

# Depolymerization of polyethylene terephthalate (PET) under mild conditions by Lewis/Brønsted acidic deep eutectic solvents

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## Abstract

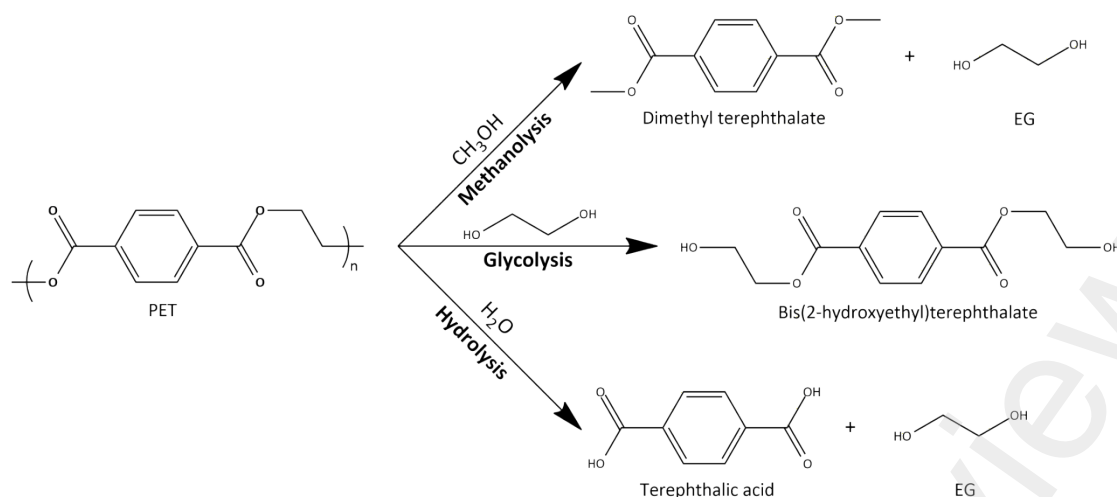
Modern society urgently needs new recycling methods to handle the impressive amount of plastic items that are annually discarded. Deep Eutectic Solvents (DESS) have shown interesting results in the depolymerization of polyethylene terephthalate (PET), but most of the procedures still need harsh conditions of temperature and pressure. In this contribution, we propose a bifunctional Lewis/Brønsted acidic DES composed of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , cheap and scarcely toxic, in combination with a variety of acids, both mineral and organic, including some of natural origin (citric and acetic acid). We show that some Lewis/Brønsted acidic DESs are capable to quantitatively depolymerize PET under mild conditions, with a temperature of 100 °C and a reaction time of 1 h for the solvents  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /sulfonic acids, affording high purity terephthalic acid in high yield. The best solvent has been thoroughly characterized and re-used multiple times.

## Introduction

Polyethylene terephthalate (PET) is a thermoplastic polymer used for its great versatility. Excellent barrier properties against oxygen, carbon dioxide and moisture, light weight, high durability, excellent resistance to wear, excellent thermal stability, good chemical resistance, and high tensile strength have been provided for its development in a huge variety of fields.[1] The global PET market size is expected to grow from \$35.47 billion in 2021 to \$57.19 billion in 2026 at a compound annual growth rate (CAGR) of 9.9%.[2]

Reduce, reuse, and recycle should always be the priorities, but the PET production is increasing and only a fraction of the PET items is recycled, the rest going to landfill or incineration.

Nowadays, most of the recycling procedures are mechanic, which imply items cleaning, shredding into pellets and reprocessing. These methods are limited by cost, degradation of mechanical properties, and general production of downgrading materials. Some of these drawbacks could be avoided by using chemical recycling methods, as complementary to traditional recycling processes, especially when they selectively return the polymer to its monomeric feedstocks (Scheme 1).[3–5]



35  
36 Scheme 1. General reactions involved in the chemical recycling of PET.

37  
38 Such methods can be divided by the conditions used (acidic,[6] basic[7] or neutral[8]) or by the employed  
39 nucleophile (glyco-, [9] hydro-, [10] methano- [11] and aminolysis [12]). Generally, all these methods require  
40 harsh conditions of temperature (often higher than 180 °C) and pressure (1-5 MPa). In the last years, many  
41 studies focused on the use of new solvents to depolymerize PET, as ionic liquids (ILs, which are salts with a  
42 melting point lower than 100 °C [13]-[14-17]) and deep eutectic solvents (DESs, which are mixtures of two  
43 or three substances with a resulting melting point much lower than those of isolated components [18]-[19-  
44 22]). DESs, in particular, are interesting because of their structural and functional versatility, their ease of  
45 preparation and purification and their potential scalability. [23] Depending on their composition, they can be  
46 biodegradable, [24] synthesized from natural compounds (NADES), and with tunable properties, as  
47 acidic [25] or basic. [26,27]

48 In 2015, Wang et al., reported for the first time a fast and selective glycolysis of PET into bis(2-  
49 hydroxyethyl) terephthalate (BHET), using urea/ZnCl<sub>2</sub> DES. In this reaction, the cooperation of the H-bonds  
50 and coordination bonds between the DES and ethylene glycol (EG) supposedly plays an essential role in the  
51 high efficiency of the reaction. [19] More recently, Attallah et al., announced the first application of DESs on  
52 PET hydrolysis via microwave-assisted process. The interaction between the DES (constituted by *m*-cresol  
53 and choline chloride) and PET, together with microwave irradiation, plays a crucial role in facilitating the  
54 reaction with depolymerization agent (NaOH): in 90 s, it was achieved 84% PET conversion with 91.55%  
55 terephthalic acid monomer yield from post-consumer bottle. [21] As both Lewis [10] and Brønsted [28] acids  
56 have been tested as catalysts for PET depolymerization, it was interesting to test a solvent made of both of  
57 them, with the aim to maximize their concentration and, hopefully, their synergy. Some bifunctional  
58 Lewis/Brønsted acidic DESs (LBDESs) have been recently prepared and applied in the desulfurization of  
59 diesel fuels [29] and bio-mass treatment, [30-32] but, to the best of our knowledge, no report about their  
60 application in PET depolymerization is available to date. In one case, a zeolite with Lewis and Brønsted  
61 acidic sites has been used (reaction temperature between 130 and 230 °C, reaction time between 10 and 40  
62 min), [33] showing that their synergy is important to enhance the depolymerization yield.

