COMMUNICATION

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

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Supporting Information

Contents

General Experimental

Poly(ethylene 2,5-furandicarboxylate) (PEF) was synthesized at our lab by a bulk polyesterification reaction adapted from elsewhere [1,2], using previously synthetized dimethyl 2,5-furandicarboxylate (DMFDC) [3], an excess of quantity of ethylene glycol (molar ratio DMFDC/EG= 1/2.2) and titanium(IV) butoxide (400 ppm). In the first stage, the temperature was raised gradually from 150 to 170 °C for 5 h. In the second stage, the reaction proceeded under vacuum and the temperature was gradually increased to 230 °C over the course of 4h. Then, the reaction mixture was dissolved in chloroform (*ca.* 25 ml) with some drops of trifluoroacetic acid and the polymer precipitated (68 % average yield) by pouring into an excel of cold methanol (*ca.* 500 ml), filtered, and dried.

Afterwards, rectangular-shape films of PEF (1x8 cm) were prepared by melting approach in a Teflon surface plate. The films were cut to flake form (*ca*. 5 mm square). FITR (λ/cm^{-1}): 3121 (=C-H stretching, furan ring); 2971 (asymmetric and symmetric C-H stretching); 1718 (C=O stretching); 1577 (C=C bending); 1266 (asymmetric and symmetric stretching vibrations of C-O bonds); 1141 (=C-O-C=, furan ring); 967, 836, 763 (=C-H out-of-plane deformation, furan ring); ^{1}H NMR (300 MHz, TCE-d2 + CF_3COOD, δ/ppm): 7.35 (s, H3 and H4, 2H), 4.72 (s, CH_2CH_2, 4H), 4.58 (t, $CH_2C\mathit{H_2}OC\mathit{H_2}CH_2$, tr), 4.11 (t, $C\mathit{H_2}CH_2OCH_2C\mathit{H_2}$, tr); ^{13}C NMR (75 MHz, TCE-d2 + CF_3COOD, δ/ppm): 159 (C=O); 146 (C2); 120 (C3); 64 (CH_2).

All other reagents were purchased commercially and used as received, ethylene glycol (EG, 99.8%), titanium(IV) butoxide (TBT, 97%), trifluoroacetic acid (TFA, 99%), 1,1,2,2-tetrachloroethane (TCE, ≥9 8.0%) zinc acetate ($ZnAc_2$, 99.99%), zinc chloride ($ZnCl_2$, ≥ 98%), choline chloride (ChCl, ≥99%), urea (99.0-100.5%), N,N'-dimethylurea (DMU, ≥ 95.0%), deuterated chloroform ($CDCl_3$, 99.8 atom% D), deuterated 1,1,2,2-tetrachloroethane (TCE-d2, ≥ 99.5 atom% D), deuterated trifluoroacetic acid (TFA-d, 99.5 atom% D), were purchased from Sigma-Aldrich Chemicals Co. Methanol (≥ 99.8%) was acquired from Honeywell, hydrochloridric acid (37%) was purchased from PanReac., chloroform (analytical grade) was purchased from Fischer Chemical. 2,5-Furandicarboxylic acid (FDCA, > 98%) was acquired from TCI Chemicals.

Instrumentation

Attenuated total reflection Fourier transform infrared (ATR FTIR) spectra of the main products were obtained using a PARAGON 1000 Perkin Elmer FTIR spectrophotometer equipped with a single horizontal Golden Gate ATR cell. The resolution was 8 cm^{-1} at 128 scans, in the range 500-4000 cm^{-1}.

^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) analyses of samples dissolved in TCE-d2 or $CDCl_3$-d with a few drops of TFA-d2 were recorded using a Bruker AMX 300 Spectrometer operating at 300.13 MHz and 75.47 MHz, respectively. All chemical shifts were expressed as parts per million (ppm) downfield from tetramethylsilane used as the internal standard.

Gas chromatography-mass spectroscopy (GC–MS) analysis of the derivatized glycolysis reaction products was performed using a GCMS-QP2010 Ultra mass spectrometer (Shimadzu, Kyoto, Japan) using helium as carrier gas (35 cm s^{-1}) equipped with a DB-1 J&W capillary column (30 m×0.32 mm i.d., 0.25 m film thickness, Clara, CA, USA), as described elsewhere.[4] The chromatographic conditions were as follows: isothermal at 80 °C for 5 min, ramped from 80 to 200 °C (4 °C min^{-1}); injector temperature, 250 °C; transfer line temperature, 290 °C; split ratio, equal to 1:50. Prior to GC-MS analysis, ≈5 mg of the sample was trimethylsilylated, as described before[5]: the residue was dissolved in pyridine (250 µL), and components containing hydroxyl and carboxyl groups were converted to their trimethylsilyl (TMS) ethers and esters, respectively, by adding bis(trimethylsilyl)trifluoroacetamide (250 µL) and trimethylchlorosilane (50 µL). After the mixture had stood at 70 °C for 30 min, the TMS derivatives were analyzed by GC-MS.

