Supporting information

The unexpected susceptibility of poly(ethylene furanoate) to UV-irradiation: a warning light for furandicarboxylic acid (FDCA)?

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1. Experimental

1.1. Chemicals and materials

Ethylene glycol (EG, 99.8%), titanium(IV)isopropoxide (Ti(OiPr)_4, 97%), and o-xylene (≥99%) were obtained from Sigma-Aldrich (the Netherlands). Dimethyl terephthalate (DMT, >99%) was obtained from Acros Organics. Hexafluoroisopropanol (HFIP, ≥99%) was obtained from Fluorochem Ltd. (UK). Methanol (≥99.98%) was obtained from Biosolve B.V. (the Netherlands). 2,5-Furandicarboxylic acid dimethyl ester (FDME) was kindly provided by Archer Daniels Midland Company (ADM, USA). All chemicals were used as received.

1.2. Polymerization procedure

A pre-dried 250 mL three-necked round bottom flask equipped with a magnetic drive overhead mechanical stirrer (Buchi bmd075), nitrogen gas inlet, and Claisen distillation head with Liebig condenser was charged with the dimethyl ester and ethylene glycol (see Table S1 for detailed reaction parameters). The set-up was evacuated and refilled with nitrogen gas five times. The reaction mixture was heated using a DrySyn at 160 °C (externally measured) for 20 min under constant stirring (150 rpm). After observing the complete melt of the mixture, the catalyst Ti(OiPr)_4 in 5 mL o-xylene was added into the flask under a continuous flow of nitrogen. The temperature was then increased to 175 °C (PEF) or 225 °C (PET). In the following 4 h, the temperature was further increased to 195 °C (PEF) or 245 °C (PET). Afterwards, vacuum was gradually applied reaching 0.02 mbar in 30 min. The temperature was subsequently further increased to 235 °C (PEF) or 270 °C (PET), and the reaction mixture was stirred for 3 h under vacuum. The stirring speed was gradually decreased to 50 rpm as the viscosity of the melt increased. After completion of the reaction, the mixture was cooled down to room temperature under a nitrogen atmosphere. The cooled polymer was milled using a Retsch ZM 1000 centrifugal grinding mill equipped with a 0.5 mm sieve. Optical microscopy images of the milled polymers are shown in Figure S1.

Part of the polymer was precipitated by first dissolving the polymer in HFIP, followed by precipitation in cold methanol. The precipitates were washed with excess methanol, and dried in vacuo at 40 °C overnight.

Table S1: Overview of reaction parameters for the polymerization of PEF and PET.

|           | PEF | PET |
|-----------|-----|-----|
| FDME      | 80.3 g / 0.44 mol | - |
| DMT       | -   | 110.2 g / 0.57 mol |
| EG        | 56.6 g / 0.91 mol | 46.2 g / 0.74 mol |
| EG equivalent | 2.1 | 1.3 |
| Ti(OiPr)_4 relative to dimethyl ester | 0.02 mol% | 0.06 mol% |
| T_transesterification | 175-195 °C | 225-245 °C |
| T_high vacuum | 235 °C | 270 °C |
Figure S1: Optical microscopy images of a) PEF and b) PET after milling. Both polymers show a particle size distribution from 10 µm up to 500 µm.

1.1. Q-SUN UV-stability testing

Weathering tests were performed in a Q-SUN Xe1s (Q-lab) according ISO 4892 in dry mode. A total UV-intensity (TUV) of 60 W/m² and a black panel temperature of 65 °C was used. The irradiance and black panel temperature were calibrated prior to the measurement. The total irradiation time was 500 h. Samples were rotated during the test, as recommended by the manufacturer\(^1\), according to the rotation scheme depicted in Figure S2 and Table S2. About 1 g of reactor grade polyester or 0.5 g of precipitated polyester was charged into quartz glass petri dishes (Behr Labor-Technik, Germany) covered with a quartz glass lid (see Figure S3). During every rotation, the polymer powder was mixed manually to ensure homogeneous exposure of the polymer to the UV-light. Each polymer was tested in duplicate. The duplicates are coded with after UV (1) and after UV (2), respectively.

Table S2: Rotation schedule as planned and as realized. The total experiment time represents at which moment the samples were rotated to that position, i.e. the samples were moved to position two after 48 hours. The time at position indicates the time the samples have spent at a certain position, i.e. the samples have been at position two for 87 hours. The experiment times indicated with an asterisk (*) indicate that at this rotation moment photographs are taken.

| Position | Total experiment time (h) | Time at position (h) |
|----------|--------------------------|----------------------|
|          | Planned | Realized | Realized |
| Position 1 | 0      | 0       | 48       |
| Position 2 | 49     | 48      | 87       |
| Position 3 | 136    | 135*    | 76       |
| Position 4 | 212    | 211     | 68       |
| Position 5 | 280    | 279*    | 84       |
| Position 6 | 328    | 327     | 52       |
| Position 7 | 380    | 378*    | 68       |
| Position 8 | 448    | 447     | 53       |
1.2. Characterization

