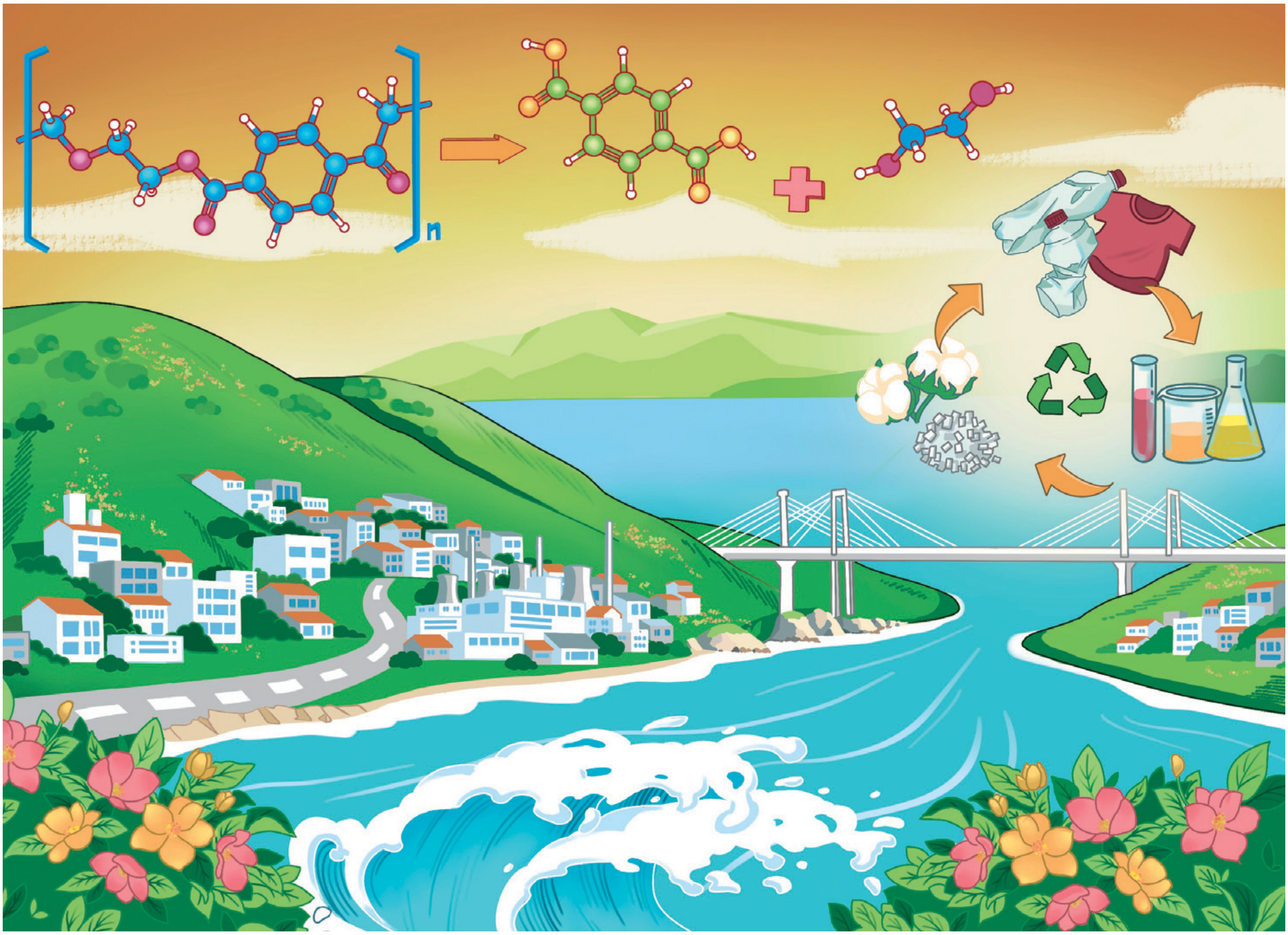

Showcasing research from Kotohiro Nomura's laboratory, Tokyo Metropolitan University, Tokyo, Japan.

Depolymerization of PET with ethanol by homogeneous iron catalysts applied for exclusive chemical recycling of cloth waste

The acid-, base-free exclusive depolymerization of PET with ethanol catalyzed by $FeCl_3$ affording DET and EG, and the selective depolymerization of PET from textile waste have been demonstrated.

As featured in:

See Kotohiro Nomura *et al.*,
Ind. Chem. Mater., 2025, **3**, 49.

