Electronic Supplementary information for

Role of enhanced solubility in esterification of 2,5-furandicarboxylic acid with ethylene glycol at reduced temperatures: energy efficient synthesis of poly(ethylene 2,5-furandicarboxylate)

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1. Materials

Polymer grade ethylene glycol (EG) and terephthalic acid (TPA) were purchased from Fisher Scientific. 2,5-furandicarboxylic acid (FDCA) (99.27% by titration) was purchased from Chem-Impex International Inc. Reagents were used as received without any further purification.

2. Methods

2.1. Solubility determination

Known quantities of the diacid and EG were added to a glass tube equipped with hose connection for nitrogen inlet. The contents were well mixed using a magnetic stirrer. The glass tube was immersed in an oil bath. Temperature of the oil bath was controlled using an Omega temperature controller and was ramped at 5 °C per minute from room temperature until the clear point was achieved. Time and temperature at the clear point were recorded during the experiment. Sample was immediately removed from the oil bath and allowed to air cool. ^{1}H and ^{13}C NMR was performed on the mixture to determine if the diacid reacted with EG to produce oligomers. Experiments were run in triplicates to ensure the repeatability of the data. A temperature ramp of 5 °C per minute was used to simulate the heating ramp used during the esterification reaction.

2.2 Hoftyzer and Van Krevelen method for Solubility parameter calculation[1]

According to this method, solubility parameter (δ) is attributed to, (i) dispersion force contribution (δ_d), (ii) polar force contribution (δ_p) and (iii) hydrogen bonding force contribution (δ_h). Each of these contributions can be determined theoretically by group contribution and can be used to determine the solubility parameter using the following equation,

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

2.3 Esterification reaction

5 grams of FDCA (0.032 mol) and 4.97 grams EG (0.080 mol) were added to a three-necked flask equipped with an overhead mechanical stirrer and a condenser assembly. Molar excess of 2.5:1 for EG to the acid was chosen to compensate for the evaporation losses. Reaction mixture was heated using an oil bath with an Omega temperature controller. Reactants were well mixed for 30 minutes before starting the heating protocol as a paste making step used typically in PET synthesis.[2] During this step, the assembly was purged with industrial grade nitrogen and held under nitrogen environment for the duration of the reaction using the Schlenk line. Reaction mixture was heated from room temperature to the desired temperature at the heating rate of 5 °C per min. The reaction temperatures were chosen based on the solubility studies and published literature summarized in Table 1 in the main article. After reaching the set point, the temperature was held constant for the duration of the experiment. Samples were drawn at regular intervals and dissolved in DMSO-d_6 for NMR analysis. No catalyst or diethylene glycol (DEG) suppressor was added during the reaction.