Intrinsic viscosity measurements were carried out on an Ubbelohde type viscometer maintained at 25 ◦C in a mixture of phenol/1,1,2,2-tetrachloroethane (50/50) (wt%/wt%). PEF was dissolved in that solvent mixture (0.1 g per 20 mL). The intrinsic viscosity ([η]) was determined by the ratio of specific viscosity and PEF solution concentration (η_{sp}/c, where $\eta_{sp} = (t_1 - t_0)/t_0$ and t_0 and t_1 are the solvent mixture elution time of the solvent mixture and polyester solution, respectively).

Procedures for PEF recycling into rPEF

DES preparation

The different DES, Choline Chloride:Zinc Acetate (ChCl:$ZnAc_2$, 1:1), Dimethyl Urea:Zinc Acetate (DMU:$ZnAc_2$, 4:1), Urea:Zinc Chloride (U:$ZnCl_2$, 4:1), and Urea:Zinc Acetate (U:$ZnAc_2$, 4:1), were prepared as described in the respective literature [6–11]. Briefly the two DES components were mixed according with the designated molar ratios at 70-100 °C for 2-8h, until the two components formed a clear homogeneous liquid, and the reaction was stopped. The as prepared DESs were promptly used.

PEF one-pot recycling

The one-pot recycling procedure started with the depolymerization reaction, glycolysis, where PEF, EG and the selected DES were put in a two-neck round-bottom flask under magnetic stirring and a nitrogen atmosphere. Reactions were carried out at 180 ºC for 1h, with molar ratios of PEF/EG= 1/4 and PEF/DES=20/1 [6–9]. Control reactions with just with one of the DES components or in the absence of any catalyst were additionally carried out. The weight loss of PEF was determined gravimetrically (equation 1) by recovering the unreacted residual PEF, rinsing thoroughly with distilled water, drying and weighting:

$$PEF\ weight\ loss\ (\%) = \frac{initial\ weight\ of\ PEF\ -\ weight\ of\ residual\ PEF}{initial\ weight\ of\ PEF} \times 100\% \qquad (1)$$

Continuously, the unpurified reaction products, still with U:$ZnAc_2$ DES, were directly used in the polyesterification reaction[2], by allowing them to react for further 5 hours at 180 °C under a nitrogen atmosphere. Afterwards, high vacuum was applied for more 2 hours as the temperature was gradually raised until 210 °C. At the end of the reaction, the obtained rPEF was purified following the same procedure described for PEF synthesis (69%). This reaction was also conducted in the presence of TBT catalyst (*ca.* 1 %wt) and rPEF isolated in 91% yield. FITR (λ/cm^{-1}): 3122 (=C-H stretching vibrations of the furan ring); 2969 (asymmetric and symmetric C-H stretching vibrations); 1715 (C=O stretching vibrations); 1576 (C=C bending vibrations); 1263 (asymmetric and symmetric stretching vibrations of C-O bonds); 1128 (=C-O-C= ring vibrations, furan ring); 966, 830, 760 (=C-H out-of-plane deformation vibrations, furan ring); ^1H NMR (300 MHz, $CDCl_3$ + CF_3COOD): δ=7.31 (s, furan ring, 2H), 4.72 (s, CH_2CH_2, 4H) ppm, 4.58 (t, $CH_2CH_2OCH_2CH_2$, tr), 4.11 (t, $CH_2CH_2OCH_2CH_2$, tr); ^{13}C NMR (75 MHz, $CDCl_3$ + CF_3COOD, δ/ppm): 160 (C=O); 146 (C2); 120 (C3); 64 (CH_2).