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PAPER

View Article Online
View Journal | View Issue

Cite this: *Ind. Chem. Mater.*, 2025, **3**, 49

Received 29th June 2024,
Accepted 6th August 2024

DOI: 10.1039/d4im00081a

rsc.li/icm

Depolymerization of PET with ethanol by homogeneous iron catalysts applied for exclusive chemical recycling of cloth waste†

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Acid-, base-free depolymerization of poly(ethylene terephthalate) (PET) with ethanol catalyzed by $FeCl_3$, $FeBr_3$ (1.0–5.0 mol%) gave diethyl terephthalate (DET) and ethylene glycol (EG) exclusively (98–99%, 160–180 °C), and $FeCl_3$ showed better catalytic performance in terms of activity. The $FeCl_3$ catalyst enabled exclusive, selective depolymerization of PET from textile waste to afford DET (and recovered cotton waste), strongly suggesting the possibility of chemical recycling of cloth waste by the transesterification in this catalysis.

Keywords: Depolymerization; PET; Chemical recycling; Textile waste management; Homogeneous catalyst.

1 Introduction

Chemical recycling, chemical conversion of used plastics to raw materials (monomers), has been recognized as an important technology for addressing concerns about plastic waste,[1–4] although the percentage is still low in the world (*e.g.* 0.1% in Europe[5] and *ca.* 3% in Japan).[6] Conversion of plastic waste to value-added chemicals, called upcycling, has also been considered as an important technology in terms not only of circular economy, but also of development of chemical processes from new alternative resources to fossil oil. Polyesters, exemplified as poly(ethylene terephthalate) (PET), are widely used commodity thermoplastics, and PET has been reused as transparent bottles partly by so-called mechanical recycling through a process of collection, sorting, cleaning, melting and reprocessing. However, due to inferior quality of PET reused resin compared to the fresh material derived from petroleum, there has been a strong demand to increase the percentage of called "closed-loop recycling", and an importance of chemical recycling, conversion to the same quality as fresh resin, has been pronounced recently.[7–17]

Although many studies have been reported to date concerning depolymerization of polyesters including PET,[12–44] most methods require harsh (high temperature, pressure) conditions in the presence of excess base/acid and/or inorganic salts. For example, the method of recovery and purification of dimethyl terephthalate (DMT, known as methanolysis) or bis(2-hydroxyethyl) terephthalate (BHET, known as glycolysis) requires excess inorganic/organic bases, acids, and additives (inorganic salts, ionic liquid *etc.*). The process also requires separation of the target compound(s) with by-products and subsequent purification (and also wastewater treatment *etc.*); these cause inferior quality of the recycled materials and a concern that the recycled products are more expensive in the present process. Moreover, in some methods, the effective alcohol used is limited to methanol and use of other alcohols leads to a decrease in efficiency.

In more detail, in the depolymerization with ethylene glycol (EG), called glycolysis, PET was treated in the presence of $Zn(OAc)_2$ catalyst combined with a base such as Na_2CO_3,[24] 1,3-dimethylurea (at *ca.* 190 °C, called Lewis acid–base synergetic catalysis),[30] or a mixture of *p*-toluene sulfonic acid (or methane sulfonic acid) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 5 mol%, 180 °C),[31,32] or the reactions were conducted in the presence of transition metal-containing ionic liquids (such as $[bmin]_2[CoCl_4]$, $[bmin][FeCl_4]$, $[bmin]_2[ZnCl_4]$ *etc.*; bmin = 1-butyl-3-methylimidazolium) at 170 °C.[29] Moreover, in the depolymerization of PET with methanol, called methanolysis, harsh conditions at high temperature (*e.g.* 280–310 °C) and high pressure (*ca.* 4 MPa)