2.4 ^{1}H and ^{13}C NMR spectroscopy for determination of end group conversion

Hydroxyl and carboxyl end group conversion during esterification reaction of TPA and EG can be accurately estimated by ^{1}H and ^{13}C NMR spectroscopy respectively.[3] This study was extended to determine the end group conversion of FDCA and EG due to structural similarity between the two diacids. NMR spectra were recorded using Bruker Avance III spectrometer at 600 MHz and 150 MHz for ^{1}H and ^{13}C nuclei respectively. All samples were dissolved in DMSO-d_6. A probe temperature of 60 ^{o}C was chosen to improve the signal to noise ratio of the spectra. ^{1}H and ^{13}C NMR spectra of monomers FDCA (F) and EG (G) and side product diethylene glycol (DEG) were recorded and chemical shifts were assigned as summarized in Figure S1.
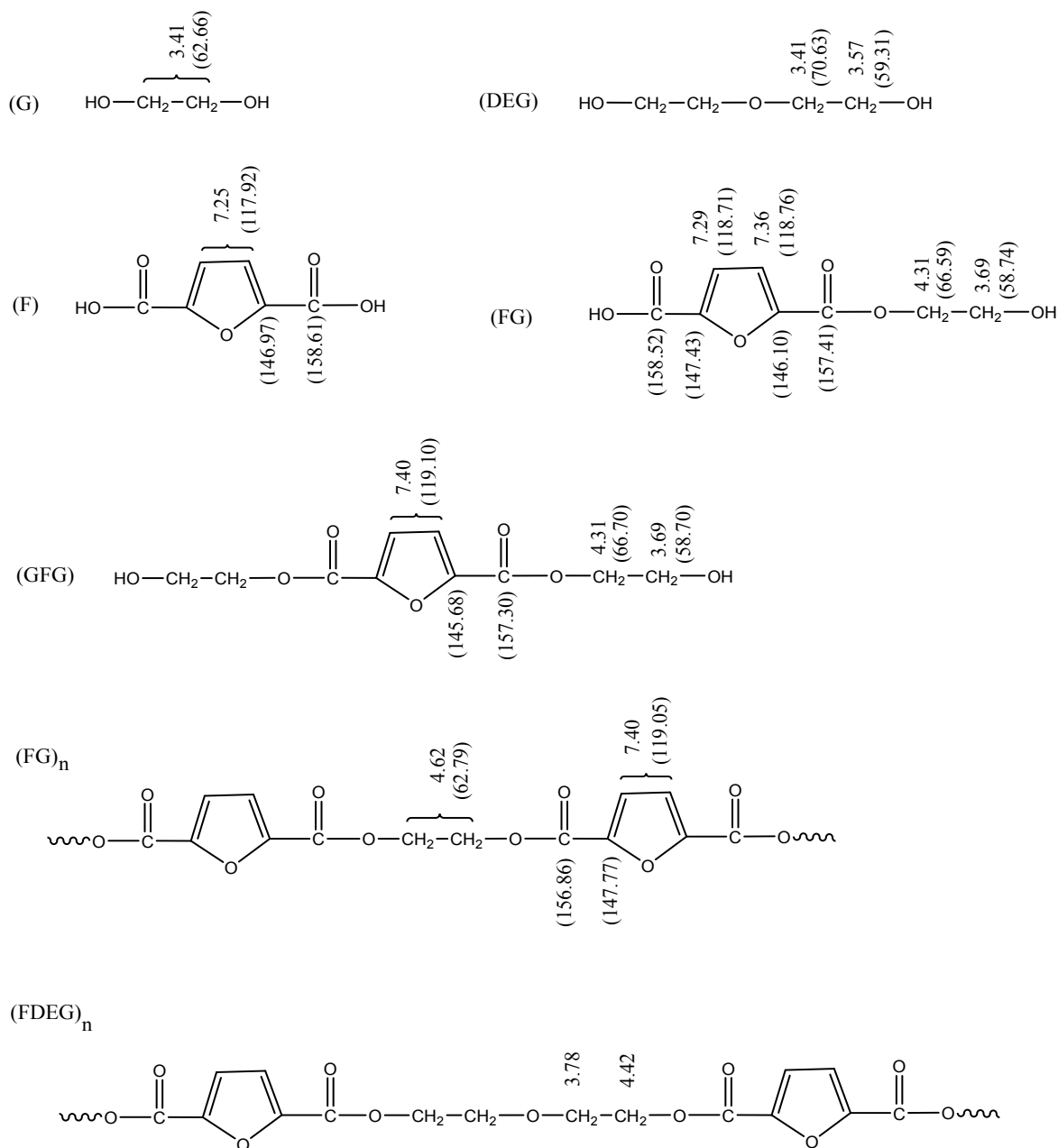
(G) HO—CH₂—CH₂—OH 3.41 (62.66)

(DEG) HO—CH₂—CH₂—O—CH₂—CH₂—OH 3.41 (70.63) 3.57 (59.31)

(F) 7.25 (117.92); HO—C(=O)—furan—C(=O)—OH (146.97) (158.61)

(FG) 7.29 (118.71) 7.36 (118.76); HO—C(=O)—furan—C(=O)—O—CH₂—CH₂—OH 4.31 (66.59) 3.69 (58.74) (158.52) (147.43) (146.10) (157.41)

(GFG) 7.40 (119.10); HO—CH₂—CH₂—O—C(=O)—furan—C(=O)—O—CH₂—CH₂—OH 4.31 (66.70) 3.69 (58.70) (145.68) (157.30)

(FG)ₙ 4.62 (62.79); ~~~O—C(=O)—furan—C(=O)—O—CH₂—CH₂—O—C(=O)—furan—C(=O)—O~~~ 7.40 (119.05) (156.86) (147.77)

(FDEG)ₙ ~~~O—C(=O)—furan—C(=O)—O—CH₂—CH₂—O—CH₂—CH₂—O—C(=O)—furan—C(=O)—O~~~ 3.78 4.42