63 In this paper,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  has been chosen as Lewis acid, because of the low price and scarce toxicity of  
 64 iron. On the other hand, many Brønsted acids have been tested, varying their strength, hydrophilicity, and  
 65 biocompatibility. In particular, the novel combinations iron chloride/sulfonic acids showed great  
 66 performance and has been thoroughly characterized, showing to be a real DES and not a simple solution or a  
 67 eutectic mixture of the components. About PET depolymerization, the effects of process parameters,  
 68 including time, temperature, progressive addition of PET's flakes, and water content were examined. The  
 69 maximum conversion of PET and yield of terephthalic acid were found to be 100% and 96% respectively,  
 70 after one hour at 100 °C and atmospheric pressure by using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /methanesulfonic acid (MSA) 1:1  
 71 (system **A1\_1**) molar ratio as DES. Analytical methods, including Fourier transform-infrared spectroscopy  
 72 (FT-IR), nuclear magnetic resonance (NMR), gas chromatography (GC) and elemental analysis were  
 73 successfully employed to check the quality of the terephthalic acid obtained from post-consumer PET  
 74 bottles, which resulted to have a purity higher than 98%.

75

## 76 **Results and Discussion**

77 **PET depolymerization.** In order to prepare mixed Lewis/Brønsted acidic mixtures, iron(III) chloride  
 78 hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was mixed and heated in different molar ratios (generally spanning from  
 79  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /acid 3:1 to 1:2) with different organic acids and substances (see Experimental Section). Table 1  
 80 shows the results of this extensive screening, highlighting the combinations that lead to homogeneous  
 81 liquids. In some cases, the liquid is kinetically unstable and turns into a heterogeneous system within some  
 82 hours (>12 h in the case of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /*p*-toluenesulfonic acid (pTSA) 1:1 molar ratio, system **B1\_1**). While  
 83 some of the presented mixtures are already known (as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /glycine and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /malonic  
 84 acid[25,32]), the liquids formed with sulfonic acids are, to the best of our knowledge, novel and particularly  
 85 interesting because of their strong acidity.

86

87 Table 1. Screening of the liquid formation with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ : hom = homogeneous, het = heterogeneous, un =  
 88 unstable. The different stoichiometry ratios refer to  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ : substance.

Substance	3:1	2:1	1:1	1:2
MSA	<b>hom</b>	<b>hom</b>	<b>hom</b>	<b>hom</b>
pTSA·H <sub>2</sub> O	het	<b>hom/un</b>	<b>hom/un</b>	<b>hom/un</b>
p-phenol-sulfonic acid <sup>d</sup>	-	-	<b>hom</b>	-
sulfuric acid	<b>hom</b> <sup>a</sup>	het <sup>b</sup>	het <sup>c</sup>	-
acetic acid	-	-	<b>hom</b>	-
citric acid	<b>hom</b>	<b>hom</b>	<b>hom</b>	-
tartaric acid	-	het	het	-
malonic acid	-	-	<b>hom/un</b>	-
levulinic acid	-	-	<b>hom</b>	-
myristic acid	-	-	het	-

succinic acid	-	-	het	-
propanoic acid	-	-	<b>hom/un</b>	-
hexanoic acid	-	het	het	het
nonanoic acid	-	-	het	-
gallic acid	-	-	het	-
oxalic acid	-	<b>hom</b>	<b>hom/un</b>	-
ascorbic acid	-	het	het	-
4-hydroxy-benzoic acid	-	het	het	-
benzoic acid	-	het	het	-
phenyl-acetic acid	-	<b>hom/un</b>	<b>hom/un</b>	-
phenyl-propanoic acid	-	-	<b>hom/un</b>	-
glycolic acid	-	-	<b>hom</b>	-
malic acid	-	<b>hom</b>	<b>hom/un</b>	-
glycine	<b>hom</b>	<b>hom</b>	het	-
L-arginine	-	het	het	-
thymol	-	het	het	-
pentaerythritol	het	het	het	-
D-mannitol	-	<b>hom</b>	het	-
glycerol	<b>hom</b>	<b>hom</b>	<b>hom</b>	<b>hom</b>
m-cresol	-	-	het	-
choline chloride	-	het	het	-

89 <sup>a</sup> With 6 equivalents of water; <sup>b</sup> with 3 equivalents of water; <sup>c</sup> with 2 equivalents of water; <sup>d</sup> in aqueous  
90 solution (65%)

91

92 In order to test the performance of the various Lewis/Brønsted mixtures in PET depolymerization, we placed  
93 0.3 g of PET flakes (derived from post-consumer colorless water bottle) in 4.0 g of system **B1\_1** at  
94 atmospheric pressure and at the temperature of 130 °C. To our delight, all the flakes were replaced after 1 h  
95 by a powdery precipitate (see Supporting Information). After this time, the heterogeneous mixture was  
96 diluted with about 10 mL of deionized water, obtaining a powder that, after purification, was proved to be  
97 pure terephthalic acid (**TA**) by IR, elemental analysis and NMR (see Supporting Information). Importantly,  
98 the Inductively Coupled Plasma (ICP) analysis evidenced that the iron content is below 0.3 ppm and  
99 comparable to the ubiquitous impurities of other heavy metals (Supporting Information), indication that all  
100 the iron present in the solvent can be washed away without leaving any significant residue in the **TA**.