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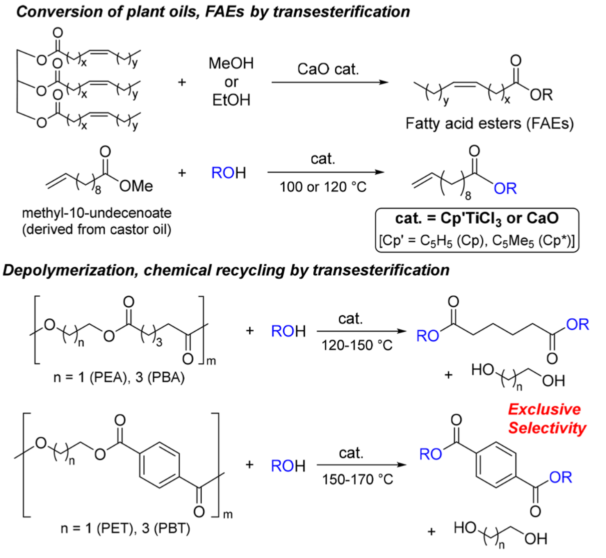
† Electronic supplementary information (ESI) available: (i) Additional results for depolymerization of PET with ethanol by $FeCl_3$ and $FeBr_3$, (ii) GC chromatograms of the resultant mixtures for depolymerization of PET through transesterification with ethanol using $FeCl_3$ and $FeBr_3$, (iii) selected ^{13}C NMR spectra of the resultant depolymerization mixtures, (iv) selected ^1H NMR spectra of the resultant depolymerization mixtures, (v) photos for selected experimental trials. See DOI: **https://doi.org/10.1039/d4im00081a**

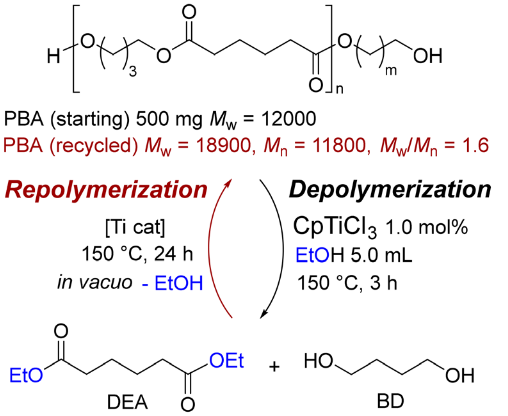
are generally required.[12–17] Copresence of inorganic base (K_2CO_3 *etc.*) was effective to reduce the harsh conditions.[12–17] The depolymerization with *n*-butanol was conducted in the presence of $ZnCl_2$ and $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl$ at 205 °C.[28]

More recently, approaches for conducting the methods (for chemical recycling and upcycling) under mild conditions (at 25 °C) by using excess K_2CO_3 (or $KOCH_3$, or TBD) in methanol–CH_2Cl_2,[38] or dimethyl carbonate in the presence of excess Li(OMe)[39,40] have also been suggested. The depolymerization of PET using $FeCl_3{\cdot}6H_2O$ combined with sulfonic acid conducted at 100 °C was also reported.[34] These methods, however, required excess base[38–40] and/or the reactions did not proceed exclusively.[34,38] Development of efficient "acid-, base-free" catalysts for chemical recycling of polyesters has thus been an attractive and important subject. Efforts should contribute to providing a simplified purification and separation process for obtaining recycled resins in a rather efficient manner (more suitable for achievement of "closed-loop chemical recycling").

We recently demonstrated that the development of efficient transesterification catalysts can solve the problem, because this type of degradation and repolymerization (polycondensation and condensation polymerization) is a transesterification. Our laboratory thus focused on using $Cp'TiCl_3$ [Cp' = C_5H_5 (Cp), C_5Me_5 (Cp*)], efficient transesterification of aliphatic fatty acid esters (FAEs),[45] and calcium oxide (CaO), efficient transesterification of triglycerides (plant oils)[46] and FAEs,[47] to depolymerize aliphatic polyesters,[45,47] and demonstrated that these catalysts enabled the depolymerization not only of poly(ethylene adipate) (PEA) and poly(butylene adipate) (PBA),[45,47] but also of PET and poly(butylene terephthalate) (PBT)[42,43] with various alcohols (Scheme 1). Moreover, $La(acac)_3$ (acac = acetylacetonato) also depolymerized PET as well as other polyesters by treating with methanol.[41,48] CaO catalyst has been widely used for transesterification of triglycerides (plant oil),[49–51] for which catalyst pretreatment (calcination at high temperature like 300 °C)[47] would be necessary. Therefore, development using simple, commercially available catalysts has been an attractive target.



Scheme 1 Acid-, base-free catalytic transesterification of methyl-1-undecenoate (fatty acid ester, FAE) and polyesters with alcohol.[42,43,45–47] Reprinted with permissions from ref. 42 (Copyright 2023 by the authors; licensee MDPI) and ref. 43 (Copyright 2024 Springer Nature).