Intermediate monomer isolation and purification

Although the focus of this work was to develop a continuous circular solution for PEF's end-of-life, the BHEFDC recover, after glycolysis, was also checked. Glycolysis reactions were carried out and the ensuing product was isolated, purified, and in-depth characterized. PEF, EG and the selected DES were reacted at 180 ºC for 1h, with molar ratios of PEF/EG= 1:4 and PEF/DES=20/1 [6–9]. Subsequently, distilled water was added to the reaction medium (*ca*. 125 ml), the unreacted PEF removed by filtration, followed by concentrating the filtrate in the rotavapor into approximately 25 ml, stored overnight in the fridge for pouring the monomers. Finally, they were filtrated, and dried at 40 °C. FITR (λ/cm^{-1}): 3393 (O-H stretching vibration), 3121 (=C-H stretching, furan ring); 2970 (asymmetric and symmetric C-H stretching); 1728 (C=O stretching); 1573 (C=C bending); 1268 (asymmetric and symmetric stretching vibrations of C-O bonds); 1148 (=C-O-C=, furan ring); 966, 833, 766 (=C-H out-of-plane deformation, furan ring); ^1H NMR (300 MHz, TCE-d2): δ=7.29 (s, furan ring, 2H), 4.65 (s, CH_2CH_2, 4H), 4.46 (t, $CH_2CH_2OCH_2CH_2$, tr), 3.94 (t, $CH_2CH_2OCH_2CH_2$, tr); ^{13}C NMR (75 MHz, TCE-d2, δ/ppm): 158 (C=O); 146 (C2); 119 (C3); 67 (OCH2); 60 (CH_2OH);.

Optimization of PEF depolymerization reaction conditions

Table S1 summarizes all the PEF glycolysis conditions tested in this study.

Table S1 Set of reaction conditions tested for PEF glycolysis using U:$ZnAc_2$ DES.

T / °C	t / min	PEF/EG (mol / mol)	PEF/U:$ZnAc_2$ (mol / mol)
160	60	1:4	20:1
200			
180	30		
	120		
	60	1:2	
		1:8	
		1:4	1:5
			5:1

rPEF ^{13}C NMR spectrum

The repolymerized product was confirmed to be PEF and in-depth characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopies.

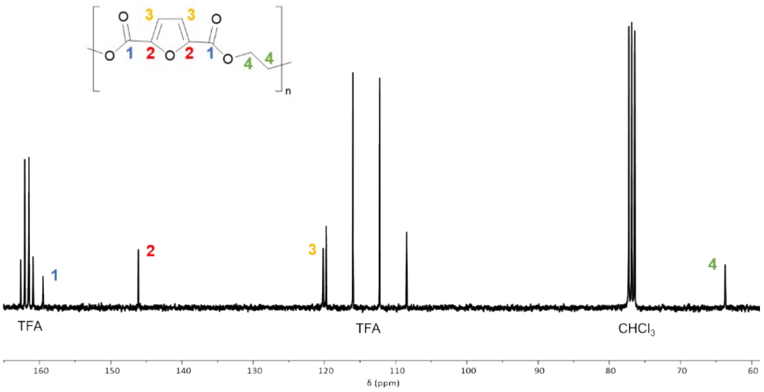

Figure S1 ^{13}C NMR spectrum of recycled PEF, in $CDCl_3$ and TFA-d.

GC-MS analysis of the glycolysis reaction media

To provide further insights into the depolymerization products, GC-MS of the crude reaction media, after glycolysis reaction, was performed (**Figures S2**- **S4**). The typical monomers identified (as TMS derivatives) include bis(hydroxyethyl)-2,5-furandicarboxylate (BHEFDC) and 2-hydroxyethyl-5-methyl-2,5-furandicarboxylate resulting from the substitution of two and one ethylene glycol units in a FDCA unit, respectively. These results indicate that the depolymerization mechanism of PEF, in Urea:$ZnAc_2$, plausibly follows glycolysis pathway, where urea-EG hydrogen bonding and metal ions-EG interaction favor ester linkage cleavage and oligomers of decreasing chain-length, and finally monomers are formed. Although, in light of the formation of 2-hydroxyethyl-5-methyl-2,5-furandicarboxylate, a more complex picture than a simple ester cleavage and ethylene glycol unit insertion, as proposed in the case of PET mechanism[12], can also be anticipated. Further studies to elucidate the PEF depolymerization (and continuous recycling) mechanism are ongoing, as mentioned in the Conclusions section.

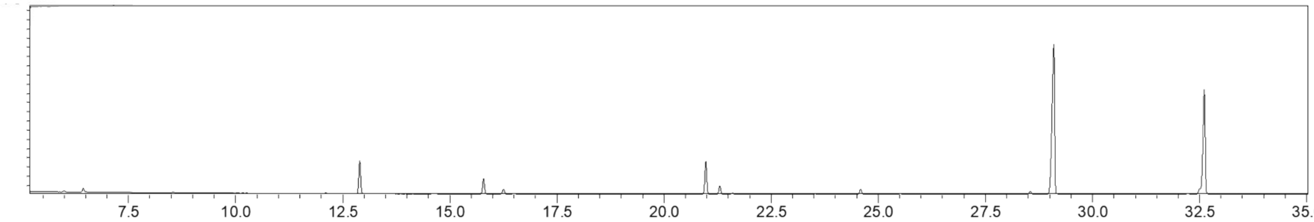

Figure S2 GC chromatogram of PEF glycolysis products (after derivatization by trimethylsilylation): 12.9 min, ethylene glycol; 21.0 min, diethylene glycol; 29.1 min, 2-hydroxyethyl-5-methyl-2,5-furandicarboxylate and 32.6 min, bis(hydroxyethyl)-2,5-furandicarboxylate.