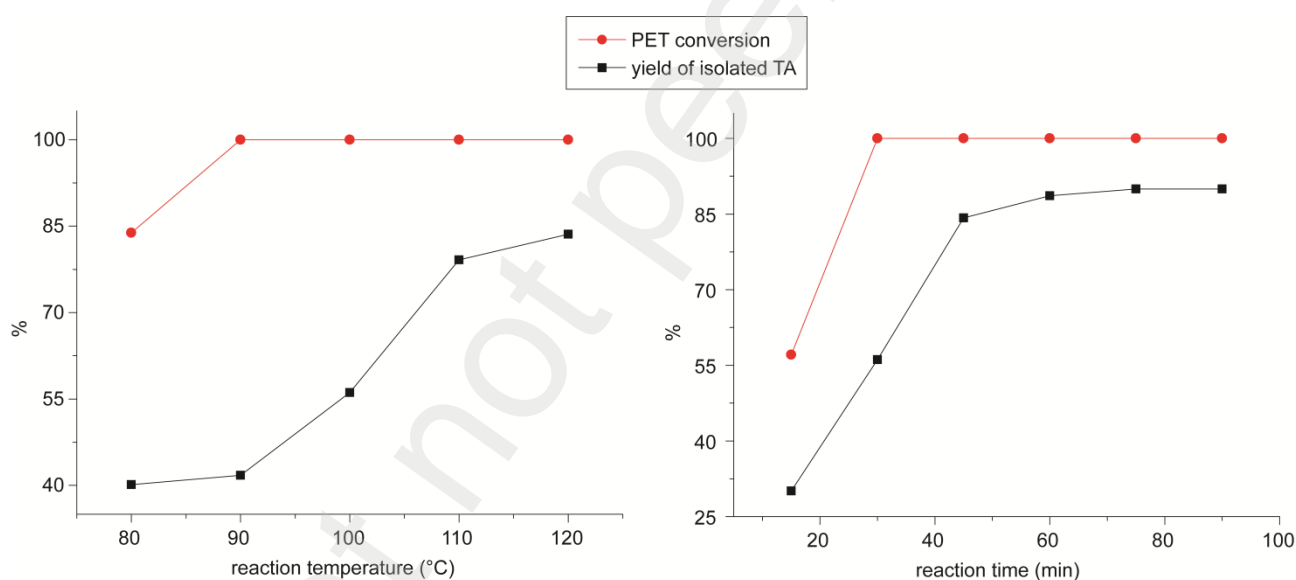
101 The depolymerization efficacy of system **B1\_1** was investigated and optimized in detail. Firstly, the effect of  
102 the temperature was studied, choosing 30 minutes as reaction time (Figure 1). The reaction already  
103 proceeded at 80 °C, with a PET conversion of 83.8% and a yield of purified **TA** of 40.1%. Differently than  
104 before, in this case a complex mixture of solids was present at the end of the reaction: unreacted PET flakes,

105 mechanically separated from the rest, TA (which is soluble in basic water) and a third white powder  
106 insoluble in both acidic and basic water. This white powder has been analyzed by IR and GPC and resulted  
107 to be PET oligomers, with a molecular weight of 1 kDa, whereas the original PET showed a molecular  
108 weight around 26 kDa (Supporting Information). Partial depolymerization explained the difference between  
109 conversion and yield.

110 Anyway, the conversion rapidly increased to 100% at 90 °C, whereas the yield after 30 minutes reached  
111 83.6% at 120 °C. Successively, depolymerization was carried out at 100 °C by changing the reaction time  
112 (Figure 1). Under the same experimental conditions (0.3 g of PET in 4 g of system **B1\_1**), the yield became  
113 88.6% after 1 h, reaching a plateau at longer reaction times. As the conversion was quantitative, the  
114 remaining 11.4% is likely lost during the work-up procedure (see Experimental Section) or persisted under  
115 the form of oligomers.

116 The reaction was also carried out by using a pTSA·H<sub>2</sub>O/H<sub>2</sub>O 1:3 mixture, not containing FeCl<sub>3</sub>·6H<sub>2</sub>O, and a  
117 FeCl<sub>3</sub>·6H<sub>2</sub>O/H<sub>2</sub>O 1:1 solution, not containing pTSA, to confirm that the synergistic effect of pTSA and FeCl<sub>3</sub>  
118 is necessary to depolymerize PET. Indeed, PET conversion was found to be null for the former and  
119 negligible (3.2%) for the latter and most of PET flakes were recovered at the end of the reaction.