Scheme 2 Closed-loop chemical recycling (one-pot depolymerization and re-condensation polymerization) of PBA by one-pot depolymerization/re-polycondensation.[42] Reprinted with permission ref. 42. Copyright 2023 by the authors; licensee MDPI.

Importantly, these depolymerizations of polyesters with alcohol especially using both titanium and calcium catalysts gave raw materials (monomers) exclusively (>99% conversion, >99% selectivity), and the finding enabled us to demonstrate one-pot closed-loop chemical recycling (one pot depolymerization–repolymerization) demonstrated by PBA with ethanol (Scheme 2).[42] Moreover, aminolysis of polyesters to afford amides could be achieved by using $Cp'TiCl_3$ catalyst.[52]

We previously communicated that $FeCl_3$ and $FeBr_3$ (readily available commercially) were effective catalysts for transesterification of FAE (methyl-1-undecenoate).[45] In this paper, we thus report that $FeCl_3$ and $FeBr_3$ are also effective as catalysts for depolymerization of PET with alcohol. Moreover, we applied this homogeneous catalysis to the selective depolymerization of polyesters from a plastic mixture (polyester and polyethylene) and a mixture of PET and cotton (often employed in our daily life as clothes) in order for this method to be applied in a chemical recycling process (obtaining raw materials) from practical wastes. We

Scheme 3 Acid-, base-free catalytic transesterification (depolymerization) of PET with ethanol catalyzed by $FeCl_3$, $FeBr_3$.

Table 1 Depolymerization of PET with ethanol catalyzed by $FeCl_3$ or $FeBr_3$[a]

Run	Catalyst[b] (mol%)	Temp. (°C)	Time (h)	Conv.[c] (%)	Yield[d] (%)
1	$FeCl_3$ (5.0)	180	18	>99	>99
2	$FeCl_3$ (5.0)	180	12	>99	98
3	$FeCl_3$ (5.0)	160	18	>99	97
4	$FeCl_3$ (5.0)	160	18	>99	98
5	$FeCl_3$ (5.0)	160	24	>99	98
6	$FeCl_3$ (5.0)	120	18	>99	46
7	$FeCl_3$ (3.0)	180	18	>99	97
8	$FeCl_3$ (3.0)	180	24	>99	>99
9	$FeCl_3$ (3.0)	180	30	>99	>99
10	$FeCl_3$ (1.0)	180	18	>99	21
11	$FeCl_3$ (1.0)	180	30	>99	97
12	$FeCl_3$ (1.0)	180	48	>99	>99
13	$FeBr_3$ (5.0)	180	18	>99	>99
14	$FeBr_3$ (5.0)	160	18	>99	87
15	$FeBr_3$ (5.0)	120	18	>99	18
16	$FeBr_3$ (3.0)	180	18	>99	>99
17	$FeBr_3$ (3.0)	180	30	>99	>99
18	$FeBr_3$ (1.0)	180	18	>99	34
19	$FeBr_3$ (1.0)	180	30	>99	97
20	$FeBr_3$ (1.0)	180	48	>99	>99

[a] Conditions: 500 mg poly(ethylene terephthalate) (PET) (prepared by cutting a PET bottle), and 5.0 mL ethanol. [b] Based on monomer unit in PET. [c] Estimated by ^{13}C NMR spectra. [d] GC yield of DET *vs.* internal standard (mesitylene).

demonstrate that the method enabled quantitative chemical recycling of cloth waste, which has been considered as an important subject for the achievement of a circular economy.[53–56]

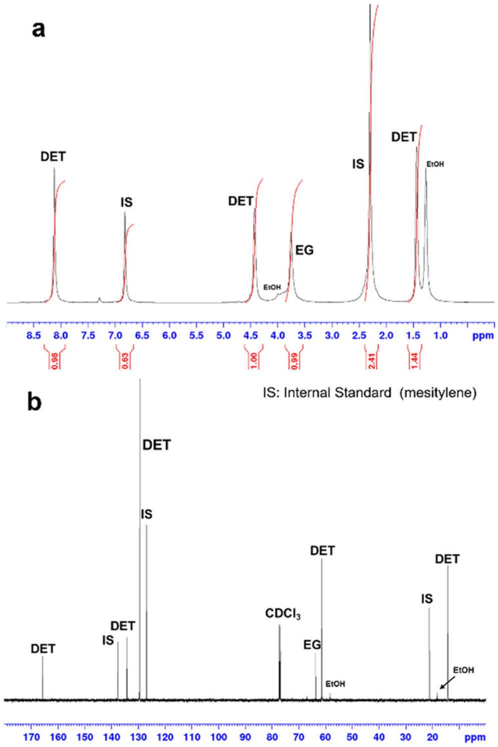


Fig. 1 (a) ^1H NMR and (b) ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of the reaction mixture (at 180 °C for 18 h, run 1) after removal of ethanol. IS (internal standard) = mesitylene.

