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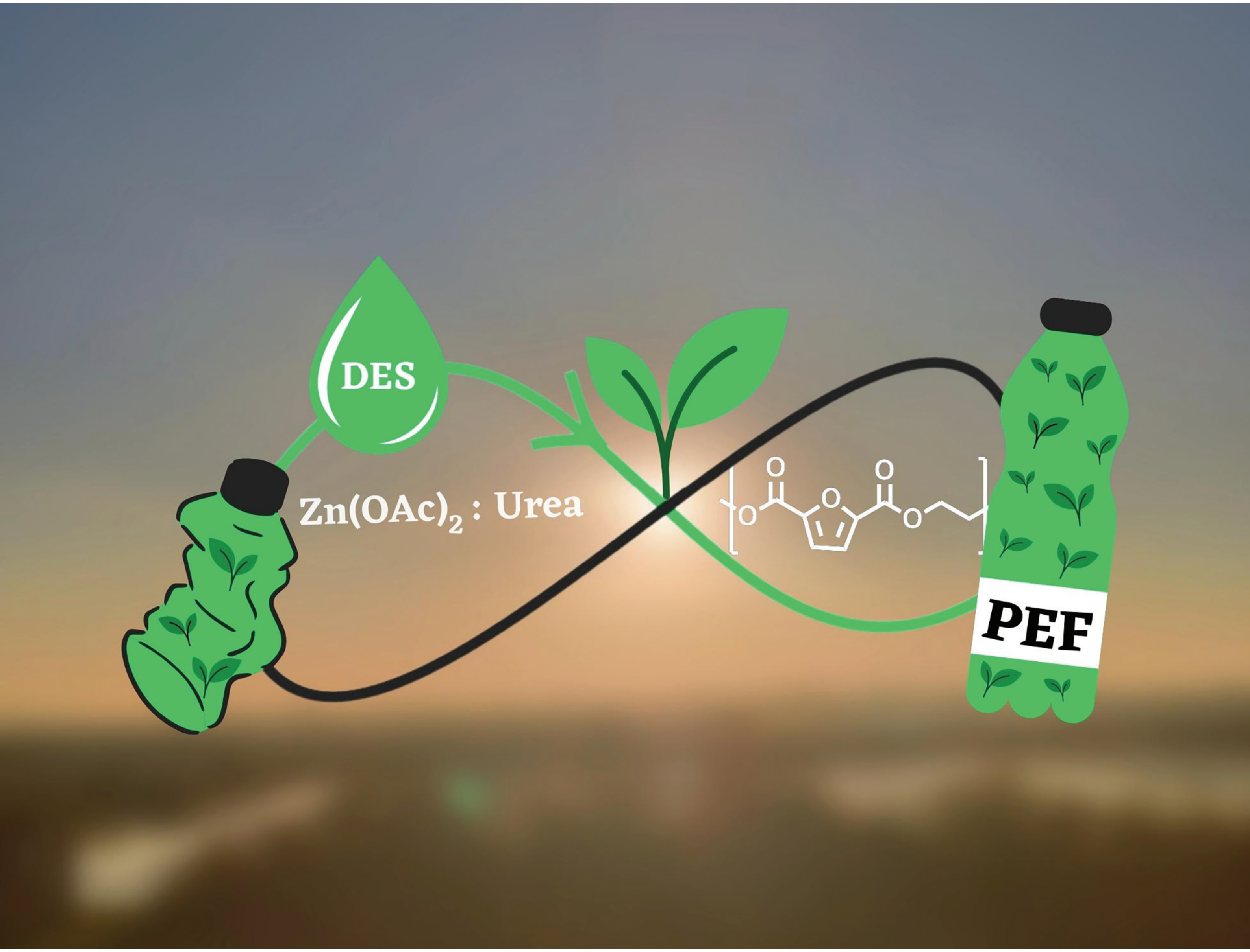

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From PEF to rPEF: disclosing the potential of deep eutectic solvents in continuous de-/re-polymerization recycling of biobased polyesters†

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Chemical attempts to recycle bio-based poly(ethylene 2,5-furandicarboxylate) (PEF) have not been reported, yet its expected global production, potential accumulation or persistence in the environment calls for innovative solutions. Here, we report the design of a urea : zinc acetate deep eutectic solvent (DES) system for a continuous, eco-friendly and closed-loop approach for recycling PEF into rPEF.