120



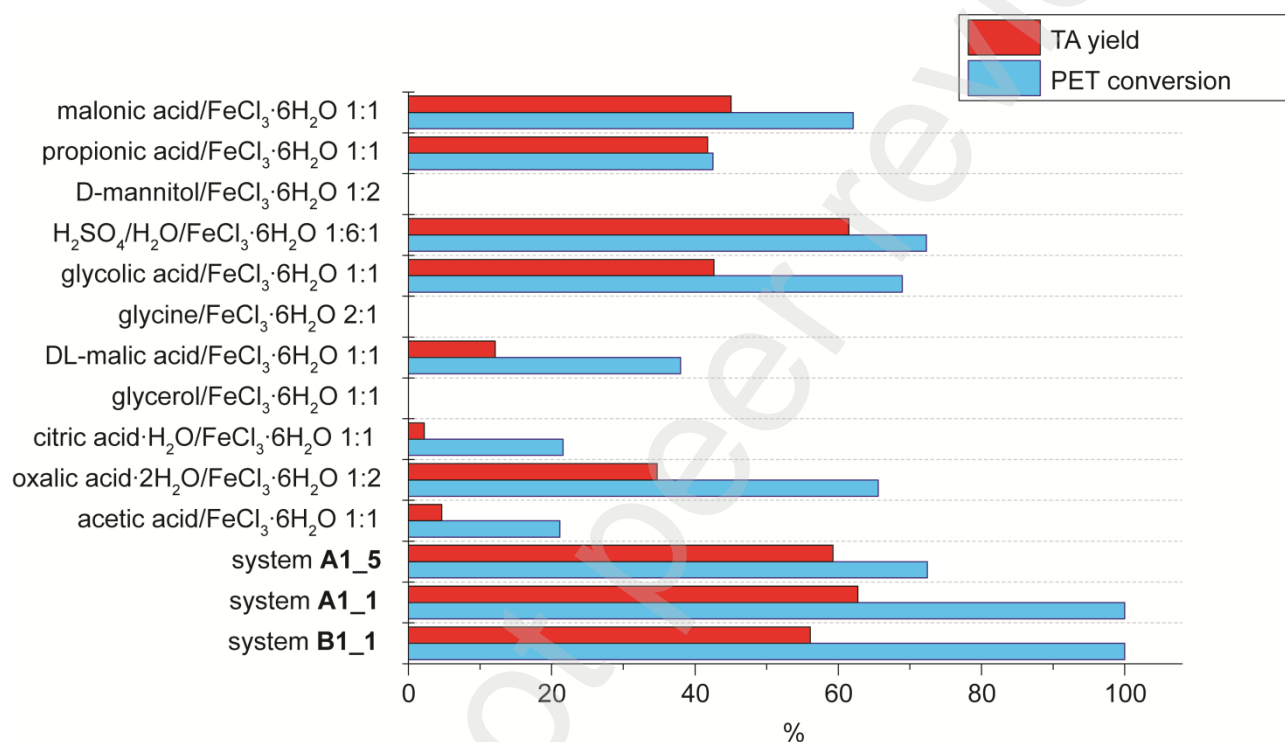
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122 Figure 1. Screening of the reaction conditions on PET conversion and TA yield. Left: reaction temperature  
123 (0.3 g of PET, 4.0 g of system **B1\_1**, reaction time = 30 min); right: reaction time (0.3 g of PET, 4.0 g of  
124 system **B1\_1**, T = 100 °C).

125

126 Successively, all the iron-based liquids reported in Table 1 were tested under the same experimental  
127 conditions (Figure 2). All the systems showed a certain ability to depolymerize the PET flakes, and stronger  
128 Brønsted acids have better conversion and yields. System containing non acidic components (as glycerol, D-  
129 mannitol and glycine) showed no conversion, indicating that iron(III) chloride is not enough to carry on the  
130 depolymerization reaction. Particularly interesting are the performances of DESs composed by natural acids

131 (as acetic and citric acids) or acids potentially obtained by biomasses and glucose, as malonic[34] and  
 132 glycolic acids[35], for their biodegradability and renewable origin. The system  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /acetic acid  
 133 showed 100% conversion and 99.7% yield after 3h at 120 °C, allowing to choose the best mixture that  
 134 balances all the different aspects (cost/sustainability/toxicology of the acid, corrosion power of the mixture,  
 135 reaction time and temperature). Anyway, only system **A1\_1** had superior performance than system **B1\_1**, in  
 136 terms of both PET conversion and yield of isolated **TA**. The real eutectic composition ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /MSA 1:5  
 137 molar ratio, system **A1\_5** see later) showed poorer performance than the 1:1 mixture **A1\_1**, likely for a non-  
 138 optimal ratio between Lewis and Brønsted acidic sites.  
 139



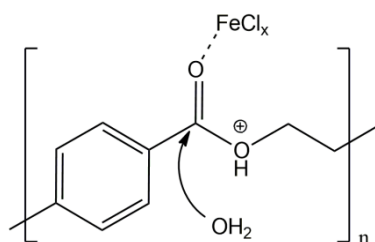
140  
 141 Figure 2. Reaction performance of different Lewis/Brønsted mixtures under the optimized reaction  
 142 conditions (0.3 g of PET, 4.0 g of LBDES, T = 100 °C, reaction time = 30 min).  
 143

144 Interestingly, a strong mineral acid as  $\text{H}_2\text{SO}_4$  showed worse performance than systems **A1\_1** and **B1\_1**  
 145 (conversion 72.3% and yield 61.5%) under our experimental conditions. Conversion and yield were also very  
 146 low (18.9% and 6.2%, respectively) when PET depolymerization was carried out under basic hydrolysis  
 147 conditions by using a concentrated solution of NaOH (30% w/w) for 30 min at 100 °C. This is consistent  
 148 with what reported in literature where higher temperatures are generally used to effectively carry out basic  
 149 hydrolysis of PET,[3] if special additives are not used.[36]

150 All the previous experiments concur in proving that the synergy between Lewis and Brønsted species is  
 151 pivotal for the effective depolymerization of PET under the mild conditions of this work. A possible  
 152 mechanism might involve the double activation of the ester group, with the iron atom that coordinates the  
 153 oxygen of the carbonyl moiety and the Brønsted acid which protonates the other oxygen, making the ester

154 carbon more prone to the nucleophilic attack from water (Scheme 2). This double activation might, therefore,  
155 be responsible for the low temperature and short reaction time necessary for the complete depolymerization  
156 of PET.