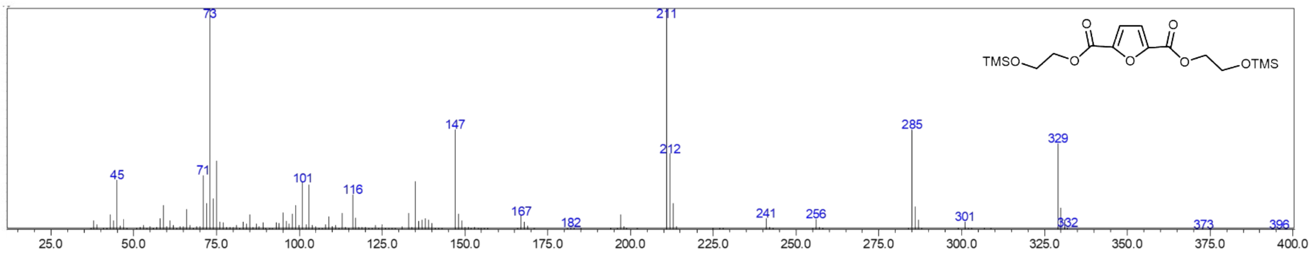

Figure S3 MS spectrum of trimethylsililated BHEFDC.

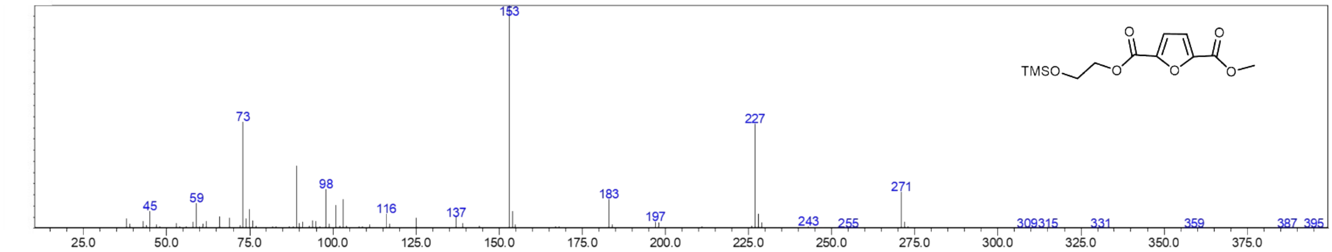

Figure S4 MS spectrum of trimethylsililated 2-hydroxyethyl-5-methyl-2,5-furandicarboxylate.

Isolated BHEFDC ^{13}C NMR spectrum

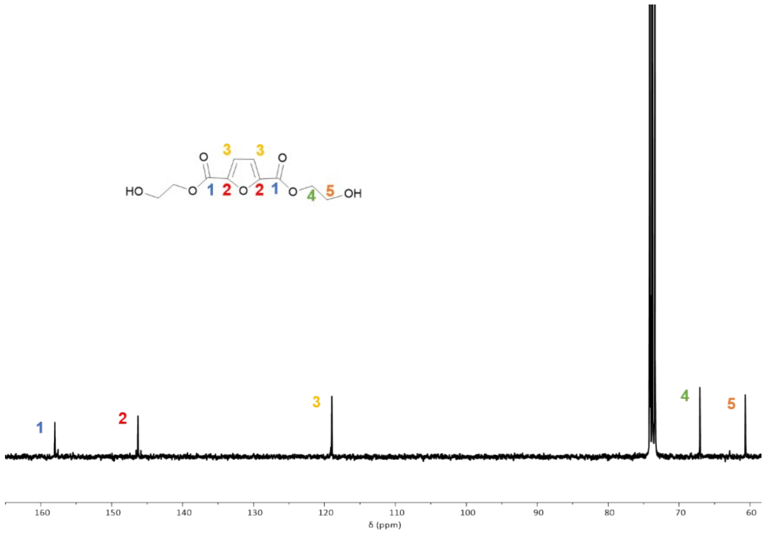

Figure S5 ^{13}C NMR spectra of intermediate BHEFDC product, in TCE-d2 and TFA-d.

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