Figure S1: ¹H and ¹³C chemical shifts of EG (G), DEG (DEG), FDCA (F), monoester of EG and FDCA (FG), diester of EG and FDCA (GFG), polyethylene furandicarboxylate oligomers ((FG)ₙ) and polydiethylene glycol furandicarboxylate ((FDEG)ₙ) using DMSO-d₆ as a solvent

Oxyethylene protons of EG (O-CH_2-CH_2-O) show different chemical shifts depending on mono-esterification (FG) or di-esterification (GFG) of the hydroxyl groups. Oxyethylene protons of free diethylene glycol (DEG) and DEG incorporated in the backbone (($DEG)_n$) can also be detected in the same chemical shift region. As the reaction progresses, area under the curve of these peaks changes as shown in Figure S2. By integrating the area under these peaks in a ^{1}H spectra, hydroxyl end group conversion, and percent of hydroxyl end groups in the form of DEG incorporated in the backbone can be determined using correlations developed by Petiaud et al.[3]

$$Hydroxyl\ end\ group\ conversion: X_{OH} = \frac{AUC[(c) + 0.5 * (b)]}{AUC[(a) + (b) + (c)]}$$

$$Mole\ \%\ of\ hydroxyl\ groups\ as\ DEG\ in\ chain$$
$$= \frac{100 * 0.5 * AUC(e)}{AUC[(a) + (b) + (c) + 0.5 * (d) + 0.5 * (e)]}$$

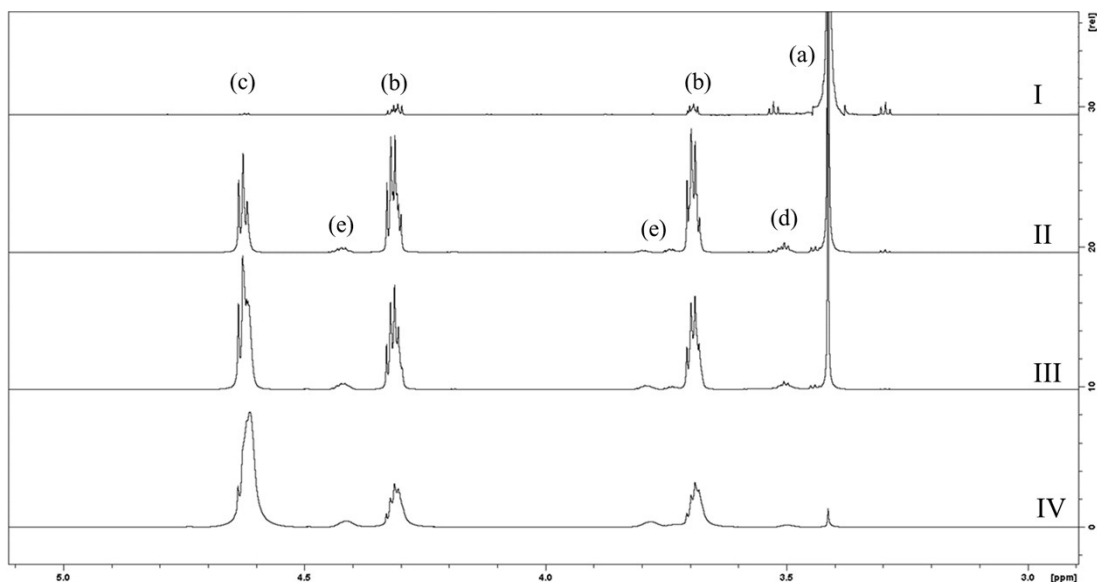$$Mole\ \%\ of\ hydroxyl\ groups\ as\ free\ DEG = \frac{100 * 0.5 * AUC(d)}{AUC[(a) + (b) + (c) + 0.5 * (d) + 0.5 * (e)]}$$

Figure S2: ^1H chemical shifts of oxyethylene protons of ethylene glycol monomer (a), ethylene glycol as an end group (b), ethylene glycol incorporated in polymer backbone (c), free diethylene glycol (d) and diethylene glycol incorporated in polymer backbone (e) after 0 minutes (I), 30 minutes (II), 60 minutes (III) and 120 minutes (IV) at 210^0 C.