The titanium concentration in the polymers directly after melt polycondensation was measured using inductively coupled plasma mass spectrometry (ICP-MS). The samples were pre-treated using acid digestion with a microwave oven (MARS express, CEM Corporation, Matthews, NC, USA). For the microwave digestion 10 mL of concentrated nitric acid (69% Instra-analyzed nitric acid, J.T. Baker, Phillipsburg, NJ, USA) was added to 0.1 g of sample in Teflon digestion vessels. The samples were digested in the microwave oven at a temperature of 210°C. The digests were quantitatively transferred to 50 ml polypropylene (PP) centrifuge tubes (Greiner Bio-One, Frickenhausen, Germany) and diluted with de-ionized water to a final volume of 50 ml. The digests were diluted prior to analysis with a final acid concentration of 2.8% v/v. The titanium concentration was determined at m/z 47 using ICP-MS (NexION 300D, Perkin Elmer, Waltham, MA, USA). Samples were introduced into the ICP-MS using an SC-FAST autosampler (ESI, Omaha, NE, USA). The ICP-MS was equipped with a PFA-ST nebulizer, a quartz cyclonic spray chamber and a quartz torch with a sapphire injector. The ICP-MS was operated in collision mode (KED) with helium as collision gas. Concentrations were determined using external calibration curves with rhodium as internal standard.

Color was measured using a Konica Minolta CM-5 spectrophotometer in reflectance mode equipped with a CM-A195 target mask and CM-A157 mini petri dish. The CIELAB color value was calculated as the average of five measurements and is expressed in L* (lightness from black (0) to white (100)), a* (green (-) to red (+)), and b* (blue (-) to yellow (+)). The color difference was calculated according CIE76, which is a method to calculate the distance between two points in a three dimensional space, given in the equation below:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

UV-absorption spectra were recorded in HFIP on a Jasco V-730 spectrophotometer equipped with a thermostatted cell holder. Polymer concentrations were 1.9 mg/mL (PET) or 1.8 mg/mL (PEF), respectively. Measurements were performed at 25°C using quartz glass cuvettes with an optical path of 10 mm (Hellma Analytics). Spectra were recorded from 340-200 nm, with a 0.5 nm resolution; each spectrum was taken as the average of three measurements.

Gel Permeation Chromatography (GPC) measurements were performed using an Omniseq HP-SEC system on HFIP (model CHR6000 sn. MAL 1202615) provided with a (standard) injection volume of 100 µL, flow of 0.7 ml/min and oven temperature of 35°C and effluent HFIP + 0.02M KTFA. Accurately weighted samples were dissolved overnight in 3.0 mL of effluent in 4 ml HPLC vails. The polymer concentration was 4-5 mg/L. Filtering is done before measuring through 0.45 um PFTE syringe filters. Narrow standard PolyCal PMMA 60kD (from Viscotek) was used for absolute calibration of the system (Mw = 59.575, DPI = 1.05). A dn/dc value of 0.2562 or 0.238 was used to calculate the molecular weight for PET and PEF, respectively.

DSC analysis was carried out with a PerkinElmer DSC 8000 with autosampler. RVS pans sealed with a rubber ring were used. An empty sealed pan was used as blank (reference) measurement. Calibration was done with indium as reference material. Samples were heated from 0 to 250 °C (PEF) or 300 °C.
(PET) with 10 °C/min, cooled to 0 °C with 10 °C/min, hold at 0°C for 3 min, followed by a second heating from 0 to 250 °C (PEF) or 300 °C (PET) with 10 °C/min. The results were evaluated with Perkin Elmer Pyris software.

The degree of crystallinity $X_c$ was calculated by:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_0}$$

$\Delta H_0$ for PET was taken as 140 J/g and for PEF as 137 J/g. When no cold crystallization was observed, $\Delta H_c$ was taken as 0 J/g.

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer STA 6000 (simultaneous thermal analyzer). Temperature calibration was performed using melting standards. The sample masses (approximately 15 mg) were determined after an isothermal stage at 65 °C for 30 min under an N$_2$ flow (20 mL/min). Mass loss measurements were run from 65 to 600 °C with a heating rate of 10 °C/min under an N$_2$ flow of 20 mL/min.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded in attenuated reflection mode (ATR) on an ALPHA II spectrometer (Bruker, Germany) equipped with a diamond crystal. Spectra were recorded using 32 scans and a resolution of 4 cm$^{-1}$.

$^1$H-NMR (400.17 MHz) & $^{13}$C NMR (100.62 MHz) spectra were recorded on a Bruker Avance III spectrometer at 298K. The used solvent was a 6:1 mixture of deuterated chloroform and trifluoroacetic acid (6:1 CDCl$_3$:TFA-d). All spectra were internally referenced to the tetramethylsilane (TMS, $\delta = 0$ ppm) signal.

