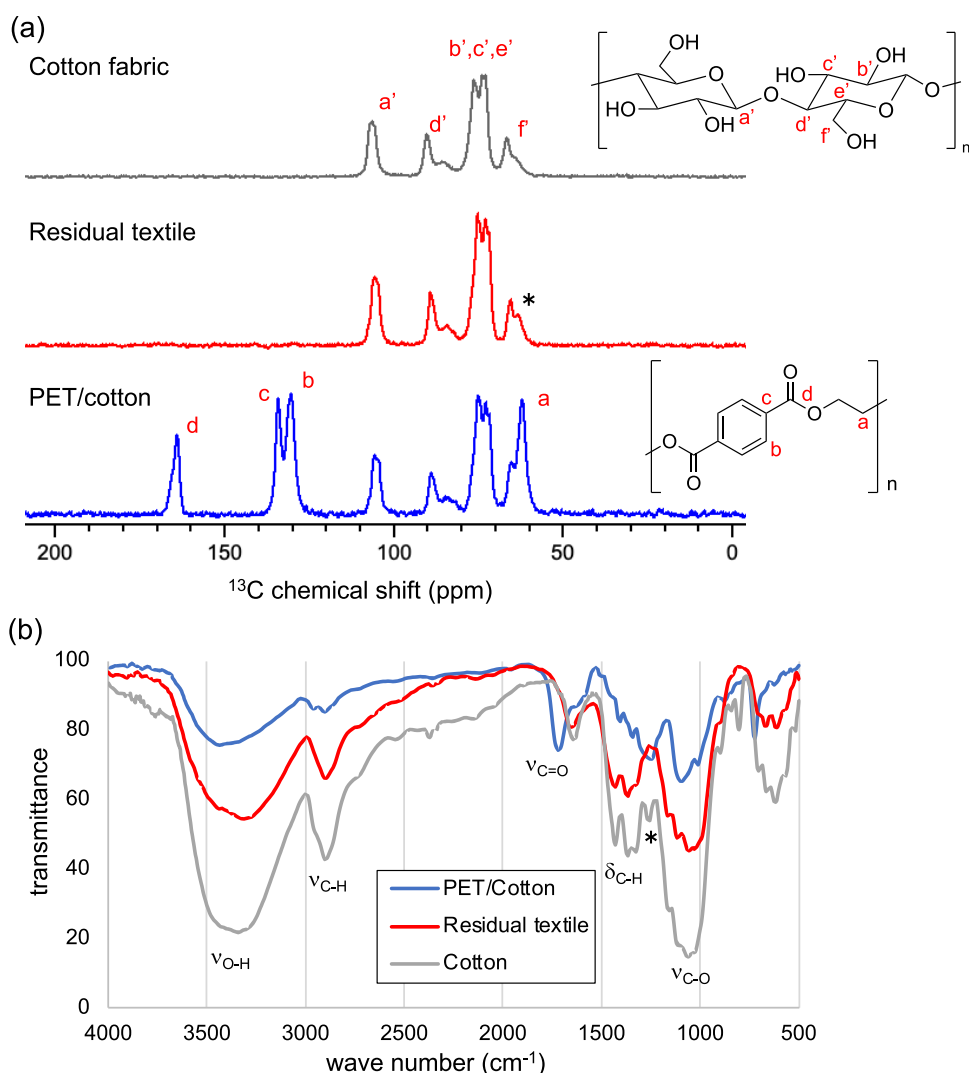


Figure 6. Solid-state ^{13}C CPMAS NMR spectra (a) and FTIR spectra (b) of PET/cotton (65/35) and the residual textile after the DCAM reaction.

reaction maintained the shape of the textile and was analyzed by solid-state NMR, Fourier transform infrared (FTIR)

spectroscopy (Figure 4a,b), thermal gravimetric analysis (TG) (Figure S18), and DSC (Figure S19) using a commercial