Similar to TPA, aromatic and carbonyl carbons of furan ring in FDCA resonate at distinct regions and can be used to determine acid end group conversion. Specifically, carbonyl carbons resonate in two different regions 158.4-158.7 ppm and 156.7-157.5 ppm depending on the presence of ester linkage. Free FDCA (F) exhibits the carbonyl carbon peak at 158.6 ppm. As the reaction progresses, intensity of this peak decreases and new peaks corresponding to mono-esterified (end group) and di-esterified FDCA carbonyl carbons appear as observed in Figure S3. Area under these peaks can be used to determine carboxyl end group conversion.

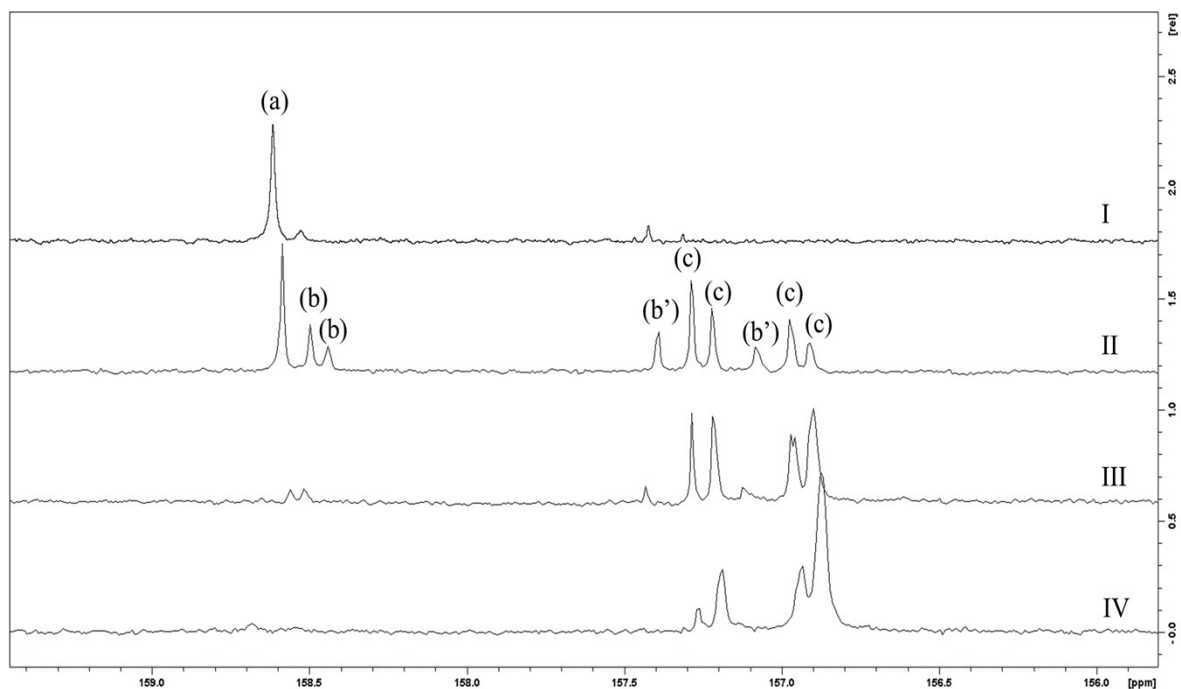$$Carboxyl\ end\ group\ conversion: X_{COOH} = \frac{AUC[(c) + (b')]}{AUC[(a) + (b) + (b') + (c)]}$$

Figure S3: ^{13}C chemical shifts of carbonyl carbons of furan ring for FDCA monomer (a), FDCA as an end group (b, b') and FDCA incorporated in polymer backbone (c) after 0 minutes (I), 30 minutes (II), 60 minutes (III) and 120 minutes (IV) at 210^0 C. Peaks (b) and (b') arise from the same structure but are annotated differently for simplification of the C_{COOH} formula