Matrix assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS) analysis was performed with an Ultraflex mass spectrometer workstation (Bruker Daltonics, Bremen, Germany). Samples were dissolved in 1,1,1,3,3,3-hexafluor-2-propano (HFIP) containing 1.82% (w/v) trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and 0.05% (w/v) potassium trifluoroacetate (KTFA). Polyethylene glycol 2,000 and maltodextrins (MD20) were used for calibration. Measurements were performed in reflective mode, and positive ions were examined. Ten spectra with a total of 50 shoots per spot were collected using the lowest possible laser intensity that led to a good quality spectrum.

The molecular weight of the end-groups was derived from the following formula:

$$m/z = M_{end\text{-}groups} + n \cdot M_{repeating\text{ }unit} + M_K$$
2. Residual titanium

**Table S3:** The amount of residual titanium in the polyesters as determined by ICP-MS showing that there is no significant difference between the reactor grade and precipitated polymers. The difference in calculated initial catalyst loading and measured residual titanium is attributed to experimental errors in both the weighing of the catalyst and the ICP-MS measurements.

|        | Initial catalyst loading (mol% relative to DMT/FDME) | Initial catalyst loading (mg/kg) | Residual titanium (mg/kg) |
|--------|------------------------------------------------------|---------------------------------|---------------------------|
| PET    |                                                      |                                 |                           |
| Reactor grade | 0.06                                         | 150                              | 187                       |
| Precipitated | 0.06                                         | 150                              | 184                       |
| PEF    |                                                      |                                 |                           |
| Reactor grade | 0.02                                         | 53                               | 83                        |
| Precipitated | 0.02                                         | 53                               | 63                        |
3. Color formation

Figure S4: Photographs of reactor grade and precipitated PEF during UV-irradiation.

Figure S5: Photographs of reactor grade and precipitated PET during UV-irradiation.
Table S4: CIELAB color values and total color difference (ΔE, CIE76) after UV-exposure for PET and PEF. Errors represent the 95% confidence interval calculated over five measurements.

| Sample          | L*    | a*    | b*    | ΔE    | Sample          | L*    | a*    | b*    | ΔE    |
|-----------------|-------|-------|-------|-------|-----------------|-------|-------|-------|-------|
| PET reactor grade |       |       |       |       | PET reactor grade |       |       |       |       |
| Virgin          | 95.6 ± 0.1 | -0.7 ± 0.02 | 6.9 ± 0.2 | 0.02 | Virgin          | 93.8 ± 0.3 | -0.8 ± 0.04 | 5.2 ± 0.1 | 0.2  |
| After UV (1)    | 96.3 ± 0.2 | -2.1 ± 0.03 | 10.5 ± 0.2 | 0.03 | After UV (1)    | 81.4 ± 1.4 | 2.3 ± 0.9 | 34.1 ± 1.4 | 1.4  |
| After UV (2)    | 95.5 ± 0.4 | -1.7 ± 0.1 | 10.9 ± 0.9 | 0.1  | After UV (2)    | 82.7 ± 1.9 | 1.5 ± 1.0 | 32.1 ± 3.0 | 3.0  |
| PET precipitated|       |       |       |       | PEF precipitated|       |       |       |       |
| Virgin          | 98.8 ± 0.04 | 0.3 ± 0.02 | 2.3 ± 0.01 | 0.01 | Virgin          | 98.6 ± 1.3 | -0.2 ± 0.01 | 1.3 ± 0.1 | 0.1  |
| After UV (1)    | 99.0 ± 0.1 | -0.7 ± 0.02 | 2.6 ± 0.04 | 0.04 | After UV (1)    | 89.8 ± 0.7 | 0.4 ± 0.1 | 24.5 ± 1.2 | 1.2  |
| After UV (2)    | 98.9 ± 0.1 | -0.8 ± 0.01 | 2.9 ± 0.01 | 0.8  | After UV (2)    | 91.1 ± 0.4 | 0.2 ± 0.2 | 23.3 ± 1.1 | 1.1  |

Figure S6: CIELAB color values for PEF and PET before and after UV-exposure. Error bars represent the 95% confidence interval calculated over five measurements.
4. UV(-VIS) absorption

**Figure S7**: UV absorption of a) reactor grade PEF, and b) precipitated PEF before and after UV-exposure. All spectra were recorded in HFIP, polymer concentrations were 1.8 mg/mL. Only one main absorption peak is found, with three local absorption maxima at 260, 266, and 278 nm, respectively.

**Figure S8**: UV absorption of a) reactor grade PET, and b) precipitated PET before and after UV-exposure. All spectra were recorded in HFIP, polymer concentrations were 1.9 mg/mL. Local absorption maxima are found at 244, 256, 290, and 303 nm, respectively. The first two correspond to the main absorption peak, whereas the latter two smaller absorption peaks originate from symmetry forbidden transitions.
5. Possible photodegradation mechanisms of PEF

Scheme S1: Possible photodegradation mechanisms of PEF via Norrish type I and type II (β-elimination) reactions. P = polymer residue.
6. Molecular weight (SEC)

Figure S9: Molecular weight distribution of a) reactor grade PEF and b) precipitated PEF before and after UV-irradiation. Both show the formation of high molecular weight species. Additionally, especially the precipitated PEF shows also the formation of low molecular weight species.