157



158

159 Scheme 2. Proposed mechanism of double activation of the ester group by the Lewis and Brønsted acids.

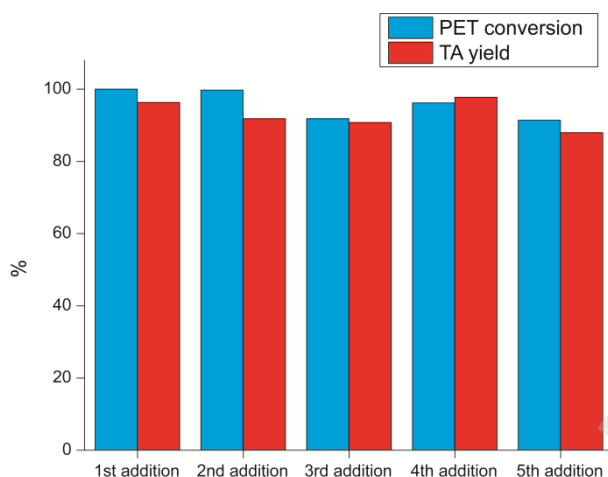
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161 Our hypothesis is indirectly supported by the dilution effect: indeed, adding other 10 equivalents of water to  
162 the systems **A1\_1** and **B1\_1**, both conversion and yield sensibly decreased from 100% and 96.4% to 23.8%  
163 and 15.5% (system **A1\_1**) and from 100% and 88.6% to 6.2% and 1.8% (system **B1\_1**), respectively. By  
164 waiting 5 h the performance of diluted **A1\_1** increased to 46.9% and 36.5%. Intuitively, a three-body adduct  
165 as those formed by iron, the ester and the acid proton is favored only at very high concentrations, justifying  
166 the use of a DES.

167 Different sources of post-consumer PET samples have been tested, and for each one the properties of the  
168 starting material have been determined (Supporting Information). No appreciable difference has been noted  
169 using colorless or colored items, as well as samples from water/milk/carbonated drink bottles or from 100%  
170 polyester textile.

171 In order to increase the amount of PET depolymerized by our solvents, we tried different strategies: loading  
172 of a larger amount of PET is possible, but some flakes are not covered by the solvent and tend to adhere to  
173 the reactor walls, hampering the necessary PET/liquid contact. For example, by loading 4 g of PET in 4 g of  
174 system **A1\_1**, at 100 °C for 5 h, the conversion and yield were 47.9% and 48.3%, respectively. Alternatively,  
175 we tried to add a larger amount of PET by different aliquots of 0.3 g per hour of reaction, leaving the workup  
176 at the end of the reaction. After each addition, also 56 μL of deionized water were added, with the aim to  
177 reintroduce in the solvent the water lost in the hydrolysis. This strategy allowed to depolymerize 1.2 g of  
178 PET with 4 g of **A1\_1** (final conversion 96.2%, yield 97.8%). The fifth addition showed lower performance  
179 (final conversion 91.4%, yield 88.0%), likely because of the solid **TA** accumulated in the reaction mixture.  
180 To avoid this, the heterogeneous mixture can be filtered at the end of the reaction and the clear liquid can be  
181 used again, without any loss of performance. The only drawback here is that the solid materials (unreacted  
182 PET, PET oligomers and **TA**) remain impregnated of the solvent, making its quantitative recover difficult.

183



184

185 Figure 3. Progressive addition of 0.3 g of PET flakes to 4.0 g of system **A1\_1** (reaction temperature = 100  
 186 °C, reaction time = 1.2 h for each addition). In each case, the work-up has been made after the indicated  
 187 number of additions.

188

189 Finally, the procedure was also successfully scaled up, using 100 g of system **A1\_1** and 30 g of post-user  
 190 PET flakes, added in 2 aliquots of 15 g with a total reaction time of 3 hours, with unaltered quantitative  
 191 conversion and high yield.

192

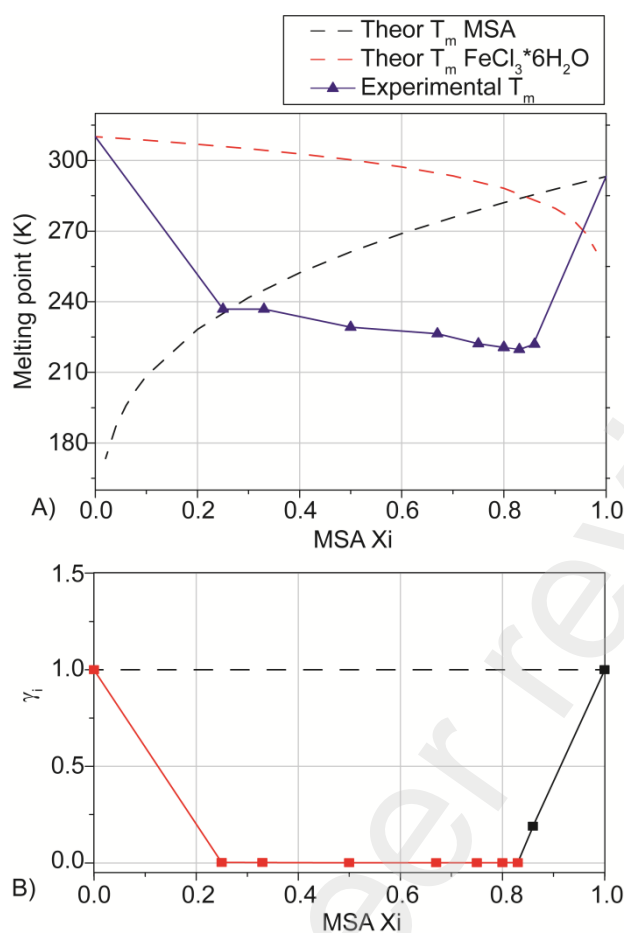
193 **DES characterization.** System **A** gives stable homogeneous red liquids in many stoichiometric ratios, from  
 194 6:1 to 1:3. In addition, it is the best solvent for the PET depolymerization, and therefore it deserves an in-  
 195 depth characterization.