2 Results and discussion

2.1 Depolymerization of PET with ethanol catalyzed by $FeCl_3$, $FeBr_3$

Depolymerizations of PET with ethanol were conducted in a sealed glass reaction tube containing a PET sheet (by cutting a PET drink bottle, as reported previously),[42,52] ethanol (5.0 mL, anhydrous) and a prescribed amount of $FeCl_3$ or $FeBr_3$ (anhydrous), and the reaction mixture was stirred magnetically at 180 °C (or 160 °C *etc.*; Scheme 3). According to the method in our previous report,[42] the conversions of PET were estimated by ^{13}C NMR spectra and the yields of DET were analyzed by GC [*vs.* internal standard (IS, mesitylene) using a calibration curve]. As described below, the reaction mixtures (carried out under the conditions in Table 1) after careful removal of the volatile (ethanol) were completely soluble in $CDCl_3$ (without any insoluble precipitates), and, as reported previously,[42] no residual resonances ascribed to carbonyl groups except those of

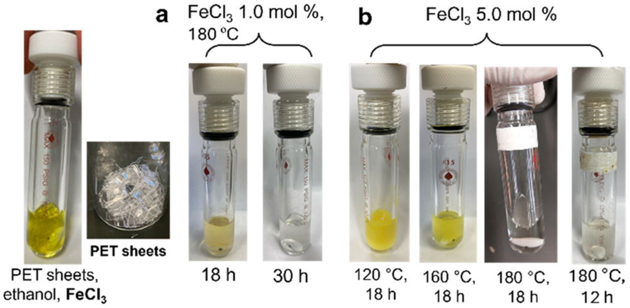


Fig. 2 Reaction mixture of PET depolymerization with ethanol in the presence of $FeCl_3$. Reaction mixture with (a) $FeCl_3$ (1.0 mol%) at 180 °C (runs 10, 11) and (b) $FeCl_3$ (5.0 mol%) (runs 1–3, 6).

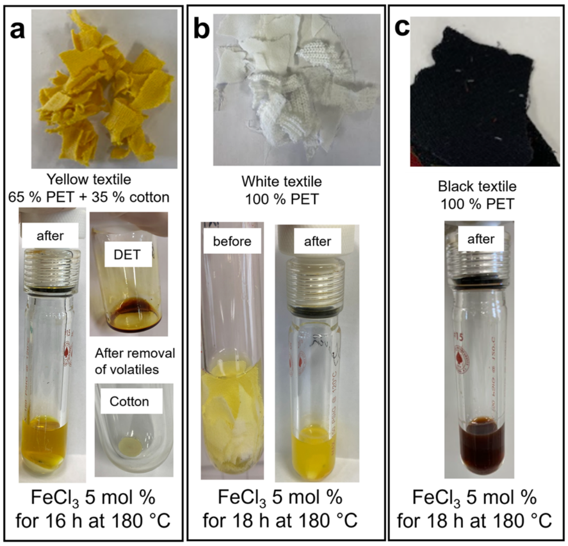


Fig. 3 Photographs of textile samples (top), and the reactions of textile samples with ethanol in the presence of $FeCl_3$ (5.0 mol%) at 180 °C. Photographs of (a) yellow sample (65% PET, 35% cotton) after the reaction, (b) white sample (100% PET), before (left) and after (right) the reaction, (c) black sample after the reaction.

DET were seen after dissolving the reaction mixture in $CDCl_3$. Detailed procedures are described in the Experimental section and selected NMR spectra and GC charts are shown in the ESI.† Selected results are summarized in Table 1.

It was revealed that, as expected from the results of the transesterification of methyl-10-undecenoate with alcohol,[39] depolymerizations of PET with ethanol in the presence of $FeCl_3$ (5.0 mol%) proceeded at 180 °C to afford DET quantitatively (runs 1 and 2). The recovered yields consisting of EG and DET after careful removal of ethanol were very close to those calculated (Table S1†). The exclusive formation of DET and EG was also confirmed by ^{1}H NMR and ^{13}C NMR spectra (Fig. 1; additional NMR spectra are shown in ESI†). The reactions conducted in the presence of 3.0 mol% of $FeCl_3$ at 180 °C (runs 7–9) or conducted at 160 °C (5.0 mol% $FeCl_3$, runs 3–5) also gave DET and EG exclusively, and the results are reproducible (runs 3 and 4). DET was obtained as a sole product after removal of volatiles (including EG partially), as shown in Fig. S18† (time course monitored by ^{13}C NMR spectra).