Figure S10: Molecular weight distribution of a) reactor grade PET and b) precipitated PET before and after UV-irradiation showing that there is no significant effect on the molecular weight distribution.

Table S5: Molecular weight of PET and PEF before and after UV-irradiation. All values are an average of two measurements. n.c.: not calculated, *: Mn could not be calculated accurately.
Figure S11: Refractive index detector signal of SEC measurements of a) reactor grade PEF, and b) precipitated PEF. Both show peak broadening on the left-hand (higher molecular weight) as well as the right-hand side (lower molecular weight) as compared to the virgin material peak. This indicates that both chain extension/cross-linking as well as chain scission after UV-irradiation occurs. However, the extent of chain scission is significantly higher for the precipitated PEF, as can be seen from the increase in intensity at higher retention volumes, i.e. at lower molecular weights.

Figure S12: Overlay of the right angle laser scattering (RALS) and refractive index (RI) detector signal for a) reactor grade PEF virgin, b) reactor grade PEF after UV (1), c) reactor grade PEF after UV (2), d) precipitated PEF virgin, e) precipitated PEF after UV (1), f) precipitated PEF after UV (2). The UV-irradiated samples show a steep increase in the RALS signal at lower retention volumes as compared to the RI signal, which is an indication of branching. The bimodal distribution in the RALS signal can, therefore, be attributed to branched and linear species.
Figure S13: Refractive index detector signal of SEC measurements of a) reactor grade PET, and b) precipitated PET.

Figure S14: Overlay of the right angle laser scattering (RALS) and refractive index (RI) detector signal for a) reactor grade PET virgin, b) reactor grade PET after UV (1), c) reactor grade PET after UV (2), d) precipitated PET virgin, e) precipitated PET after UV (1), f) precipitated PET after UV (2).
7. Thermal properties (DSC & TGA)

**Figure S15:** DSC graphs of a) reactor grade PEF and b) precipitated PEF before and after UV-exposure.

**Figure S16:** DSC graphs of a) reactor grade PET and b) precipitated PET before and after UV-exposure.
Table S6: Thermal properties of reactor grade and precipitated PEF before and after UV-exposure. n.o.: not observed.

| Sample          | 1st heating |          |         |          |          | 2nd heating |          |         |          |          |
|-----------------|-------------|----------|----------|----------|----------|-------------|----------|----------|----------|----------|
|                 | Tg (°C)     | ΔHcc (J/g) | Tcc (°C) | ΔHm (°C) | Tm (°C)  | Tg (°C)     | ΔHcc (J/g) | Tcc (°C) | ΔHm (°C) | Tm (°C)  |
| PET reactor grade Virgin | n.o.         | -19       | 159      | 49       | 215      | 74          | -36       | 163      | 47       | 214      |
| After UV (1)     | 76           | n.o.      | n.o.     | 32       | 208      | n.o.        | n.o.      | 63       | -11      | 163      | 10       | 199      |
| After UV (2)     | 74           | n.o.      | n.o.     | 23       | 205      | n.o.        | n.o.      | 61       | -10      | 157      | 17       | 195      |
| PET precipitated Virgin | 65           | -12       | 116      | 53       | 214      | -25         | 143       | 69       | -6       | 143      | 45       | 213      |
| After UV (1)     | n.o.         | -32       | 116      | 17       | 183      | n.o.        | n.o.      | 26       | n.o.     | n.o.     | n.o.     | n.o.     |
| After UV (2)     | n.o.         | -38       | 116      | 20       | 184      | n.o.        | n.o.      | 23       | n.o.     | n.o.     | n.o.     | n.o.     |

Table S7: Thermal properties of reactor grade and precipitated PET before and after UV-exposure. n.o.: not observed. The Tg of PET found for the first heating cycle is relatively low. We attribute this to some moisture in the sample.

| Sample          | 1st heating |          |         |          |          | 2nd heating |          |         |          |          |
|-----------------|-------------|----------|----------|----------|----------|-------------|----------|----------|----------|----------|
|                 | Tg (°C)     | ΔHcc (J/g) | Tcc (°C) | ΔHm (°C) | Tm (°C)  | Tg (°C)     | ΔHcc (J/g) | Tcc (°C) | ΔHm (°C) | Tm (°C)  |
| PET reactor grade Virgin | 68           | n.o.      | n.o.     | 57       | 254      | -62         | 215       | 78       | n.o.     | 57       | 252      |
| After UV (1)     | 77           | n.o.      | n.o.     | 59       | 254      | -60         | 211       | 77       | n.o.     | 54       | 252      |
| After UV (2)     | 77           | n.o.      | n.o.     | 60       | 253      | -59         | 211       | 77       | n.o.     | 55       | 250      |
| PET precipitated Virgin | 66           | -6        | 81       | 65       | 255      | -59         | 214       | 79       | n.o.     | 51       | 250      |
| After UV (1)     | 73           | -7        | 98       | 64       | 254      | -56         | 211       | 78       | n.o.     | 50       | 248      |
| After UV (2)     | 74           | -5        | 97       | 64       | 254      | -56         | 210       | n.o.     | n.o.     | 47       | 248      |