196 In order to elucidate the nature of system **A**, an analysis of the melting point at the different stoichiometric  
 197 ratios was conducted. In particular, all the systems going from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{MSA}$  1:6 to 3:1 have been  
 198 prepared and the melting points ( $T_m$ ) have been evaluated and compared with the theoretical trend of melting  
 199 points of the pure substances (therefore in the absence of any interaction), both for MSA and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$   
 200 (Supporting Information). This approach is necessary in order to determine if the novel liquid mixture is a  
 201 DES or a simple eutectic liquid.[37] In Figure 1, the experimental melting points and the theoretical curves  
 202 (Panel A), and the activity coefficients of the mixtures (Panel B) are reported.

203

204





205

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207 Figure 4. Panel A: experimental/theoretical solid-liquid phase diagrams for the  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /methanesulfonic  
 208 acid LBDES; Panel B: activity coefficients of the components in the LBDES. Dashed line indicates an ideal  
 209 mixture.

210

211 The experimental melting points are much different from the theoretical curves (Figure 4, Panel A), in  
 212 particular they are much lower. A eutectic point is detected at the molar ratio of MSA of 0.83 (1:5 molar  
 213 ratio, system **A1\_5**). Theoretical curves show an intersection about the same value of the molar fraction of  
 214 acid, but with a much higher melting point ( $\Delta T_m$  over 65 °C). Also, the activity coefficients  $\gamma_i$  (Figure 4,  
 215 Panel B) are very far from 1 at all the investigated molar ratios (see Supporting Information), indicating the  
 216 strong non-ideality of the mixture. The values of  $\gamma_i$  are close to zero in all the cases. Therefore, on the basis  
 217 of the deepening of the melting point, the difference from the theoretical curves and the shifts in the activity  
 218 coefficients, the mixture can be defined as a deep eutectic solvent.

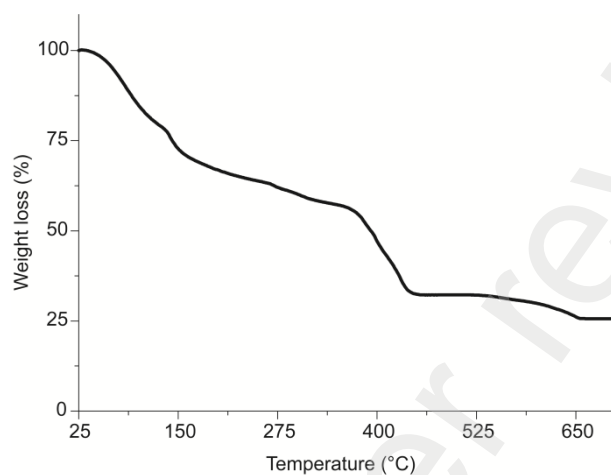
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220 The ionic conductivity of DES **A** was also measured, in order to have information on the structural features  
 221 of the liquid in terms of ionic species present in the mixture. The conductivity at room temperature is 42.1  
 222 and 21.4 mS/cm, for systems **A1\_1** and **A1\_5** ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /MSA 1:5 molar ratio), similar to those of  
 223 concentrated aqueous solutions of MSA (38.3 and 37.4 mS/cm for MSA:  $\text{H}_2\text{O}$  1:1 and 1:5, respectively) and  
 iron chloride (6.26 and 22.1 mS/cm for  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ :  $\text{H}_2\text{O}$  1:1 and 1:5, respectively). The values are higher  
 than the ones observed typically in DESs, but very similar to the ones reported for other iron-based Deep

224 Eutectic Solvents.[32] This could be due to the higher presence of ionic species in the DES and to their easy  
225 mobility in the liquid, facilitated by the low viscosity (below 100 cP, see Experimental Section).

226 The thermogram of system **A1\_1** (Figure 5)[38] shows that water is readily lost even before 100 °C. This  
227 induces to think that the six molecules of water are not strongly bound to iron. Rather, they are likely  
228 displaced, partially at least, from the coordination sphere of the metal and free to diffuse in the liquid,  
229 contributing to lower the viscosity of the system.

230



231

232 Figure 5. Thermogravimetric analysis curve for system **A1\_1** (10 °C/min).

233

234 The system **B1\_1** gave, after heating, a dark red, homogeneous liquid, but after some days a solid phase  
235 began to form, therefore the liquid is not stable. Furthermore, varying the molar composition always led to a  
236 heterogeneous system, which is not suitable for our scope. In addition, fresh system **B1\_1** shows a quite high  
237 ionic conductivity (26.7 mS/cm at room temperature), much higher than in the case of benzyl-triethyl-  
238 ammonium chloride/pTSA and choline chloride/pTSA mixtures[39,40] and similar to that of system **A1\_1**. A  
239 more complete characterization of systems **A1\_1**, **A1\_5** and **B1\_1** is available in the Supporting Information  
240 (IR spectra and thermograms, Supporting Information).

241

## 242 Conclusions

243 The synergy between Lewis and Brønsted acids in the depolymerization of post-consumer PET has been  
244 tested and reported, allowing to the quantitative recovery of high purity terephthalic acid in 1 h at 100 °C.  
245 The trend of melting point and activity coefficient with the molar composition have been characterized for  
246 the novel (and best performing) LBDES (FeCl<sub>3</sub>·6H<sub>2</sub>O/MSA), revealing a strong deviation from ideality and  
247 confirming the real DES nature of the liquid.

248 Many other acids can be used in combination with FeCl<sub>3</sub>·6H<sub>2</sub>O, with lower but still acceptable results: for  
249 example, using acetic acid the yield is quantitative after 3 h. The suggested mechanism for PET  
250 depolymerization is the double activation of the ester group, with the metal that coordinates the carbonyl  
251 moiety and the acid that protonates the ether oxygen, sensibly increasing the carbon electrophilicity. The  
252 method resulted robust in the treatment of different PET sources (textile, thicker bottles for carbonated

253 drinks or milk, colorless and not... ) under the same experimental conditions and with the same final TA  
254 purity.

255 At the end of the reaction, other PET can be added without any loss of performance (four additions) and  
256 when the solid TA saturates the reactor, the solvent can be filtered and reused, with the only addition of  
257 water to carry on the hydrolysis.