Among the most promising bio-based polymers is indisputably poly(ethylene 2,5-furandicarboxylic acid) (PEF), derived from C6 sugars like D-fructose or D-glucose feedstocks,[1] which is estimated to reach the market by 2023.[2]

PEF has attracted a lot of attention due to a myriad of relevant thermal and mechanical properties,[3–5] as well as standout barrier features (*e.g.* a reduction in CO_2 permeability of 19 times compared to poly(ethylene terephthalate) (PET)).[6] All these together make PEF a feasible replacement for commercially available PET in packaging, and also in textile fibers and films among many other general applications.[1,4,7] Despite the foreseen PEF industrialization and imminent market introduction,[2] its end-of-life (EoL) options have been generally overlooked, as we have recently highlighted.[7] Thus, if PEF is inadequately handled, it will inevitably accumulate in the environment.[8]

Furthermore, recycling of disposed polymers is an issue of utmost importance in the context of moving from a linear to a circular economy model of development as requested by the United Nations[9] and European Union directives (within the so-called *Green Deal*).[10] Nevertheless, in the present state-of-the-art, polyester recycling, of any kind, has some relevant drawbacks. Repeated cycles of mechanical recycling lead to molecular weight decay.[11] Likewise, chemical recycling is not economically feasible nor sustainable because it is conventionally conducted under harsh operating conditions,[12] typically using high temperatures and strong alkaline or acidic conditions.

Even when more sustainable processes are followed, for example using enzymes such as PETase[13] or cutinases (*Thermobifida cellulosilytica* (Thc_Cut1))[14–17] which are suitable for both PET and PEF depolymerization, the processes are hampered by their high cost and long reaction times (up to 96 h).

Beyond enzymes, there are some alternative approaches making use of organocatalysis[18] and ionic liquids (ILs),[19] although some pending issues can be identified, such as the use of volatile organic solvents (VOCs) or the often questioned toxicity profile, like the case of the tested IL 1-butyl-3-methylimidazolium chloride.[20,21]

A few studies used instead the ability of DESs to catalyze the mild glycolysis of PET.[22–26] Under the optimized conditions, a DES of urea and zinc chloride led to fast glycolysis of PET, yielding BHET, under atmospheric pressure at 170 °C.[22] Similar results were obtained by Liu *et al.*,[23] who used a DES based on 1,3-dimethylurea and zinc acetate (4 : 1) to yield BHET but at a slightly higher temperature (190 °C), reaching up to 100% yield.

Besides PET glycolysis, DES-mediated alcoholysis,[25] aminolysis,[26] and very recently also hydrolysis[27] were efficiently advanced. They were all revealed to be promising in PET mild depolymerization, but they have not been used in PEF, nor even in a continuous circular approach. In fact, in general terms, all the catalytic depolymerization approaches studied so far yield a variety of monomers but do not touch on the (continuous) repolymerization aspect completing the recycling cycle, despite the evident cost and time advantages of not having to isolate or purify the monomers.

