

Electronic Supporting information (ESI)

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A) Materials

1,3-propanediol was purchased from Sigma-Aldrich; antimony trioxide was supplied by Carlo Erba. 2,5-furandicarboxylic acid (FDCA) was provided by Tetrapak. PET was produced by Invista (trade name: 7001 resin). All the reagents were supplied in high purity and therefore used without further purifications.

B) Synthesis of Poly(propylene 2,5-furandicarboxylate) (PPF)

15.61 g (0.100 mol) of FDCA, 13.70 g (0.180 mol) of 1,3-propanediol and 220 mg ($7.5 \cdot 10^{-4}$ mol) of antimony trioxide were charged into a glass reactor, equipped with a stirrer, a temperature programmer, a vacuum controller and a torque meter which gives an indication of the viscosity of the reaction melt. The reactor was immersed into a salt bath preheated to 180°C for 30 min. The first stage was conducted at 200°C, atmospheric pressure under nitrogen atmosphere and the mixture was allowed to react for 120 min under stirring (200 rpm) with continuous removal of water. In the second stage the reaction was heated from 220 to 240°C while the pressure was gradually reduced to 0.07 mbar. These conditions were reached within 90 min, using a linear gradient of temperature and pressure, and maintained for 60 min. Finally, the reaction temperature was further increased till 250°C and stirred for 90 min.

C) Film preparation by compression molding and ageing experiments

1.40 g of ground PPF were weighted and scattered on a Teflon foil. The foils were placed between the plates of the Carver press and heated at 200°C, under 5-6 bars over 5 minutes. Then the film was quickly cooled to room temperature, led to room pressure and finally separated by the Teflon foils. The films were aged in an oven at 135°C for 5, 10, 15, 20, 30 minutes in order to change their crystalline degree.

D) Physico-chemical characterization of PPF powder and films

The ¹H NMR analysis on the PPF polymer was performed at room temperature on samples dissolved in a mixture of deuterated chloroform /deuterated trifluoroacetic acid 80/20 (V/V), using a Varian Inova 600 spectrometer at 600 MHz.

Gel permeation chromatography (GPC) analyses on PPF powder and films were carried out by dissolving the materials in a mixture of chloroform/hexafluoroisopropanol (HFIP) (95/5, V/V) and by using chloroform as eluent (elution rate of 0.3 mL min⁻¹) on a HP 1100 Series apparatus equipped with a TSK gel SuperMultiporeHZ-M column and a IR detector. Calibration was performed with polystyrene standards.

The calorimetric analyses were performed by a Perkin–Elmer DSC-6, calibrated with high purity standards. The samples (about 10 mg) were heated from room temperature to 250°C at 20°C min⁻¹ and kept at this temperature for 1 min in order to erase the thermal history. Then, they were cooled to 0°C at 10°C min⁻¹ and maintained 1 min at 0°C. Finally, they were heated from 0°C to 250°C at 10°C min⁻¹ (2nd scan). The glass transition temperature (T_g) was taken as the temperature of the inflection point during the 2nd scan. T_{cc} and ΔH_{cc} refer to cold crystallization process. i.e. crystallization occurring during the heating scan.

The aged films were analyzed from 10 to 240°C at 10°C/min in DSC.

The X-ray diffraction measurements (WAXD) were carried out at room temperature with a Bragg/Brentano diffractometer system (Philips PW1050/81), equipped with a graphite monochromator in the diffracted beam. Cu anode was used as X-ray source. Data were collected in the range from 5 to 60° of 2 θ .