^{1}H spectra of solubilized FDCA in EG confirming the presence of oligomers

^{1}H NMR was performed on the dissolved FDCA samples to identify the onset of esterification and presence of esterified oligomers (Figure S4). For the samples with clear point temperatures (T_{cp}) higher than 140 °C, peaks (b) from Figure S2 were observed in the spectra. These peaks correspond to the monoesterified FDCA.
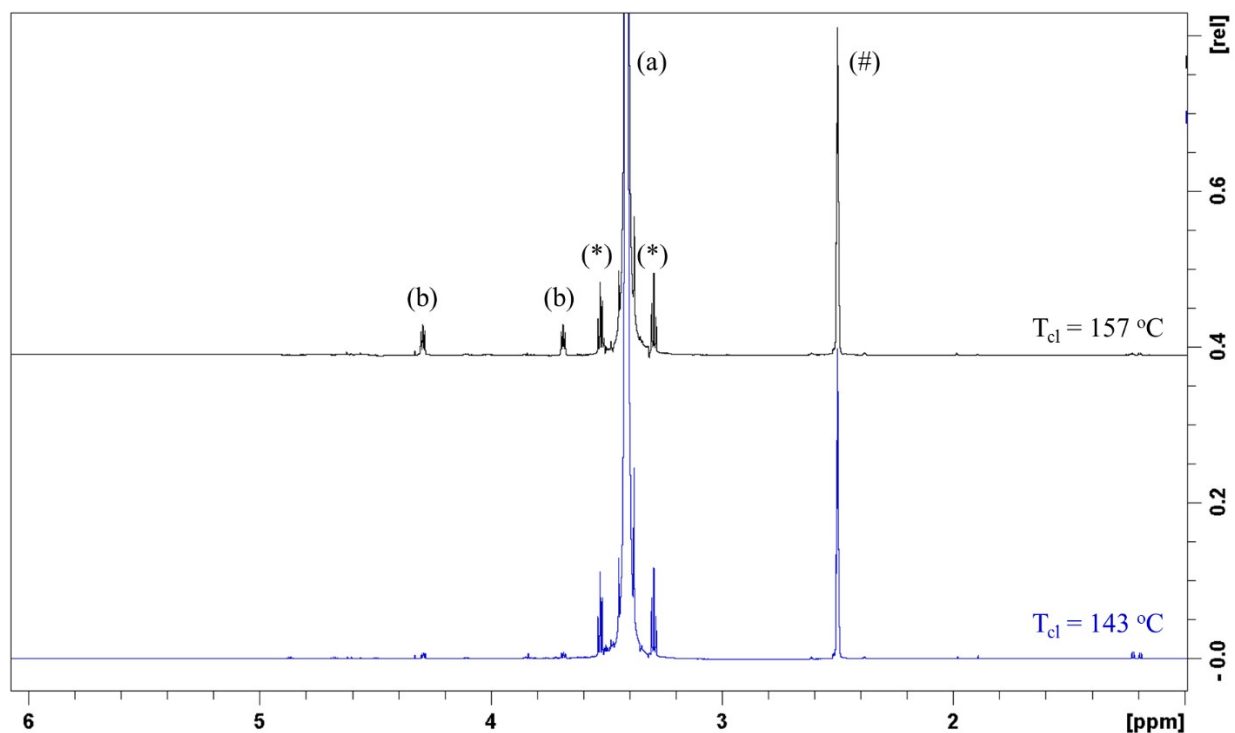

Figure S4: ^{1}H spectra of dissolved FDCA samples in EG corresponding to clear point temperatures of 143 and 157 °C. Peaks (b) arise from the esterified oligomers as described in Figure S2. (#) is DMSO-d$_6$ peak and (*) are satellite peaks of the oxyethylene protons of EG.

2.5 End group analysis by titration

The carboxyl end group conversion of oligomers was determined by titration.[4] For this analysis, 0.1 gram of the sample was dissolved in 10 ml of benzyl alcohol with moderate heating. The solution was titrated with 0.1 M sodium hydroxide (NaOH) and phenol red was used as an indicator. By determining the acid value (AV) of the samples at initial time and desired time for each reaction temperature, the carboxyl group conversions were calculated.

2.6 Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-ToF-MS)