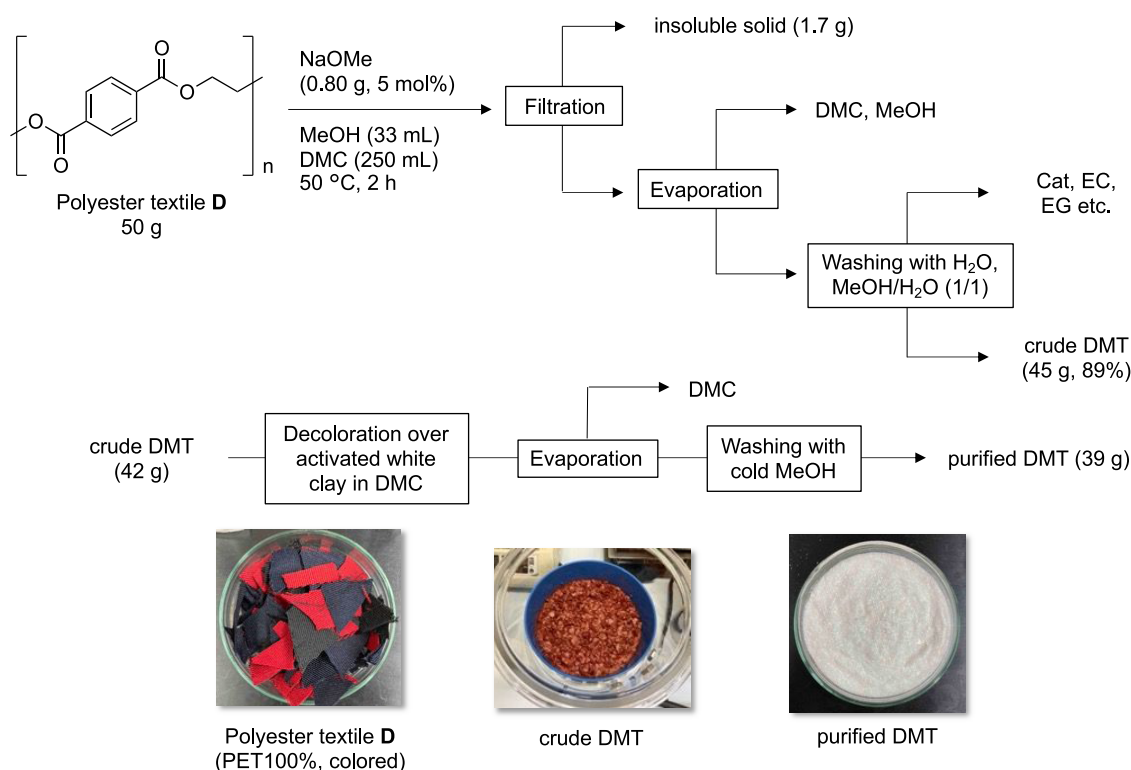


Figure 7. Depolymerization of colored polyester textiles (D) (PET 100%) by DCAM.

PU elastic fiber as a reference. In solid-state ^{13}C CPMAS NMR, sets of signals assignable to the methylenediphenyl 4,4'-diisocyanate unit (signals a', b', c', d', e', and f') and the polyTHF unit (signals g', h', I' and j') were observed from the residual textiles,⁴¹ and signals due to PET (signals a, b, c, and d) were not observed (Figure 4a). In addition, FTIR spectra of the residual textile showed a ν_{NH} peak at 3316 cm^{-1} and a ν_{CO} peak at 1724 cm^{-1} assignable to the carbamate unit (Figure 4b). Observation of strong peaks at 2936 and 2856 cm^{-1} due to the alkyl group together with a strong peak at 1105 cm^{-1} due to vibration signals from ether linkage indicated the presence of the polyTHF unit with keeping the structure intact (Figure 4b).⁴² A TG curve of the residual textile showed a similar pattern as that of the PU reference (Figure S18), and a DSC endothermic peak (second heating) due to phase transition of the soft segment⁴³ was observed at $22\text{ }^\circ\text{C}$ from all samples measured (Figure S19). Notably, the mild conditions of this approach enabled the facile separation of the PU component from blended textiles. A similar textile separation approach was recently reported for polyester/polyamide¹⁹ and polyester/PU textiles,⁴⁴ but an application for PU was still challenging, presumably due to its liability under high-temperature hydrolysis/alcoholysis conditions.¹⁹