Table S8: Degree of crystallinity Xc of PET and PEF before and after UV-exposure calculated from the DSC data. a ΔHcc > ΔHm resulting in a negative value for the crystallinity. b no melting peak observed, Xc couldn’t be calculated.

| Sample          | Xc,1st heating (%) | Xc,2nd heating (%) | Sample          | Xc,1st heating (%) | Xc,2nd heating (%) |
|-----------------|---------------------|---------------------|------------------|---------------------|---------------------|
| PET reactor grade Virgin | 41                  | 41                  | PEF reactor grade Virgin | 22                  | 9                   |
| After UV (1)     | 42                  | 39                  | After UV (1)     | 23                  | 0                   |
| After UV (2)     | 43                  | 39                  | After UV (2)     | 17                  | 5                   |
| PET precipitated Virgin | 42                  | 36                  | PEF precipitated Virgin | 30                  | 28                  |
| After UV (1)     | 41                  | 36                  | After UV (1)     | -10*                | b                   |
| After UV (2)     | 42                  | 34                  | After UV (2)     | -13*                | b                   |
Figure S17: TGA graphs under nitrogen atmosphere of a) reactor grade PEF and b) precipitated PEF before and after UV-exposure. Both reactor grade and precipitated PEF show an earlier onset of mass loss after UV-irradiation. In addition, both show a higher residual mass as compared to the virgin material, which is an indication for cross-linking (also confirmed by GPC). The virgin precipitated PEF, and precipitated PEF after UV-irradiation show a minor mass loss at 100 °C due to the evaporation of water. We attribute this to adsorbed water that is included in the crystalline phase during precipitation of the polymer. Because of the low diffusion rate of water in the crystalline domains, this water is not removed during the isothermal phase prior to the mass loss measurement. Indeed, when the polymer is dried above its $T_g$, significantly enhancing water diffusion, we do not observe a mass loss around 100 °C (data not shown).

Figure S18: Overlay of TGA graphs of reactor grade (black lines) and precipitated PEF (grey lines) after UV-exposure. Precipitated PEF shows a higher mass loss rate at lower temperatures as compared to the reactor grade PEF. The residual mass, however, is comparable for the precipitated and reactor grade PEF.
8. ATR-FTIR

![ATR-FTIR spectra of a) reactor grade PEF and b) precipitated PEF as obtained directly after UV-irradiation. The spectrum before UV-exposure is given in black whereas the spectra of the duplicate measurements after UV-exposure are given in blue. All spectra were normalized relative to the absorption at 764 cm\(^{-1}\). After UV-irradiation a broad signal from 3700-2200 cm\(^{-1}\) is observed caused by hydroxyl groups. Also the carbonyl signals broaden due new carbonyl groups with absorption maxima around 1660 cm\(^{-1}\) (carboxylic acid) and 1785 cm\(^{-1}\).](image-url)
**Figure S20**: A possible solution of the peak deconvolution of the carbonyl region in the ATR-FTIR spectra of PEF into three (virgin) or four (after UV) Gaussian curves (see Table S9). All spectra were baseline corrected prior to deconvolution. a) Reactor grade virgin, b) reactor grade after UV (1), c) reactor grade after UV (2), d) precipitated virgin, e) precipitated after UV (1), f) precipitated after UV (2). The measurement data are given in black, the sum of the Gaussians in blue, and the second derivative in red. The main absorption peak consists of Gaussians found at ~1715 cm\(^{-1}\) and at ~1745 cm\(^{-1}\), which are attributed to amorphous and crystalline carbonyl regions, respectively\(^4\). The shoulder around ~1660-1640 cm\(^{-1}\) is attributed to carboxylic acid groups (see reference spectra in Figure S22), and the shoulder at ~1780cm\(^{-1}\) is most likely attributed to anhydride groups (see reference spectra in Figure S23). However, the formation of (aliphatic) aldehyde or perester groups cannot be excluded due to overlap of the absorptions (Figure S23).