Here, we demonstrate the first example of PEF recycling combining the potential of DESs as innovative and potentially greener catalysts for PEF glycolysis (Scheme 1(a)) and approaching its dual capacity to also catalyze polyesterification

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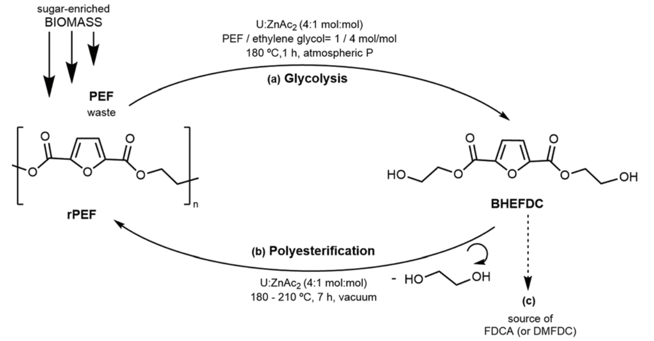

Scheme 1 PEF continuous circular recycling method by using a small amount of urea : zinc acetate, as the DES, and mild conditions to catalyze glycolysis (a) and polyesterification (b) reactions. The potential recovery of FDCA (or its dimethyl ester) (c) is also considered.

reactions by a continuous circular recycling method directly yielding the starting polymer (rPEF) (Scheme 1(b)).

Learning from both previous experience on glycolysis[23,24,28] and the extant non-toxicity and biodegradability data of choline chloride, dimethylurea and urea, a test group of four deep eutectic solvents based on them, with decreasing freezing points,[22,23,25] were screened[29] for glycolysis, namely: choline chloride : zinc acetate (ChCl : $ZnAc_2$, 1 : 1); dimethylurea : zinc acetate (DMU : $ZnAc_2$, 4 : 1); urea : zinc chloride (U : $ZnCl_2$, 4 : 1); and urea : zinc acetate (U : $ZnAc_2$, 4 : 1).

PEF samples, synthesized and processed as films at our lab,[3,30] with an intrinsic viscosity equal to 0.2675 dl g^{-1}, were initially ground to *ca.* 5 mm square shapes with 0.7 mm thickness and mixed with a small amount of each DES (around 2 wt%), and then glycolysis reactions were allowed to proceed under conventional fixed conditions (T = 180 °C for 1 h and normal pressure). The first screening of the PEF glycolysis efficiency, expressed in terms of the specimens' weight loss, is shown in Fig. 1.

Our results show that all studied DESs were successful in catalyzing the glycolysis reaction, yielding as the main product bis(hydroxyethyl 2,5-furandicarboxylate) (confirmed by FTIR and ^1H and ^{13}C NMR, as will be discussed in more detail below in Fig. 4, 6 and Fig. S4 in the ESI,† respectively). The best results were achieved with U : $ZnAc_2$ with a PEF weight loss of 85%. Control reactions with only $ZnAc_2$ or urea as the catalyst, and without the presence of any DES, showed that PEF can undergo depolymerization to some extent but cannot reach the optimum values of those with DES (35–54% *vs.* 85%). These observations are in agreement with some reports on the use of $ZnAc_2$ as a catalyst for the depolymerization of PET through glycolysis[31] or other approaches,[32,33] but, under the same standard reaction conditions, the conversions obtained in these studies were lower than those of all tested DESs.

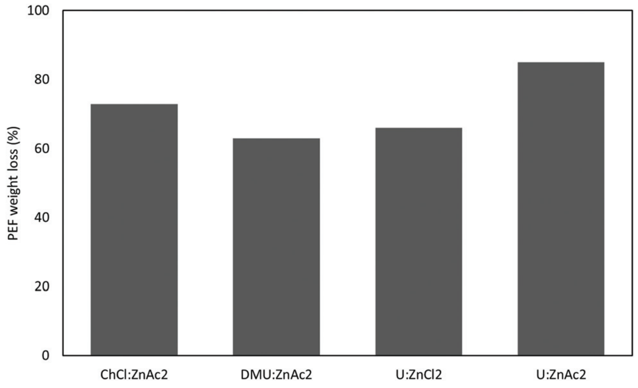

Fig. 1 Screening the efficiency of DESs for PEF glycolysis under standard reaction conditions: T = 180 °C, 1 h, normal pressure, PEF/DES = 20/1 and PEF/EG = 1/4 mol/mol.

