1. Detailed experimental procedure

1.1. Materials

The reagents dimethyl L-tartrate (99%), paraformaldehyde (95%), sodium sulfate (99%), LiAlH₄ (95%), 1,4-butanediol (99%), dimethyl terephthalate (99+) and the catalyst dibutyl tin oxide (DBTO, 98%) were purchased from Sigma-Aldrich. PBT was a kind gift from DSM. Deuterated chloroform (CDCl₃, 99.8% atom d) and deuterated trifluoroacetic acid (TFA-d, 99% atom d) were obtained from Cambridge Isotope Laboratories. Solvents used for purification and characterization were purchased from Panreac and Biosolve and these were all of either technical or high-purity grade. All chemicals were used as received unless stated otherwise.

1.2. General methods

¹H and ¹³C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 °C operating at 300.1 and 75.5 MHz, respectively. Samples were dissolved in a mixture of
deuterated chloroform and deuterated trifluoroacetic acid (9:1), and spectra were internally referenced to tetramethysilane (TMS). Approximately 10 and 50 mg of sample dissolved in 1 mL of the solvent mixture were used for $^1$H and $^{13}$C NMR, respectively. Sixty-four scans were acquired for $^1$H and 1,000-10,000 for $^{13}$C with 32 and 64-K data points as well as relaxation delays of 1 and 2 s, respectively. **Elemental analysis was performed by the Microanalysis Laboratories of the CSIC, Barcelona, Spain.** Size-exclusion chromatography (SEC) was performed on a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector working at 40 °C, a Waters 2707 autosampler, and a PSS PFG guard column followed by a 2PFG-linear-XL (7 μm, 8·300 mm) columns in series at 40 °C. HFIP with potassium trifluoroacetate (3 g·L$^{-1}$) was used as eluent at a flow rate of 0.8 mL·min$^{-1}$. The molecular weights were calculated against polymethyl methacrylate standards (Polymer Laboratories, Mp= 580 Da up to Mp= 7.1·10$^6$ Da). Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC Pyris 1 equipment. DSC thermograms were obtained from 3 to 5 mg samples at heating/cooling rates of 10 °C·min$^{-1}$ under a nitrogen flow of 20 mL·min$^{-1}$. Indium and zinc were used as standards for temperature and enthalpy calibration. The glass-transition temperatures were determined from the third heating run at a heating rate of 20 °C·min$^{-1}$ from rapidly melt-quenched polymer samples. The treatment of the samples for isothermal crystallization experiments was the following: the thermal history was removed by heating the sample up to 250 °C and keeping the sample at this temperature for 5 min, subsequently it was cooled at 20 °C·min$^{-1}$ to the selected crystallization temperature, where it was left to crystallize until saturation. Thermogravimetric analyses were performed under a nitrogen flow of 20 mL·min$^{-1}$ at a heating rate of 10 °C·min$^{-1}$, within a temperature range of 30 to 600 °C, using a Perkin Elmer TGA 6 equipment. Sample weights of about 10-15 mg were used in these experiments. Wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku Geigerflex Bragg-Brentano Powder Diffractometer using Cu radiation, wavelength 1.54056 Å, at 40 kV and 30 mA. The scans were performed with 0.02 ° steps and a dwell time of 3 s in the 20 range from 10 ° till 35 °. The analyses were performed on the crude
copolyester samples. Scanning electron microscopy (SEM) images were taken with a field-emission JEOL JSM-7001F instrument (JEOL, Japan) from platinum/palladium coated samples.

**1.3. Monomer synthesis**

A mixture of dimethyl L-tartrate (15 g, 84.3 mmol) and paraformaldehyde (15 g, 498 mmol) was heated to 60 °C under stirring. Subsequently, 20 mL of sulfuric acid 98% was added drop wise and the resulting mixture was stirred until complete dissolution. The resulting solution was repeatedly extracted with chloroform. The organic layers were combined and washed with an aqueous solution of ammonia (25% w/w) and water, and finally dried over anhydrous sodium sulfate. The chloroform was evaporated and the obtained material was purified by vacuum distillation to obtain an oil, dimethyl 2,3-O-methylene-L-tartrate (yield: 60%).

To a cooled solution of 5 g of dimethyl 2,3-O-methylene-L-tartrate (26.3 mmol) in 40 mL of dry diethyl ether, 2.67 g LiAlH4 (68.1 mmol) in 40 mL dry diethyl ether was added under nitrogen atmosphere. The mixture was stirred for 12 h after which it was cooled to 0 °C. Successively 7 mL H2O, 8 mL of a aqueous NaOH (15% w/v) solution, and 25 mL H2O were slowly added to the reaction mixture. The resulting mixture was filtrated and the solids were extracted with hot acetone. The combined extracts were evaporated to dryness and purified by vacuum distillation, to obtain an yellowish oil, 2,3-O-methylene-L-threitol (yield: 75%). Found: C, 44.9; H, 7.6. Calc. for C5H10O4: C, 44.8; H, 7.5%.