In contrast, the reaction conducted with low $FeCl_3$ loading (1.0 mol%, runs 10–12) revealed that DET yield (by GC) was low after 18 h, and the yield increased with time and eventually reached >99% after 48 h [DET yield 21% (18 h), 97% (30 h), >99% (48 h), 180 °C], as observed in the depolymerization of PET with ethanol using $Cp'TiCl_3$ (ref. 36) and CaO (ref. 37) catalysts. The activity of $FeCl_3$ thus was rather low compared to that of $Cp'TiCl_3$ under the same conditions [DET yield 92% ($CpTiCl_3$), 94% (Cp^*TiCl_3, Ti 1.0 mol% at 150 °C after 24 h)].[42]

The reaction catalyzed by $FeCl_3$ conducted at 120 °C led to a decrease in the yield of DET (run 6). In both cases (runs 6 and 10), only one resonance ascribed to the carbonyl group in DET was observed in the region around 155–170 ppm (ascribed to carbonyl carbon), whereas the reaction mixtures after removal of volatiles were completely soluble in $CDCl_3$ [Fig. S17 (run 6) and S19† (run 10)]. Several resonances (probably ascribed to the oligomer) were seen in the spectra with observation of several additional peaks (with their retention time longer than those of DET) in the GC chromatogram. These results thus suggest that, as observed in the depolymerization of PET with ethanol catalyzed by $Cp'TiCl_3$ (ref. 36) and CaO (ref. 37) catalysts, PET was first depolymerized to afford an oligomer mixture and eventually converted to DET over the time course of the reaction. One probable explanation we may consider is the formation of ethyl(hydroxyethyl) terephthalate (EHTP), as an intermediate in this depolymerization event, as demonstrated in the reaction of PET with ethanol catalyzed by CaO.[37]

Fig. 2 shows selected photographs of the reaction mixture in the depolymerization of PET catalyzed by $FeCl_3$ under various conditions. As shown in Fig. 2a, the reaction mixture with low $FeCl_3$ loading at 180 °C first became cloudy pale yellow after 18 h (Fig. 2a left) and became a clear solution after 30 h (Fig. 2a right) with quantitative formation of DET (confirmed by GC and NMR spectra). Similar colour changes are observed in Fig. 2b, and the reaction mixture with incomplete conversion to DET was a cloudy pale yellow, the colour eventually changing to a clear solution with complete conversion to DET. These observations could also suggest the above assumption that PET was first converted to an oligomer mixture and then converted to DET eventually.

Similarly, depolymerization of PET with ethanol proceeded in the presence of $FeBr_3$, and the reactions conducted at 180

Table 2 Depolymerization of textile waste samples containing PET with ethanol catalyzed by $FeCl_3$ at 180 °C[a]

Run	Textile sample[b] (composition)	Time (h)	PET conv.[c] (%)	DET yield[d] (%)	Cotton[e] (wt% (mg))
21	Yellow (PET 65%, cotton 35%)	12	>99	96	>99 (69 mg)
22	Yellow (PET 65%, cotton 35%)	16	>99	>99	>99 (70 mg)
23	White (PET 100%)	18	>99	>99	—
24	White (PET 100%)	18	>99	98	—
25	Black (PET 100%)	18	>99	>99	—

[a] Conditions: textile pieces 200 mg, ethanol 5.0 mL, $FeCl_3$ 5.0 mol% for PET (calculated on the basis of monomer unit in PET only). [b] Samples shown in Fig. 3. [c] Estimated by ^{13}C NMR spectra. [d] GC yield *vs.* internal standard (mesitylene). [e] Based on weight recovered as solid after filtration and drying *in vacuo*.