With the optimal DES in hand, we optimized the reaction conditions in terms of temperature and time, as well as PEF/EG and PEF/U : $ZnAc_2$ molar ratios (Table S1 in the ESI†). The yield peaked at a standard temperature of 180 °C (Fig. 2(a)), and it decreased upon either increasing the temperature to 200 °C or decreasing it to 160 °C. The variation of the reaction time also revealed the optimum conditions for the standard 1-hour total reaction time (Fig. 2(b)). Decreasing time to only 30 minutes or increasing it up to 2 hours had a negative effect on the PEF weight loss yield, decreasing it to 67% and 55%, respectively.

When it came to the amount of the DES (Fig. 3(a)), we concluded that the best results (85%) were obtained with a very low molar amount of the DES, the lowest one tested, *i.e.*, a

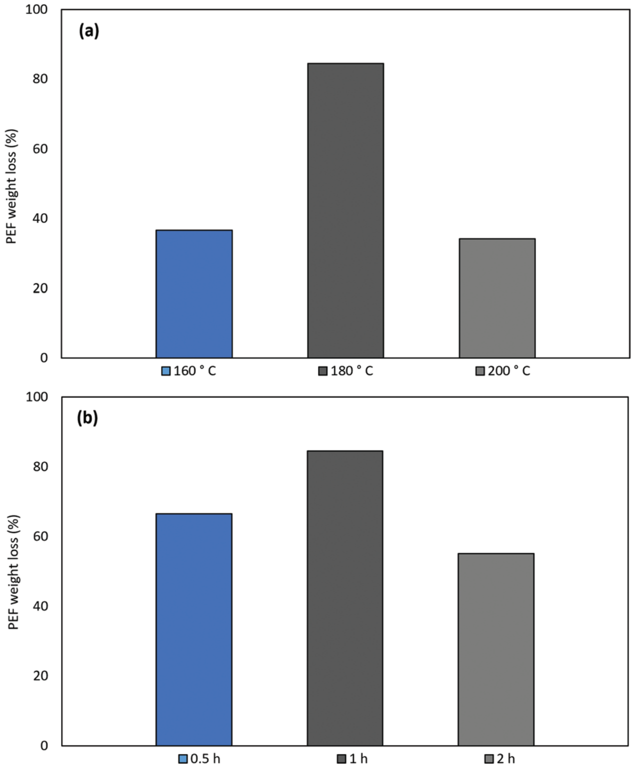

Fig. 2 Optimization of PEF reaction conditions: (a) temperature and (b) time under standard reaction conditions: normal pressure, PEF/DES = 20/1 and PEF/EG = 1/4 mol/mol.

PEF/U : ZnAc$_2$ ratio of 20/1. For the ethylene glycol ratio (Fig. 3(b)), the standard intermediate conditions obtained the best result (PEF/EG = 1/4).

Given the outstanding performance of U : ZnAc$_2$ to initiate PEF glycolysis under mild conditions, we adopted this DES in the continuous recycling of PEF to rPEF. We successfully reacted ground PEF (0.5 g) with EG and the selected DES in a two-neck round-bottom flask (Scheme 1(a)); we did not need to isolate the main intermediate product (bis(hydroxyethyl)-2,5-furandicarboxylate, BHEFDC) nor even remove the DES, but instead we used the unpurified reaction products and the ability of U : ZnAc$_2$ to catalyze polyesterification reactions to repolymerize BHEFDC into rPEF (Scheme 1(b)). It should be noted, however, that the unreacted PEF was removed from the medium before repolymerization to doubly prove that repolymerization was actually happening and a simple PEF dissolution was not occurring. The conversion rate of PEF that reacted in the depolymerization step to form rPEF was high, around 69%. In the case of adding an additional amount of a classic polyesterification catalyst to the system, *e.g.* titanium(IV) butoxide (1 wt%), the yield reached 91%.