**Table S9**: Wavenumber (\(\tilde{\nu}\)) and absorbance (A) of the maxima of the Gaussian curves found by peak deconvolution of the carbonyl region into three or four Gaussians of the ATR-FTIR spectra.

| Sample                  | Gaussian 1 | Gaussian 2 | Gaussian 3 | Gaussian 4 |
|-------------------------|------------|------------|------------|------------|
|                         | \(\tilde{\nu}\) (cm\(^{-1}\))/ A (a.u.) | \(\tilde{\nu}\) (cm\(^{-1}\))/ A (a.u.) | \(\tilde{\nu}\) (cm\(^{-1}\))/ A (a.u.) | \(\tilde{\nu}\) (cm\(^{-1}\))/ A (a.u.) |
| PEF reactor grade       |            |            |            |            |
| Virgin                  | not present| 1745/0.39  | 1715/0.80  | 1686/0.21  |
| After UV (1)            | 1775/0.14  | 1745/0.47  | 1713/1.14  | 1668/0.27  |
| After UV (2)            | 1778/0.08  | 1746/0.46  | 1714/1.17  | 1665/0.18  |
| PEF precipitated        |            |            |            |            |
| Virgin                  | not present| 1740/0.65  | 1717/0.88  | 1691/0.15  |
| After UV (1)            | 1778/0.14  | 1726/0.91  | 1709/0.74  | 1643/0.18  |
| After UV (2)            | 1776/0.11  | 1724/1.13  | 1712/0.32  | 1648/0.11  |
**Figure S21**: A possible solution of the peak deconvolution of the carbonyl region in the ATR-FTIR spectra of PEF into six Gaussian curves (see Table S10). From the second derivative, it can be concluded that the ATR-FTIR spectrum of the carbonyl region consists of more than three or four Gaussians. Therefore, the carbonyl region was fitted with a maximum of six Gaussians. Again, the measurement data are given in black, the sum of the Gaussians in blue, and the second derivative in red. a) Reactor grade virgin, b) reactor grade after UV (1), c) reactor grade after UV (2), d) precipitated virgin, e) precipitated after UV (1), f) precipitated after UV (2). The shoulders that appear on both the right- and left-hand side of the main carbonyl absorption after UV-irradiation can be fitted as sum of two Gaussians with absorption maxima at ~1800 and ~1775 for the left-hand side, and ~1670-1680 and ~1640 cm$^{-1}$ for the right-hand side.

**Table S10**: Wavenumber ($\tilde{\nu}$) and absorbance (A) of the maxima of the Gaussian curves found by peak deconvolution of the carbonyl region up to six Gaussians of the ATR-FTIR spectra.

| Sample          | Gaussian 1 $\tilde{\nu}$ (cm$^{-1}$) / A (a.u.) | Gaussian 2 $\tilde{\nu}$ (cm$^{-1}$) / A (a.u.) | Gaussian 3 $\tilde{\nu}$ (cm$^{-1}$) / A (a.u.) | Gaussian 4 $\tilde{\nu}$ (cm$^{-1}$) / A (a.u.) | Gaussian 5 $\tilde{\nu}$ (cm$^{-1}$) / A (a.u.) | Gaussian 6 $\tilde{\nu}$ (cm$^{-1}$) / A (a.u.) | Gaussian 7 $\tilde{\nu}$ (cm$^{-1}$) / A (a.u.) |
|-----------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| **PEF reactor grade**                                      |                                               |                                               |                                               |                                               |                                               |                                               |
| Virgin          | not present                                   | not present                                   | 1746 / 0.41                                   | not present                                   | 1714 / 0.94                                   | 1676 / 0.21                                   | 1631 / 0.09                                   |
| After UV (1)    | 1796 / 0.09                                   | 1772 / 0.12                                   | 1746 / 0.59                                   | not present                                   | 1712 / 1.28                                   | 1675 / 0.17                                   | 1642 / 0.17                                   |
| After UV (2)    | 1794 / 0.05                                   | 1767 / 0.10                                   | 1742 / 0.74                                   | not present                                   | 1712 / 1.10                                   | 1684 / 0.33                                   | 1644 / 0.14                                   |
| **PEF precipitated**                                     |                                               |                                               |                                               |                                               |                                               |                                               |
| Virgin          | not present                                   | not present                                   | 1746 / 0.44                                   | 1730 / 0.22                                   | 1718 / 0.94                                   | 1683 / 0.12                                   | 1630 / 0.03                                   |
| After UV (1)    | 1800 / 0.08                                   | 1774 / 0.12                                   | not present                                   | 1724 / 1.08                                   | 1709 / 0.56                                   | not present                                   | 1638 / 0.18                                   |
| After UV (2)    | 1802 / 0.07                                   | 1774 / 0.10                                   | not present                                   | 1728 / 0.95                                   | 1715 / 0.56                                   | 1667 / 0.17                                   | 1625 / 0.10                                   |
Figure S22: ATR-FTIR spectra of furan-based reference compounds. a) overlay of all furan-based reference compounds from 3350-1350 cm$^{-1}$. b-g) Full spectra of 2,5-furandicarboxylic acid (2,5-FDCA), 2-methyl 2,5-furandicarboxylate (2,5-FMME), dimethyl 2,5-furandicarboxylate (2,5-FDME), dibutyl 2,5-furandicarboxylate (2,5-DBF), methyl 2-furoate (M2F), 5-formyl-2-furancarboxylic acid methyl ester (MeFFA), and 5-formyl-2-furancarboxylic acid ethyl ester (EtFFA), respectively.
**Figure S23:** ATR-FTIR spectra of other reference compounds. a) overlay of the carbonyl region of all reference compounds (1950-1550 cm\(^{-1}\)). b-k) Full spectra of heptanal (HA), benzyloxyacetaldehyde (BOA), phthalic anhydride (PA), homophthalic anhydride (HPA), trimellitic anhydride (TMA), succinic anhydride (SA), diglycolic anhydride (DGA), maleic anhydride (MA), itaconic anhydride (IA), and tert-butyldihydrobenzoate (tBPB), respectively.
**Figure S24:** ATR-FTIR spectra before and after drying (*in vacuo* overnight at 40 °C) of a) reactor grade PEF and b) precipitated PEF after UV-exposure. The spectrum before drying is shown in grey whereas the spectra of the same material after drying is shown in black. All spectra are normalized relative to the absorption at 764 cm\(^{-1}\). The reactor grade PEF shows only a minor decrease in intensity in the 3700-2200 cm\(^{-1}\) region, proving that this absorption is mainly caused by non-volatile hydroxyl groups. In contrast, there is a decrease in intensity for the same absorption in the precipitated PEF, showing that some water was present which is in agreement with the TGA results. Both show a decrease in the absorption of carboxylic acid groups at 1660 cm\(^{-1}\) upon drying.
Figure S25: ATR-FTIR spectra of a) reactor grade PET and b) precipitated PET as obtained directly after UV-irradiation. The spectrum before UV-exposure is given in black whereas the spectra of the duplicate measurements after UV-exposure are given in blue. All spectra were normalized relative to the absorption at 724 cm$^{-1}$. 
9. $^1$H-NMR and $^{13}$C-NMR