Also, polyester textiles (10 g) blended with cotton (polyester textile C, PET/cotton 65:35) obtained from a commercial lab coat for chemical experiments were selectively depolymerized to afford crystalline DMT (6.2 g, 94% yield; Table 2 entry 3, Figure 5). Additional catalyst loading (0.30 g, 15 mol % on PET) was needed to achieve high efficiency, probably due to the hygroscopic nature of cotton.⁴⁵ The recovered cotton (3.1 g) was obtained as its original textile form and analyzed by solid-state NMR, FTIR (Figure 6a,b), TG, and DSC (Figures S20 and S21) using the commercial cotton textile as a reference. The ^{13}C CPMAS NMR spectrum clearly showed

that the PET signals completely disappeared, and only a set of signals assignable to cellulose type I (signals a', b', c', d', e', and f')^{46,47} was observed after the reaction (Figure 6a). A shoulder peak at 63.5 ppm (Figure 6a, asterisk) appeared in residual textiles, presumably due to partial methylation of the hydroxy group by DMC in basic conditions.⁴⁸ The FTIR spectra also showed a typical broad peak due to ν_{OH} ($3100\text{--}3650\text{ cm}^{-1}$) together with ν_{CO} ($1000\text{--}1150\text{ cm}^{-1}$) from residual textiles (Figure 6b), which are consistent with reported spectra from cellulose type I.⁴⁵ A weak peak at 1250 cm^{-1} (Figure 6b, asterisk) due to OH in-plane bending observed in the cotton reference did not appear in the spectra of residual textiles, indicating partial consumption of OH groups in cellulose. A TG curve of the residual textile showed a pattern similar to that of the cotton reference with a 5% loss temperature (T_{d5}) at $325\text{ }^\circ\text{C}$ for the residual textile and $320\text{ }^\circ\text{C}$ for cotton (Figure S20). A DSC curve (second heating) showed no peak in the range from -40 to $270\text{ }^\circ\text{C}$ (Figure S21). These observations indicated that the polymeric structure of the cellulose was maintained after depolymerization of the PET component, while hydroxyl groups were partially methylated due to DMC. It should be noted that the study focused on the recovery of cotton/viscose from blended polyester textiles was recently reported by Lu et al.⁴⁹ and Motte et al.,⁵⁰ yet the method to recover both cotton/viscose and the PET monomer in a high yield and high purity is rarely explored.

Polyester fibers colored with dyes (i.e., disperse dyes) are a challenging target as dyes and/or their decomposed compounds may deactivate the catalyst and retard depolymerization. Thereby, dyes generally need to be separated by high-temperature pretreatment of textiles in organic solvents,¹⁵ which is energetically costly and decreases the amount of recoverable monomers. Our approach enables the depolymer-

rization of colored polyester textiles (**D**) (PET 100%) obtained from a commercial colored apron (black/red/blue) without any pretreatment. The colored textile (**D**) (50 g) was depolymerized under the same conditions as those for the other textiles (Figure 7). The crude DMT was first rinsed with MeOH/H₂O (3:1) to remove most of the contaminating dye and further purified over activated white clay. After these treatments, the residual nitrogen element in the DMT was quantified as 4.4 ppm (Table S1). This value is sufficiently small¹⁵ and even smaller than that obtained from the colorless polyester textile (35 ppm, Table S1), confirming that the dyes were completely removed after the DCAM reaction and simple purification processes.

CONCLUSIONS

In summary, we demonstrated that the DCAM approach is a powerful method for low-energy chemical recycling of polyester textiles, comprising robust crystalline PET, which is a challenging target in this field. Polyester textiles were efficiently depolymerized under mild conditions in a short reaction time using inexpensive alkali-metal methoxide catalysts. Furthermore, we showcased the facile depolymerization of various polyester textiles utilized in modern society, including blended and colored textiles. The state of recovered textiles (e.g., PU and cotton) after the DCAM reaction was investigated using solid-state NMR, FTIR, TG, and DSC analyses. Colored polyester textiles in a 50 g scale were depolymerized into pure DMT through the DCAM approach and simple purification processes, thus paving the way for recycling wasted polyester textiles that are mostly incinerated or disposed of in the environment. Further application of our DCAM approach toward other blended materials and polymers, as well as a scale-up experiment including optimization of purification processes, is ongoing in our group.