Table 3 Selective depolymerization of PET with ethanol catalyzed by $FeCl_3$ (180 °C, 18 h)[a]

Run	Sample[b] (composition)	PET conv.[c] (%)	DET yield[d] (%)	Cotton[e] (wt% (mg))
26	PET (500 mg) + cotton (200 mg)	>99	98	>99 (200 mg)
27	PET (500 mg) + PE (200 mg)	>99	>99	>99 (198 mg)

[a] Conditions: 500 mg poly(ethylene terephthalate) (PET) prepared by cutting a drink bottle, 200 mg of PE or cotton textile, and 5.0 mL ethanol. [b] Samples shown in Fig. 4. [c] Estimated by ^{13}C NMR spectra. [d] GC yield *vs.* internal standard (mesitylene). [e] Based on weight recovered as solid after filtration and dried *in vacuo*.

°C (with $FeBr_3$ at 3.0 and 5.0 mol%) gave DET in quantitative yields (runs 13, 16, 17), whereas the DET yield in the reaction with low $FeBr_3$ loading (1.0 mol%) was initially low (34%, run 18) and reached a quantitative value after 48 h (run 20). However, the conversions at 160 °C (run 14) and 120 °C (run 15) were low compared to those in the presence of $FeCl_3$ (runs 3, 4, 6). It is thus concluded that $FeCl_3$ is a suitable catalyst in PET depolymerization. The colour in the reaction mixture initially showed red and changed from cloudy pale red to a clear solution with quantitative formation of DET (Fig. S38†).

2.2 Selective depolymerization of PET with ethanol from a mixture with polyethylene and cloth waste

It should be noted that depolymerizations of textile waste samples (yellow, white, black, shown in Fig. 3) with ethanol catalyzed by $FeCl_3$ afforded DET quantitatively. As shown in Fig. 3a as well as in Table 2 (runs 21 and 22), the yellow textile sample consisting of a mixture of PET (65%) and cotton (35%) was treated with ethanol in the presence of $FeCl_3$ (5.0 mol% to PET) to afford DET (>99% yield, very small amount of dyes remaining) along with recovery of cotton quantitatively (>99% recovery yield); the complete conversion to DET could be achieved in 16 h (run 22). Similarly, reactions of the white textile sample (Fig. 3b, 100% PET) and the black sample (Fig. 3c, 100% PET) with ethanol also afforded PET (runs 23–25, Table 2), and the results were reproducible (runs 23, 24). Moreover, as shown in Fig. S20 and S21,† no other resonances ascribed to DET (and EG remaining) were observed in the NMR spectra after removal of volatiles from the reaction mixture. These results thus clearly indicate that the present method can be applied to chemical recycling of cloth waste to afford raw materials exclusively without any accompanying by-products.

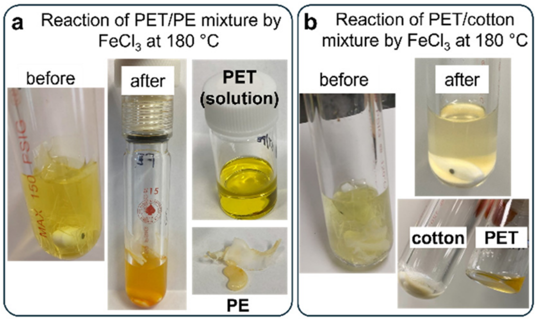


Fig. 4 Photographs of selective depolymerization of PET from (a) a mixture of PET sheets (by cutting a PET drink bottle) and cotton and (b) PET sheets and polyethylene (PE) with ethanol in the presence of $FeCl_3$ (5.0 mol%) at 180 °C for 18 h.

Moreover, as summarized in Table 3 as well as Fig. 4, the method can be applied to the selective depolymerization of PET from a mixture of PET and cotton or polyethylene (PE). Importantly, DET was recovered from the mixture in quantitative yields (runs 26 and 27) along with quantitative recovery of cotton or PE. These results also indicate that the present method can be applied to separation of polyesters from PE and cotton waste by the exclusive depolymerization.

3 Conclusions

We have demonstrated that $FeCl_3$ ($FeBr_3$) catalyzed acid-, base-free depolymerization (transesterification) of PET with ethanol to afford diethyl terephthalate (DET) and ethylene glycol (EG) exclusively (98–99% yield, 1.0–5.0 mol% Fe, 160–180 °C); $FeCl_3$ showed better catalyst performance in terms of activity. The reaction gave by-products in negligible amounts that facilitates the purification. Use of $FeCl_3$ should be emphasized in terms of wide availability (cheap, used in industry) without pretreatment (as required for CaO catalyst, calcination at 300 °C *etc.*),[37,40] whereas the observed catalytic activity by $FeCl_3$ was rather low compared to that of $Cp'TiCl_3$.[35] The method can be applied to selective depolymerization of PET from textile (cloth) waste to afford DET with exclusive recovery of cotton waste. The method can also be applied to selective depolymerization of polyesters from a mixture of plastic waste (consisting of polyolefins *etc.*). We believe that the method could provide a possibility of a clean chemical recycling process in the presence of a commercially available catalyst ($FeCl_3$). We are currently exploring the possibility of conducting the reactions under mild conditions without compromising the exclusive selectivity *via* catalyst development.