The success of this innovative one-pot recycling approach was further confirmed by identifying the repolymerized product as PEF with an intrinsic viscosity equal to 0.409 dL g^{-1}. This result was confirmed by rPEF FTIR spectroscopy (Fig. 4), with the spectrum not displaying visible OH-band stretching (around 3390 cm^{-1}), but instead showing the furan =C–H stretching (3120 cm^{-1}), antisymmetric and symmetric stretching C–H vibrations (*ca.* 1273 cm^{-1}) and the ester C=O stretching vibration (1728 cm^{-1}). The ^{1}H NMR spectrum in Fig. 5 also corroborates the expected rPEF structure: furan ring and methylene proton resonances at 7.32 ppm (H3, H4) and 4.72 ppm (H1′), respectively. Two trace resonances at 4.12 and 4.58 ppm due to etherification side-reactions[34] are also present.

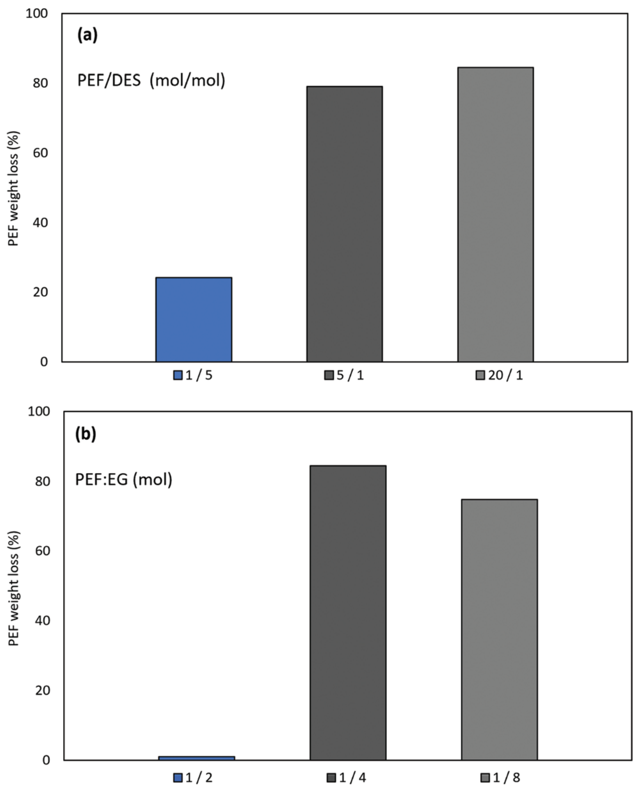

Fig. 3 Optimization of PEF reaction conditions: (a) PEF/U : ZnAc$_2$ and (b) PEF/EG molar ratios.

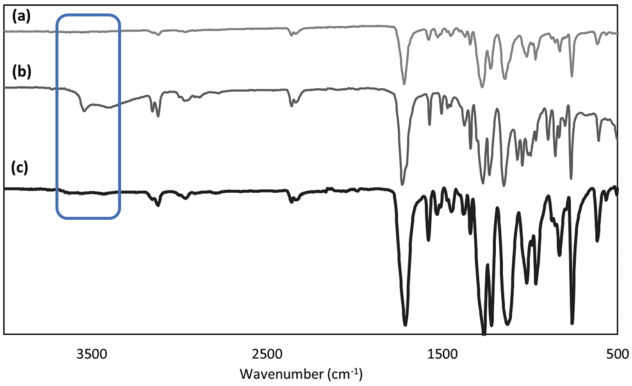

Fig. 4 FTIR spectra of (a) the initial PEF, (b) the intermediate BHEFDC product, and (c) rPEF.

The ^{13}C NMR spectra (Fig. S1 in the ESI†) also corroborate the expected rPEF structure.