EXPERIMENTAL SECTION

General

Commercially available polyester textiles were used in this study (colorless lab coat for the analytical experiment (**A**) [PET 100%], colorless functional undershirt (**B**) [PET88%/PU12%], colorless lab coat for the chemical experiment (**C**) [PET 65%/cotton 35%], and apron (**D**) [PET 100%, black, blue, red]). The textiles were cut with scissors into ca. 10 mm × 10 mm size and used for experiments as is. Chemicals were purchased from chemical suppliers (DMC, MeOH, NaOMe, activated white clay from Fujifilm-WAKO, KOMe, LiOMe from Sigma-Aldrich, TBD from TCI). 2-Hydroxyethyl methyl carbonate (HEMC) was prepared from DMC and EG according to the literature.³⁸ DMC, MeOH, and toluene were dried over activated MS4A before use. Solution NMR was measured with a Bruker Avance III spectrometer (600 MHz for ¹H nuclei) using a cryoprobe. All spectra were recorded at 25 ± 1 °C. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0 ppm for ¹H. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 using a DB-WAXETR column (0.25 mm × 30 m, Agilent Technologies, program: 80 to 260 °C (rate 15 °C/min) and held at 260 °C for 10 min). All samples were analyzed and quantified by using biphenyl as an internal standard. Fourier transform infrared (FTIR) spectroscopy was conducted with an FT/IR-4100 (JASCO) using the KBr disk method. Solid-state NMR was measured with an Avance NEO spectrometer (400 MHz for ¹H nuclei) using a 3.2 mm MAS probe. Standard ramped cross-polarization (CP) with 3 ms of contact time was used to transfer polarization from the ¹H nuclei to the nucleus of interest (¹³C). SPINAL-64 ¹H heteronuclear decoupling was applied during acquisition. ¹³C chemical shifts were

referenced to tetramethylsilane at 0 ppm using adamantane as an external standard (38.52 ppm).

Procedure for the Catalytic Reaction

General Procedure for Optimization of Conditions. In a vial (volume: 5 mL), the polyester textile (**A**) (100 mg (0.52 mmol based on an alternating unit: 192.17 g/mol)) and DMC were charged. A catalyst (5 mol %) dissolved in MeOH was added to give a colorless suspension. The vial was placed in an aluminum block heater whose temperature setting was stabilized and magnetically stirred for 1–2 h. The resulting reaction mixture was filtered using a syringe equipped with a PTFE filter (pore size: 0.22 μ m). Extra DMC (1 mL) was used for the collection of residual chemicals in the vial and filtered. To the mixture, then, the measured amount of biphenyl (as an internal standard) was added, and an aliquot was used for the GC-FID measurement. Molar amounts of DMT, EG, EC, HEMC, and DDH were determined by the standard calibration curve method, and yields of each product were calculated based on the following equation.

$$\text{yield (\%)} = \frac{\text{molar amount of product (mol)}}{\frac{\text{weight of PET in textile (g)}}{\text{molecular weight of PET alternating unit (g/mol)}}} \times 100$$

Ten Gram Scale DCAM Reaction Using Polyester Textiles (A) (PET). In a 100 mL round-bottom flask, the polyester textile (**A**) (PET 100%, 10 g, 5.2 mmol based on an alternating unit: 192.17 g/mol) and the DMC (50 mL) were charged. NaOMe (0.16 g, 5 mol % based on PET) dissolved in MeOH (6.5 mL) was added. The mixture was magnetically stirred at 50 °C for 2 h using an oil bath, followed by filtration at 50 °C using additional DMC (100 mL). The filtrate was concentrated under reduced pressure to give a wet solid that was rinsed with water (100 mL). The residue was further treated with MeOH/H₂O (v/v:1:1) (100 mL), affording DMT as a white crystalline solid (9.5 g, 94%).

For mechanistic investigations, the reaction was stopped after 0.5 h. In this case, unreacted PET in the textile form (2.1 g) was obtained after the first hot filtration. The filtrate was treated in the same way to give DMT (6.8 g, 67%).

Ten Gram Scale DCAM Reaction Using Polyester Textiles (B) (PET/PU). In a 100 mL round-bottom flask, the polyester textile (**B**) (PET/PU = 88:12, 10 g, 4.6 mmol based on an alternating unit: 192.17 g/mol) and DMC (50 mL) was charged. NaOMe (0.16 g, 6 mol % based on PET) dissolved in MeOH (6.5 mL) was added. The mixture was magnetically stirred at 50 °C for 1 h using an oil bath, followed by filtration at 50 °C using additional DMC (100 mL). PU (0.98 g) was recovered in a textile form. The filtrate was concentrated under reduced pressure to give a wet solid that was rinsed by water (100 mL). The residue was further treated with cold EtOAc (25 mL), affording DMT as a white crystalline solid (7.2 g, 80%).