258 Finally, the strategy of synergically combining Lewis and Brønsted acids confirmed its feasibility for PET  
259 depolymerization, and it will be tested under different experimental conditions (for example using  
260 ultrasounds, microwave heating and additives) and with other polymers having similar functional groups.

261

## 262 **Experimental details**

263 **Materials.** PET plastics were collected directly from the department garbage containers, washed thoroughly  
264 with distilled water, dried and cut into flakes (approximate size 1x1 cm). Iron(III) chloride hexahydrate  
265 ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was purchased from Alfa Aesar. Methanesulfonic acid (MSA), *p*-toluenesulfonic acid  
266 monohydrate (pTSA·H<sub>2</sub>O), acetic acid, L-arginine, glycine, citric acid·H<sub>2</sub>O, pentaerythritol, glycerol,  
267 levulinic acid, choline chloride, succinic acid, propanoic acid, hexanoic acid, nonanoic acid, gallic acid,  
268 sulfuric acid, oxalic acid, ascorbic acid, 4-hydroxy-benzoic acid, benzoic acid, phenyl-acetic acid, phenyl-  
269 propanoic acid, m-cresol, malic acid, tartaric acid, thymol, D-mannitol, myristic acid, malonic acid, glycolic  
270 acid, p-phenol sulfonic acid (aqueous solution 65%), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), hydrochloric acid (HCl 37%),  
271 sodium hydroxide (NaOH) were purchased from Sigma Aldrich. All the chemicals in this study were used  
272 without further purification.

273

274 **Synthesis of Lewis/Brønsted mixtures.** Different mixtures were synthesized by mixing  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with  
275 different hydrogen bond donors in suitable quantities under mild heating until a homogeneous red dark liquid  
276 appeared. Table 1 shows the mixtures tested and prepared.

277

278 **Solid-liquid phase curves determination.** The DES A were characterized in terms of comparison between  
279 the theoretical solid-liquid phase diagrams with the experimental melting points at different molar  
280 ratios.[37,41] The melting points were measured with a thermometer via immersion of the samples in a  
281 Dewar with  $\text{CO}_2$ /acetone mixture. The melting points were taken in triplicate to avoid kinetic effect on the  
282 melting of the mixtures.

283 The solid-liquid theoretical curves were determined by using the equation (1) that represents the solid-liquid  
284 equilibrium curve:

285

$$286 \ln(\chi_i \cdot \gamma_i) = \frac{\Delta_m h_i}{R} \cdot \left( \frac{1}{T_{m,i}} - \frac{1}{T} \right) + \frac{\Delta_m C p_i}{R} \cdot \left( \frac{T_{m,i}}{T} - \ln \frac{T_{m,i}}{T} - 1 \right) \quad (1)$$

287

288 where  $\chi_i$  is the mole fraction of component i,  $\gamma_i$  is its activity coefficient in the liquid phase,  $\Delta_m h_i$  and  $T_{m,i}$  are  
289 its melting enthalpy and temperature, respectively,  $\Delta_m C p_i$  is its heat capacity change upon melting, R is the

290 ideal gas constant, and T is the absolute temperature of the system. This equation can be simplified by  
291 considering the heat capacity change upon the melting of a substance as negligible, therefore equation (2)  
292 was used:

$$294 \ln(\chi_i \cdot \gamma_i) = \frac{\Delta_m h_i}{R} \cdot \left( \frac{1}{T_{m,i}} - \frac{1}{T} \right) \quad (2)$$

295  
296 The theoretical melting temperatures were determined from the theoretical curves by considering the activity  
297 coefficients  $\gamma_i = 1$ . The eutectic points were determined as the minimum in the experimental curves and they  
298 were compared to the theoretical ones.

299 The experimental  $\gamma_i$  values were determined via equation (3) by using the experimentally observed melting  
300 temperatures:

$$301 \gamma_i = \frac{\exp \left[ \frac{\Delta_m h_i}{R} \left( \frac{1}{T_{m,i}} - \frac{1}{T} \right) \right]}{\chi_i} \quad (3)$$

304 **General procedures for PET hydrolysis.** For the catalytic experiments, a 25 mL flask equipped with a  
305 magnetic stirrer and reflux condenser was filled with 300 mg of post-consumer PET and 4.0 g of DES.  
306 Hydrolysis reactions were carried out in a temperature range from 80 to 120 °C for 15-90 min. When the  
307 reaction was completed, about 10 mL of distilled water was added to the reaction solution to precipitate  
308 terephthalic acid (TA), which was then collected by sedimentation after centrifugation. Supernatant (straw  
309 yellow color) contains an aqueous solution of used DES and EG from PET depolymerization. Then, TA was  
310 re-solubilized with an aqueous solution of NaOH (1M), giving di-sodium terephthalate. Unreacted PET (if  
311 any) and PET oligomers, insoluble in alkaline medium, was removed manually and by filtration,  
312 respectively. PET conversion was calculated using the following equation (4)

$$314 \text{ PET conversion (\%)} = \frac{W_1 - W_2}{W_1} \cdot 100 \quad (4)$$

315  
316 where  $W_1$  is the initial weight of PET flakes and  $W_2$  is the weight of unreacted PET.

317 TA was finally precipitated by adding 2 mL of hydrochloric acid (37%) and then collected by filtering. The  
318 obtained white powder of TA was then washed with water several times and dried at 80 °C overnight. TA  
319 yield was calculated using the following equation (5)

$$321 \text{ TA yield} = \frac{W_{TPA} \cdot M_{PET}}{M_{TPA} \cdot W_1} \cdot 100 \quad (5)$$

322  
323 where  $W_{TPA}$  is the weight of TA,  $M_{TA}$  is the molecular weight of TA and  $M_{PET}$  is the molecular weight of PET  
324 monomeric unit.