The PEF depolymerization mechanism, mediated by urea : ZnAc$_2$, follows a glycolysis pathway, where urea–EG hydrogen bonding and metal ion–EG interactions[22,35] favor ester linkage cleavage and oligomers of decreasing chain-length and finally monomers are formed as further assessed in the ESI (the GC-MS results are displayed in Fig. S2–S4 in the ESI†). Therefore, although the focus of this work was to develop a continuous circular end-of-life solution for PEF, BHEFDC recovery, after glycolysis, was also possible by a simple precipitation procedure in water (approximately 125 ml). The investigation on higher purity monomer isolation is ongoing, as an additional strategy to valorize PEF waste, and an isolation/purification yield of at least 18% in regard to the initial PEF has already been achieved. The isolated product can also be exploited as a source of FDCA (or its dimethyl ester

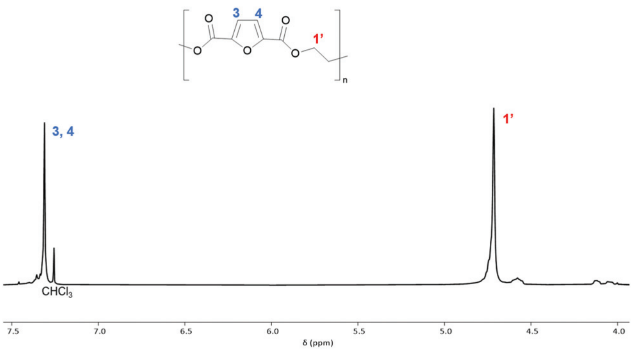

Fig. 5 ^{1}H NMR spectrum of the repolymerized PEF (rPEF), in $CDCl_3$ and TFA-d.

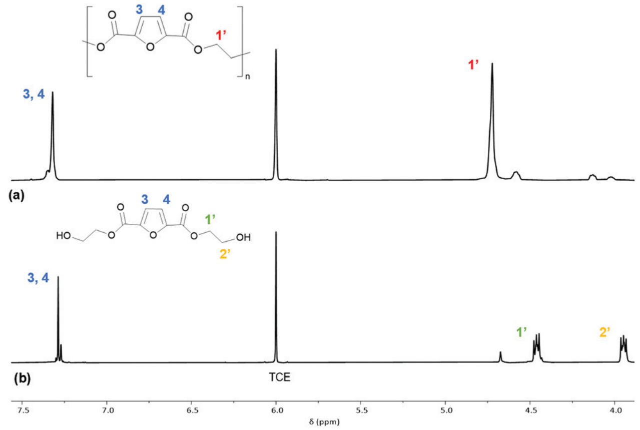

Fig. 6 ^1H NMR spectra of (a) the initial PEF and (b) the intermediate BHEFDC product, in TCE-d2.

derivative) that can be used in PEF synthesis or even other polycondensates. Full recovery of the used water was also achieved, simply *via* evaporating the supernatant followed by a condensation process. Fig. 6 shows the typical BHEFDC ^1H NMR spectrum: furan ring proton resonance (7.29 ppm, H3, H4) and methylene proton resonances (4.46, 3.95 ppm; H1′, H2′). The FTIR and ^{13}C NMR spectra (Fig. 4 and Fig. S5 in the ESI†) are also in accordance with the expected structure.

Conclusions

To the best of our knowledge, this study discloses, for the first time, the ability of a urea : zinc acetate deep eutectic solvent to assist the innovative chemical recycling of PEF to yield back its starting repolymerized polymer. A yield as high as 91% was achieved. This approach meets the requirements of green chemistry by designing a mild glycolysis reaction and advantageously circumventing the often needed laborious and high solvent and energy demanding procedures for isolating and recrystallizing the recycled monomers to meet the high purity standards of monomers for polymer synthesis. Also, in this PEF to rPEF procedure, there is no need to remove the DES. Taking advantage of the herein described procedure and the ability of the urea : zinc acetate DES to catalyze both glycolysis and esterification, there is clearly enormous potential to expand it to other polyesters. Also worth mentioning is the fact that these DES components are commercially available at competitive prices, are biodegradable and safe to handle, which may offer prospects of market exploitation and, ultimately, contribute to PEF (and beyond) EoL solutions within a circular model of development. Further studies to elucidate the U : $ZnAc_2$ mediated PEF recycling mechanism are ongoing.

Conflicts of interest

There are no conflicts to declare.

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