MALDI-ToF-MS analysis was performed using Bruker Daltonics UltrafleXtreme MALDI-TOF/TOF mass spectrometer operating in the linear positive ion mode. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix in water. Samples were purified by dissolving in CH_2Cl_2/HFP and precipitating out in methanol to separate the unreacted FDCA and EG. Then, samples were redissolved in CH_2Cl_2/HFP (~ 5 mg mL^{-1}) and deposited on the probe plate with the matrix (1/1 volume ratio) by dried-droplet approach. Solvents were evaporated at room temperature for matrix crystallization. Number average molecular weight (M_n) and polydispersity index (PDI) of the mass spectra was determined using Bruker PolyTools software. The spectra obtained from MALDI-ToF-MS analysis of purified PEF oligomer samples after 180 minutes at different temperatures are shown in Figure S5.
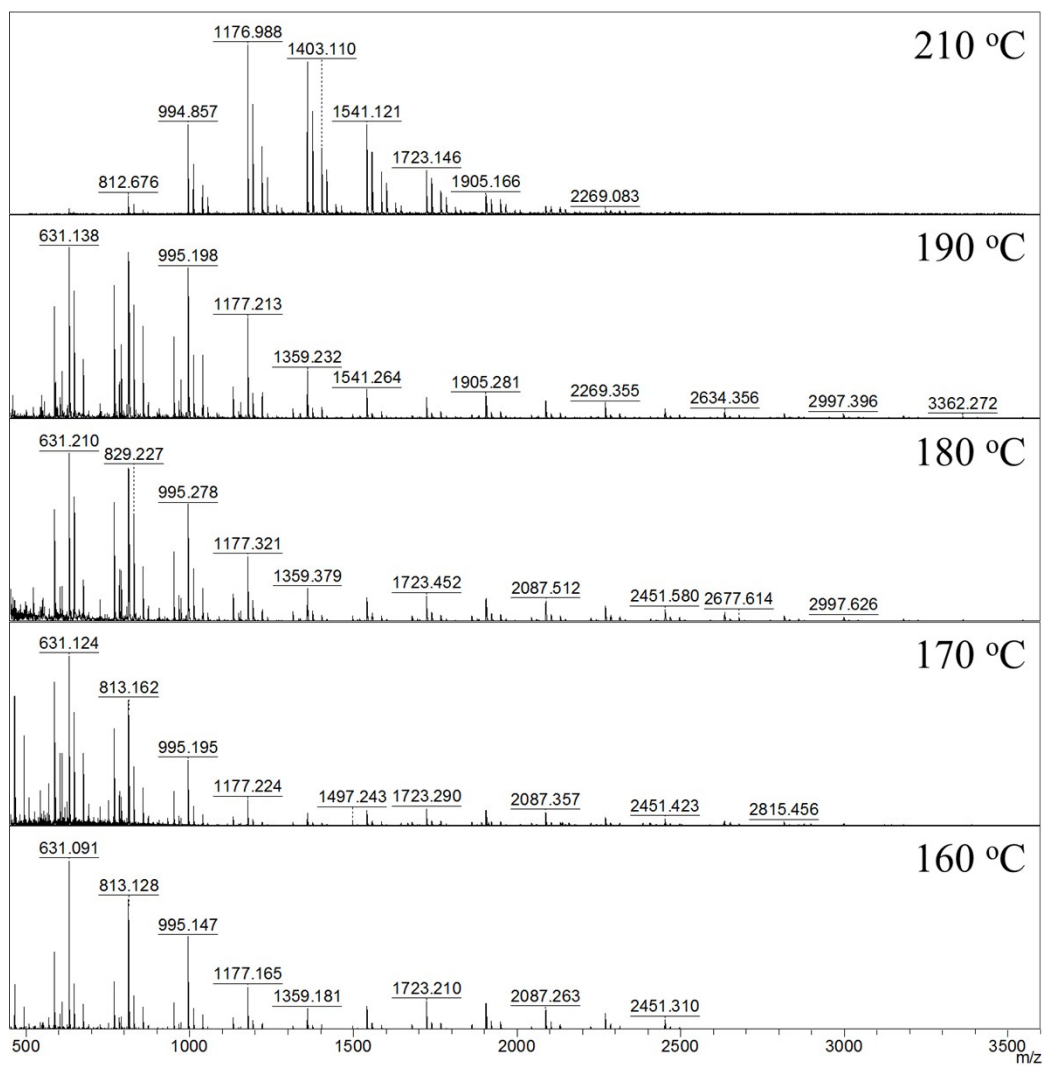
Figure S5: MALDI-MS spectra of purified PEF oligomers of the esterification reaction at different temperatures after 180 mins

3 References

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2. Aharoni, S. M., Industrial-Scale Production of Polyesters, Especially Poly(Ethylene Terephthalate). In *Handbook of Thermoplastic Polyesters*, Wiley-VCH Verlag GmbH & Co. KGaA: 2005; pp 59-103.

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