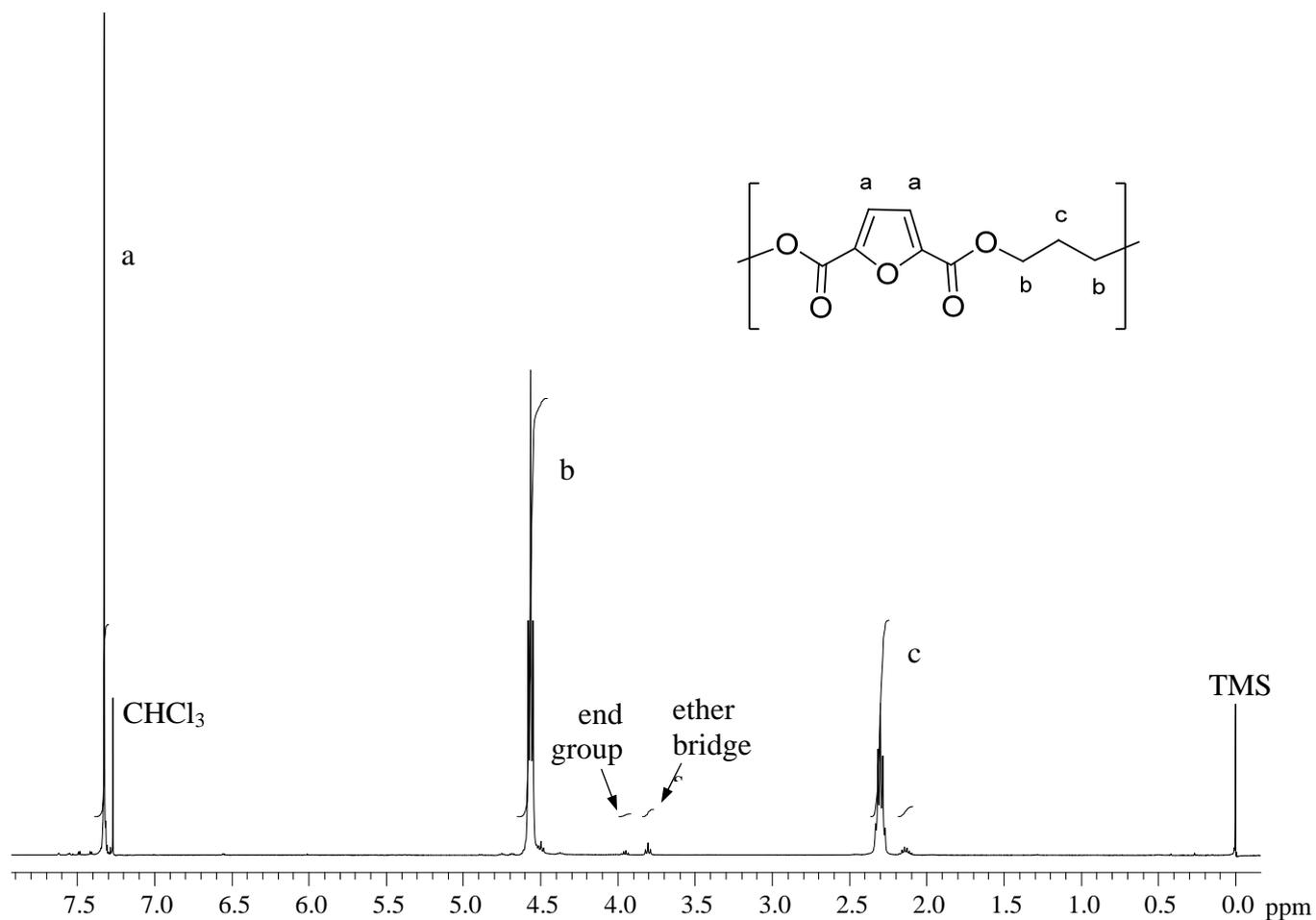
The density of films was calculated for every sample as a ratio between the weighted mass and the measured volume. The volume was determined by using a helium Penta-pycnometer Quantachrome. Every sample was introduced in the 10 cm³ chamber of the pycnometer and a definite-volume steel ball was further added to decrease the vacuum volume and increase the reliability. The samples were subjected to purging with helium gas over 1 minute prior to analysis in order to expel all the air and vapor trapped in the lattice. The analyses were conducted at ambient temperature and pressure.

Specimens for dynamic mechanical measurements were obtained by injection molding in a Mini Max Molder (Custom Scientific Instruments) equipped with a rectangular mold (30 x 8 x 1.6 mm³). Dynamic mechanical measurements were performed with a dynamic mechanical thermal analyzer (Rheometrics Scientific, DMTA IV), operated in the dual cantilever bending mode, at a frequency of 3 Hz and a heating rate of 3 °C/min, over a temperature range from -140 °C to a final temperature.

Oxygen permeability measurement was based on ASTM D3985-02 and done on a Mocon Oxtran® 2/21 instrument at 23°C while same level of relative humidity (RH) of 50 or 90% was used for both test (O₂) and carrier gas (N₂).

Water vapor permeability measurement was based on ASTM F-1249 and done on a Mocon Permatran-W® 3/33 at 37.8 C using 100% RH Nitrogen as test gas at and 0% RH Nitrogen as carrier gas.

E) Figure S1: ^1H -NMR spectrum of PPF



F) Table S1. Characteristics of crude PPF powder

Ether bridges ^{a)} [mol%]	$M_n^{b)}$ $\cdot 10^{-3}$	$M_w^{b)}$ $\cdot 10^{-3}$	$D^{b)}$	$T_g^{c)}$ [$^{\circ}\text{C}$]	$T_{cc}^{c)}$ [$^{\circ}\text{C}$]	$\Delta H_{cc}^{c)}$ [J g^{-1}]	$T_m^{c)}$ [$^{\circ}\text{C}$]	$\Delta H_m^{c)}$ [J g^{-1}]
2.91	18.2	54.6	3.0	54	138	0.8	170	1.0

^{a)} Measured by ^1H NMR; ^{b)} Measured by GPC; ^{c)} Measured in DSC during the second heating scan at $10^{\circ}\text{C min}^{-1}$.