325 For all the analyses, our TA samples were compared with samples of commercial TA (Merck, purity >  
326 98%), taken as a reference.

327

328 **Characterization.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were carried out on a FT-NMR Joel JNM-ECZ500R  
329 MHz with HFX probe at room temperature.

330 The Fourier Transform infrared-attenuated total reflectance (FTIR-ATR) spectra of terephthalic acid were  
331 recorded using FT-IR Thermoscientific Nicolet iS50 spectrometer equipped with Smart iTR with single  
332 reflection diamond crystal (sampling depth 2.03  $\mu\text{m}$  at 1000  $\text{cm}^{-1}$ , incidence angle 42°). The conditions for  
333 ATR FT-IR measurements were a scan range of 400-4000  $\text{cm}^{-1}$  with 32 scans, and a resolution of 4  $\text{cm}^{-1}$ .  
334 For the IR characterization of the LBDESs, a sample of the liquid has been examined as thin film, obtained  
335 by evaporation (under vacuum) of an aqueous solution (10 mg of LBDES in 2 mL of deionized water)  
336 deposited on a thallium bromide support.

337 Elemental analyses were performed on a Vario MICRO cube instrument (Elementar).

338 Thermogravimetric analyses were carried out using Mettler TGA Q500 thermogravimetric analyzer. Each  
339 sample (10 mg) was weighted and analyzed under nitrogen flux (60 ml/min). The selected heating speed was  
340 10 °C/min from room temperature to 700 °C.

341 Conductivity measurements were carried out with VIO series 7 conductometer with integrated temperature  
342 probe. The measurements were conducted between 20°C and 70°C.

343 Density analysis was carried out with Anton Paar DMA 55 densimeter. The densimeter was calibrated with  
344 air and water with an error of  $\pm 1 \times 10^{-5}$  g/ml for samples which have a density from 0.5 to 1.5 g/ml. The  
345 measurements were conducted between 20 °C and 70 °C.

346 GLC-MS analyses were recorded with an Agilent 6890 N gas chromatograph interfaced with an Agilent  
347 MS5973 mass detector, using an Agilent J&W DB-5ms (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) column. UPLC-MS  
348 analyses were performed on an Acquity UPLC Water instrument (Phase A 95/5H<sub>2</sub>O/ACN+ 0.1% Formic  
349 Acid, Phase B 5/95H<sub>2</sub>O/ACN + 0.1% Formic Acid; Acquity UPLC 2.1  $\times$  100 mm column, BEH C18, 1.7  
350  $\mu\text{m}$ ; Flow 0.6 mL/min) coupled with an Acquity QDa Water mass spectrometer (Probe temperature: 600 °C;  
351 ESI capillary voltage 1.5V; Cone voltage 15V; Mass range 60–1000).

352 Viscosity measurements have not been carried out because of the corrosivity of the systems **A** and **B** toward  
353 steel. Anyway, comparing the flow rate with other DESs, the viscosity has been evaluated to be lower than  
354 100 cP.

355 The number and weight average molecular weights ( $M_n$ ,  $M_w$ ) were determined by gel permeation  
356 chromatography (GPC), using a Jasco (Hachioji-shi, Tokyo, Japan) PU-2089 Plus liquid chromatograph  
357 equipped with two PL gel 5  $\mu\text{m}$  mixed-D columns, a Jasco RI-2031 Plus refractive index detector, and a  
358 Jasco (Hachioji-shi, Tokyo, Japan) UV-2077 Plus UV/vis detector. Measurements were carried out using  
359 chloroform as the mobile phase, at a flux of 1 mL/min and a temperature of 30 °C maintained by a Jasco  
360 (Hachioji-shi, Tokyo, Japan) CO 2063 Plus column thermostat. Samples were filtered with a 0.2  $\mu\text{m}$  PTFE

361 filter before injection. Polystyrene standards were used for calibration. The refractive index detector was  
362 used to obtain reported values.

363 Differential scanning calorimetry (DSC) analysis was performed with a TA Instruments Discovery DSC  
364 model 250 under the nitrogen gas flow (50 mL min<sup>-1</sup>). Each sample (3-5 mg) was weighted and hermetically  
365 sealed into an aluminum DSC pan. A heating-cooling cycle from 25 to 300 °C at 10 °C/min, followed by a  
366 second heating scan in the same conditions was performed. The characteristic temperatures of PET samples  
367 were obtained from the second heating curve.

368 The degree of crystallinity was calculated using the following equation

369

$$370 X_c (\%) = \frac{\Delta H_m}{\Delta H_m^0} \cdot 100 \quad (6)$$

371

372 where  $\Delta H_m$  is the melting enthalpy of PET sample and  $\Delta H_m^0$  is the estimated specific melting enthalpy of the  
373 neat PET (140.1 J g<sup>-1</sup>). [42]

374 Inductively Coupled Plasma – Optical Emission Spectrometry (ICP–OES) analyses were performed on a  
375 Thermo Scientific iCAP 7200 Series ICP–OES instrument. Terephthalic acid before and after purification  
376 process was hydrolyzed using a mixture of HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (30%) 8:1 v/v in a microwave reactor for 30 minutes  
377 at 180 °C. The solution was diluted with Milli-Q water to obtain a final volume of at least 15 ml and  
378 analyzed by the instrument.

379

#### 380 **CRedit authorship contribution statement**

381 **Marco Rollo, Elisa Rossi:** Investigation, Data curation. **Francesca Raffi:** Investigation. **Matteo Tiecco,**

382 **Elisa Martinelli, Gianluca Ciancaleoni:** Supervision, Conceptualization, Formal Analysis.

383

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387

#### 388 **Declaration of Competing Interest**

389 The authors declare that they have no known competing financial interests or personal relationships that  
390 could have appeared to influence the work reported in this paper.

391

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