4 Experimental

All depolymerization experiments were carried out under a nitrogen atmosphere in a drybox. PET sheets were prepared by cutting a PET drink bottle. Anhydrous-grade ethanol (>99.5%, Kanto Chemical Co., Inc.) was used as received. Anhydrous-grade $FeCl_3$ (97.0%) and $FeBr_3$ (98.0%) were purchased from Aldrich Chemical Co. and were used as received in the drybox under nitrogen atmosphere. Textile samples were received from companies (by donation for research purposes).

All ^{1}H and ^{13}C NMR measurements were performed at 25 °C with a Bruker AV500 spectrometer (500.13 MHz and 125.77 MHz, respectively) using $CDCl_3$ as a solvent. $SiMe_4$ was used as a reference at 0.00 ppm (chemical shifts were reported as ppm). The GC chromatograms were recorded using a Shimadzu gas chromatograph (GC-2014, Shimadzu Corp., Tokyo, Japan) equipped with a flame ionization detector (FID) using nitrogen as a carrier gas. Conditions were as follows (DB-1MS column, 30 m × 0.250 mm × 0.25 μm): column temperature, 80 °C (4 min) followed by increasing up to 320 °C (20 °C min^{-1}) [injection at 300 °C, flow (column) at 1.71 mL min^{-1}].

4.1 General procedure for the depolymerization of PET through transesterification

In a drybox under nitrogen atmosphere, the prescribed amount of $FeCl_3$ or $FeBr_3$ (anhydrous grade), 500 mg of PET sheets (or 200 mg of textile), and 5.0 mL of ethanol (anhydrous grade) were placed under a nitrogen atmosphere into an oven-dried 15.0 mL scale pressure reaction tube with a screw cap. The reaction mixture was stirred for a prescribed time and temperature using an alumina bath. After completion of the reaction, the mixture was cooled to room temperature and washed with $CHCl_3$ (*ca.* 3 mL). The volatiles ($CHCl_3$, ethanol, *etc.*) were removed *in vacuo*. The internal standard was added to the resultant residue then the yield was estimated using GC (quantitative analysis using a calibration curve *vs.* internal standard). The resultant reaction mixtures were analyzed by using ^{1}H (500.13 MHz) and $^{13}C\{^{1}H\}$ (125.77 MHz) NMR spectra in $CDCl_3$ at 25 °C. Selective transesterifications of PET from the mixture with polyethylene or cotton were conducted under similar conditions, except that 500 mg of PET sheets and 200 mg of cotton or polyethylene were used.

Data availability

Data are contained within the article and the ESI† including (i) additional results for depolymerization of PET with ethanol catalyzed by $FeCl_3$ and $FeBr_3$, (ii) GC chromatograms of the resultant mixtures for depolymerization of PET through transesterification with ethanol using $FeCl_3$ and $FeBr_3$, (iii) selected ^{13}C NMR spectra of the resultant depolymerization mixtures, (iv) selected ^{1}H NMR spectra of the resultant depolymerization mixtures, (v) photos for selected experimental trials.

Author contributions

KN designed the project (conceptualization, catalyst selection, methodology, supervision) including funding acquisition. NWBA and MABRH conducted reactions, analysis and MMA helped in conducting experiments, analysis (GC, NMR *etc.*) and data analysis including drawing. KN wrote the manuscript, and NWBA and MMA helped in the preparation. All authors have discussed the results and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This project was partly supported by JST-CREST (grant number JPMJCR21L5), and the authors express their thanks to Ms. Yuriko Ohki and Mr. Asahi Tanaka (Tokyo Metropolitan University) for some technical support. MABRH thanks Universiti Teknologi MARA Sarawak Branch and Faculty of Science, Tokyo Metropolitan University for financial support. KN expresses his thanks to Prof. Wenjuan Zhang (Beijing Institute of Fashion Technology) for sending the test samples of cloth waste for conducting these experiments.

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