Ten Gram Scale DCAM Reaction Using Polyester Textiles (C) (PET/Cotton). In a 100 mL round-bottom flask, the polyester textile (**C**) (PET/cotton = 65:35, 10 g, 3.4 mmol based on an alternating unit: 192.17 g/mol) and DMC (50 mL) were charged. NaOMe (0.30 g, 15 mol % based on PET) dissolved in MeOH (6.5 mL) was added. The mixture was magnetically stirred at 50 °C for 2 h using an oil bath, followed by filtration at 50 °C using additional DMC (100 mL). After washing with water, cotton (3.1 g) was recovered in a textile form. The filtrate was concentrated under reduced pressure to give a wet solid that was rinsed by water (100 mL). The residue was further treated with MeOH/H₂O (v/v:1:1) (100 mL), affording DMT as a white crystalline solid (6.2 g, 94%).

Fifty Gram Scale DCAM Reaction Using Polyester Textiles (D) (Colored PET). In a 1000 mL round-bottom flask, the polyester textile (**D**) (red, blue, and black were mixed, PET 100%, 50 g, 26 mmol based on an alternating unit: 192.17 g/mol) and DMC (250 mL) were charged. NaOMe (0.73 g, 5 mol % based on PET) dissolved in MeOH (32 mL) was added. The mixture was magnetically stirred at 50 °C for 1 h using an oil bath, followed by filtration at 50 °C using additional DMC (150 mL). The filtrate was concentrated under

reduced pressure to give a wet colored solid that was rinsed with water (300 mL \times 3). The residue was further treated with MeOH/H₂O (v/v: 1:1) (300 mL \times 2) and then MeOH/H₂O (v/v: 3:1) (300 mL \times 3), affording crude DMT (45 g, 89%). The crude DMT (42 g) dissolved in DMC (750 mL) was stirred over activated white clay (40 g) for 1 h at room temperature to remove the dyes. The resulting suspension was filtrated using celite, and the filtrate was concentrated under reduced pressure. The obtained solid was further rinsed with cold MeOH (150 mL, 100 mL), giving DMT as a crystalline form (39 g).

Gel Permeation Chromatography (GPC). GPC measurement was performed at 40 °C with a Jasco system equipped with a PU-4185 RPLC semimicro pump, a JASCO AS-4150 RPLC Autosampler, an RI-4035 semimicro refractive index detector, a CO-4065 column oven, a Gastorr FG-32 degasser, and TSKgel SuperHM-H columns (Tosoh Co. Tokyo, Japan). 1,1,1,3,3,3-Hexafluoro-2-propanol was used as an eluent at 0.3 mL min⁻¹. Data were recorded and analyzed with ChromNAV GPC software, version 2. Molecular weight (M_n , M_w) was determined relative to poly(methyl methacrylate) standards. For sample preparation for GPC, about 1 mg of PET was dissolved in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol. The solution was filtered through a poly(tetrafluoroethylene) membrane with a pore size of 0.20 μ m. Then, 20 μ L of the sample solution was injected into the GPC system.

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry was performed using a DSC-7000X (Hitachi High-Tech, Japan) in an atmosphere of nitrogen flowing at 50 mL/min. A heating rate of 10 °C min⁻¹ was applied for the temperature range from 30 to 300 °C. The degree of crystallinity (X_c) was calculated from the area of the DSC endotherm of the first heating scan using 140 J/g as the enthalpy of fusion of a 100% crystalline PET.^{51–53} The crystallinity can be obtained from

$$X_c = \frac{\Delta H_m}{\Delta H_f}$$

where ΔH_m is the measured enthalpy of fusion of PET samples and ΔH_f is the enthalpy of fusion of a 100% crystalline PET from the literature.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialsau.3c00091>.

GPC analysis of the polyester textile (A) (PET 100%); DSC analysis of the polyester textile (A) (PET 100%); NMR analysis of the insoluble part after depolymerization; NMR and GC spectra of isolated products; and total nitrogen analysis of isolated DMT; thermal analysis of residual textiles (PDF)

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Notes

The authors declare no competing financial interest.

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