**1.4. Polymer synthesis**

**1.4.1. Melt polycondensation (MP)**

Thx-based copolyesters were obtained from a mixture of 1,4-butanediol (1,4-BD), the cyclic diol 2,3-O-methylene-L-threitol (Thx) and dimethyl terephthalate (DMT) with a predetermined composition. PThxT homopolyester was obtained by reacting Thx with DMT. The reactions were performed in a three-necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a vacuum distillation outlet. A 5% molar excess of the
diol mixture to DMT was used, and dibutyl tin oxide (DBTO, 0.6% molar with respect to monomers) was the catalyst of choice. The apparatus was purged with nitrogen several times at room temperature in order to remove the last traces of air. Transesterification reactions were carried out under a low nitrogen flow at the selected temperature. Polycondensation reactions were performed at a selected temperature under a 0.03-0.06 mbar vacuum. At the end of the reaction, the reaction mixture was cooled to room temperature under a nitrogen atmosphere. The resulting polymers were dissolved in a mixture of chloroform and trifluoroacetic acid (9:1) and precipitated in an excess of methanol. Finally, the polymer was collected by filtration, extensively washed with methanol and dried under vacuum. The detailed reaction conditions are given below. The Thx-based copolyesters obtained via MP are abbreviated as \( \text{MPPB}_x\text{Thx}_y\text{T} \), where \( x \) and \( y \) are the mole percentages (mol-%) of 1,4-BD and Thx, respectively, in the resulting copolyester.

**PThxT homopolyester.** Transesterification reactions were performed at 160 °C for 2 h and at 180 °C for 1 h under a low nitrogen flow. Polycondensation reactions were performed at 180 °C for 8 h under a 0.03-0.06 mbar vacuum. \(^1\)H NMR (300.1 MHz, CDCl\(_3\)/TFA), \( \delta \) (ppm): 8.1 (s, 4H, Ar-H), 5.3 (s, 2H, OCH\(_2\)O), 4.6 (m, 4H, OCH\(_2\)CH), 4.5 (m, 2H, OCH\(_2\)CH). \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)/TFA), \( \delta \) (ppm): 167.0 (CO), 133.5, 130.3, 95.7, 75.9, 64.9.

**MP\( \text{PB}_x\text{Thx}_y\text{T} \) copolyesters.** The copolyesters were obtained by a similar procedure, with polymerization conditions slightly differing for each composition feed.

- **MP\( \text{PB}_{96}\text{Thx}_4\text{T} \).** Transesterification reactions were performed at 160 °C for 1 h, at 200 °C for 1 h and at 240 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions were performed at 250 °C for 2.5 h under a 0.03-0.06 mbar vacuum.

- **MP\( \text{PB}_{91}\text{Thx}_9\text{T} \).** Transesterification reactions were performed at 160 °C for 1 h, at 200 °C for 1 h and at 240 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions were performed at 240 °C for 3 h under a 0.03-0.06 mbar vacuum.

- **MP\( \text{PB}_{84}\text{Thx}_16\text{T} \) and MP\( \text{PB}_{82}\text{Thx}_18\text{T} \).** Transesterification reactions were performed at 160 °C for 1 h, at 200 °C for 1 h and at 230 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions were performed at 230 °C for 3.5 h under a 0.03-0.06 mbar vacuum.
**MPPB**\textsubscript{77}Thx\textsubscript{23}T and **MPPB**\textsubscript{71}Thx\textsubscript{29}T. Transesterification reactions were performed at 160 °C for 1 h, at 200 °C for 1 h and at 220 °C for 0.5 h under a low nitrogen flow. Polycondensation reactions were performed at 220 °C for 4 h under a 0.03-0.06 mbar vacuum.

NMR characterization of **MPPB**\textsubscript{x}Thx\textsubscript{y}T copolyesters. $^1$H NMR (300.1 MHz, CDCl\textsubscript{3}/TFA), $\delta$ (ppm): 8.1 (s, 4H, Ar-H), 5.3 (s, y·2H, OCH\textsubscript{2}O), 4.6 (m, y·4H, OCH\textsubscript{2}CH), 4.5 (t, x·4H, OCH\textsubscript{2}CH\textsubscript{2}), 4.5 (m, y·2H, OCH\textsubscript{2}CH\textsubscript{2}), 2.0 (t, x·4H, OCH\textsubscript{2}CH\textsubscript{2}). $^{13}$C NMR (75.5 MHz, CDCl\textsubscript{3}/TFA), $\delta$ (ppm): 168.0 (CO), 167.0 (CO), 134.2-133.2, 130.3, 130.1, 95.7, 75.9, 66.3, 64.9, 25.4.