**Figure S26:** Pictures of a,b) reactor grade and precipitated PEF and c,d) reactor grade and precipitated PET dissolved in a 6:1 mixture CDCl$_3$:TFA. Both reactor grade and precipitated PEF become partially insoluble after UV-irradiation as indicated by the yellow gel-like material at the bottom of the vial.

**Figure S27:** Full scale 1H-NMR spectra of a) reactor grade PEF and b) precipitated PEF before and after UV-exposure showing the main polymer signals. All NMR spectra are normalized to the signal at 4.71 ppm (b, ethylene glycol).
Figure S28: Zoomed 1H-NMR spectra a) reactor grade PEF and b) precipitated PEF before and after UV-exposure showing that several new signals, albeit with a very low intensity, appear after UV-irradiation. All NMR spectra are normalized to the signal at 4.71 ppm (ethylene glycol). A more detailed assignment of the PEF signals can be found in Figure S29.

Table S11: Integrals of newly formed signals in the 1H-NMR spectra of reactor grade and precipitated PEF after UV-irradiation. All integrals are relative to the furanic signal (set at a value of 2). a Overlaps with ethylene glycol signal, b overlaps with TMS signal. Only signals which have an intensity >0.001 in at least one sample are given. The formation of free carboxylic acid is not observed in the 1H-NMR data, indicating that the formation of carboxylic acid groups is probably a surface effect.

| Chemical shift (ppm) | PEF reactor grade | PEF precipitated |
|----------------------|-------------------|------------------|
|                      | after UV (1)      | after UV (2)     | after UV (1) | after UV (2) |
| 9.69                 | 0.0002            | 0.0009           | 0.0004       | 0.0011       |
| 8.01                 | 0.0049            | 0.0009           | 0.0037       | 0.0016       |
| 6.81                 | 0.0012            | 0.0007           | 0.0039       | 0.0007       |
| 6.40                 | 0.0025            | 0.0022           |              |              |
| 5.08                 | 0.0064 a          | 0.0048 a         | 0.0062       | 0.0068       |
| 4.99                 |                   | 0.0126 a         | 0.0102 a     |
| 3.97                 |                   | 0.0169           | 0.0087       |
| 3.42                 | 0.0056            | 0.0020           | 0.0163       | 0.0093       |
| 3.14                 | 0.0038            | 0.0023           | 0.0402       | 0.0575       |
| 2.81                 | 0.0006            | 0.0007           | 0.0117       | 0.0279       |
| 2.20                 | 0.0014            | 0.0022           | 0.0007       | 0.0030       |
| 1.27                 | 0.0037            | 0.0092           | 0.0059       | 0.0317       |
| 0.86                 | 0.0021            | 0.0015           | 0.0056       | 0.0095       |
| 0.41                 | 0.0009            | 0.0027 b         | 0.0020       | 0.0059       |
| 0.35                 |                   |                  |              | 0.0326       |
Figure S29: a,b) Enlarged $^1$H-NMR spectra focusing only on the main polymer signals (furan and ethylene glycol) of reactor grade and precipitated PEF, respectively c) Assignment of protons in the $^1$H-NMR spectra, peaks assigned with an asterisk (*) belong to $^{13}$C satellites, d) table of integrals obtained from the $^1$H-NMR spectra, all integrals are relative to the furan signal (proton a).

Figure S30: $^{13}$C-NMR spectra of a) reactor grade PEF and b) precipitated PEF before and after UV-exposure. All NMR spectra are normalized to the signal at 64 ppm (d, ethylene glycol).
Figure S31: Full scale 1H-NMR spectra of a) reactor grade PET and b) precipitated PET before and after UV-exposure. The signal marked with an asterisk (*) belongs to end-groups. All spectra are normalized to the signal at 4.77 ppm (b, ethylene glycol).

Figure S32: Zoomed 1H-NMR spectra a) reactor grade PET and b) precipitated PET before and after UV-exposure. The same zoom factor has been used as for the spectra of PEF. All NMR spectra are normalized to the signal at 4.77 ppm (ethylene glycol). The heptet at 4.43 ppm (J=6.0 Hz) in the PET precipitated virgin spectrum can be attributed to residual HFIP. New signals after UV-irradiation are observed at 7.66 ppm, 5.12 ppm, 5.03 ppm, 2.75 ppm, however, the intensity of these signals barely exceeds the noise in the baseline.
**Figure S33**: $^{13}$C-NMR spectra of a) reactor grade PET and b) precipitated PET before and after UV-exposure. All spectra are normalized to the signal at 64 ppm (d, ethylene glycol).
10. MALDI-TOF

Figure S34: MALDI-TOF spectra of a) reactor grade PEF and b) precipitated PEF before and after UV-exposure.

Figure S35: Enlarged MALDI-TOF spectra of one PEF repeating unit before and after UV-exposure. All spectra are normalized to the intensity at m/z 2073. The following end-groups were assigned to the signals in the virgin material spectrum: #3: cyclic or ester/ester, #6: ester/-OH, #9: -OH/-OH, #10: ester/diethylene glycol (DEG), #12: -OH/DEG. Only one new signal (#11) is observed after UV-irradiation with an end-group mass of 93 Da. Also the intensity of signal #4 (M_end-groups 17, carboxylic acid/-OH) increases upon UV-irradiation.
Table S12: Assignment of MALDI-TOF signals for both reactor grade and precipitated PEF. Note that a full assignment of all signals is out of scope for this work.

![Polypeptide Structure](image)

| Signal # | M<sub>end-groups found</sub> (Da) | Assigned end-groups | Structure assigned end-groups |
|----------|-------------------------------|---------------------|------------------------------|
| 1        | 169                           |                     |                              |
| 2        | 177                           |                     |                              |
| 3        | 1                             | cyclic (0)          |                              |
| 4        | 17                            | carboxylic acid/-OH (18.0) | HO-P-H                      |
| 5        | 25                            |                    |                              |
| 6        | 31                            | ester/-OH (32.0)    | O-P-H                       |
| 7        | 45                            |                    |                              |
| 8        | 55                            |                    |                              |
| 9        | 61                            | -OH/-OH (62.1)      | HO-O-P-H                    |
| 10       | 75                            | ester/DEG (258.2/76.1) |                            |
| 11       | 93                            |                    |                              |
| 12       | 105                           | -OH/DEG (106.1)     | HO-O-O-O-P-H                |
Figure S36: MALDI-TOF spectra of a) reactor grade PET and b) precipitated PET before and after UV-exposure.

Figure S37: Enlarged MALDI-TOF spectra of one PET repeating unit before and after UV-exposure. All spectra are normalized to the intensity at m/z 2154. The following end-groups were assigned to the signals in the virgin material spectrum; #3: cyclic or ester/ester, #6: ester/-OH, #7: not assigned M_end-groups. There are only very minor differences observed after UV-irradiation. The intensity of signal #2 (M_end-groups 179) increases, and new signals (#4: M_end-groups 17 carboxylic acid/-OH, #5: M_end-groups 25) are observed, both with an intensity <3%.
Table S13: Assignment of MALDI-TOF signals for both reactor grade and precipitated PET. Note that a full assignment of all signals is out of scope for this work.

![PET structure](image)

| Signal # | M<sub>end-groups</sub> found (Da) | Assigned end-groups | Structure assigned end-groups |
|----------|----------------------------------|---------------------|------------------------------|
| 1        | 167                              |                     |  |
| 2        | 179                              | cyclic (0)          | ![Structure image](image) |
| 3        | 2                                | ester/ester (194.2/2.0) | ![Structure image](image) |
| 4        | 17                               | carboxylic acid/-OH (18.0) | ![Structure image](image) |
| 5        | 25                               |                      |  |
| 6        | 32                               | ester/-OH (32.0)    | ![Structure image](image) |
| 7        | 46                               |                      |  |
| 8        | 62                               | -OH/-OH (62.1)      | ![Structure image](image) |
| 9        | 76                               | ester/DEG (268.3/76.1) | ![Structure image](image) |
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