### 1.4.2. Solid-state modification (SSM) of PBT

Physical mixtures of purified PBT ($M_\text{n} = 23.3$ kg·mol\textsuperscript{-1} and $M_\text{w} = 47.1$ kg·mol\textsuperscript{-1}, determined by SEC), the cyclic diol Thx, and DBTO catalyst (0.36% molar with respect to PBT) were prepared from solution, using a common solvent approach as described elsewhere,\textsuperscript{32} in which the PBT was first precipitated to remove any titanium-based catalysts. Different molar ratios of PBT and Thx were used in order to obtain copolyesters with varying compositions. The solid-state modification of PBT was performed in a reactor comprising a glass tube (inner diameter= 2.4 cm) with a sintered glass frit at the bottom. A heat exchange glass coil (inner diameter= 0.5 mm) surrounded the reactor and entered the inner glass tube at the bottom just below the glass frit. The nitrogen gas was heated by passing through this coil prior to entering the reactor, which was immersed in an oil bath kept at 160 °C. The nitrogen flow was controlled by a flow-meter. Typically, 0.4 g of the PBT/Thx physical mixture was placed on the sintered glass plate. The powder was fixed in place by addition of glass pearls (diameter= 2 mm) on top of the powder, and the reactor was purged with a nitrogen flow of 0.5 L·min\textsuperscript{-1} during 30 min prior to the reaction. Reactions were left to proceed at 160 °C under a 0.5 L·min\textsuperscript{-1} nitrogen flow until the desired molecular weights were attained, which were followed as function of reaction time using SEC. Reaction times were in the 4-20 h range. After completion of the reaction, the reactor was gradually cooled down to room temperature by removing the heat source and by continuing the purging of the reactor with nitrogen. Subsequently, the obtained polymer was
dried under vacuum. The Thx copolyesters obtained via SSM are abbreviated as \texttt{SSM}PB$_x$Th$_y$T, where \( x \) and \( y \) are the mole percentages (mol-%) of 1,4-BD and Thx, respectively, in the resulting copolyester.

NMR characterization of \texttt{SSM}PB$_x$Th$_y$T copolyesters. $^1$H NMR (300.1 MHz, CDCl$_3$/TFA), $\delta$ (ppm): 8.1 (s, 4H, Ar-H), 5.3 (s, $y$·2H, OCH$_2$O), 4.6 (m, $y$·4H, OCH$_2$CH), 4.5 (t, $x$·4H, OCH$_2$CH$_2$), 4.5 (m, $y$·2H, OCH$_2$CH), 2.0 (t, $x$·4H, OCH$_2$CH$_2$). $^{13}$C NMR (75.5 MHz, CDCl$_3$/TFA), $\delta$ (ppm): 168.0 (CO), 167.0 (CO), 134.2-133.2, 130.3, 130.1, 95.7, 75.9, 66.3, 64.9, 25.4.

1.5. Hydrolytic degradation procedures

Films for the hydrolytic degradation studies on the (co)polyesters were prepared with a thickness of approx. 200 µm by casting from solution (100 g·L$^{-1}$) in a mixture of chloroform and 1,1,1,3,3,3-hexafluoroisopropanol (5:1). The films were cut into disks with a diameter of 10 mm and a weight of 20 to 30 mg, which were subsequently dried under vacuum to constant weight. For the hydrolytic degradation, samples were immersed in vials containing 10 mL of citric acid buffer (pH 2.0) at 80 ºC. After incubation for a predetermined period of time, the samples were rinsed thoroughly with distilled water, dried to constant weight and analyzed by SEC chromatography, NMR spectroscopy and SEM microscopy.

For hydrolytic degradation studies of the monomer 2,3-\(O\)-methylene-\(L\)-threitol, samples of this diol (80 mg) were immersed in NMR tubes containing 1 mL of citric acid buffer (pH 2.0), sodium phosphate buffer (pH 7.4) or sodium carbonate buffer (pH 10.5), all of them prepared in D$_2$O, and were incubated at 80 ºC for 6 weeks. The residue left after incubation was analyzed by NMR spectroscopy.
2. Figures and tables

**Figure S1.** TGA traces of $^{MP}$PB$_{x}$Th$_{y}$T copolyesters.

**Figure S2.** TGA traces of $^{SSM}$PB$_{x}$Th$_{y}$T copolyesters.
Figure S3. WAXD profiles of $^{MP}$PB$_{x}$Th$_{y}$T and $^{SSM}$PB$_{x}$Th$_{y}$T copolyesters with indication of the $d$ in Å.

Table S1. Powder X-ray diffraction data.

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$^a$Bragg spacings measured in powder diffraction patterns for samples coming directly from synthesis. Intensities visually estimated as follows: m, medium; s, strong; w, weak. $^b$Crystallinity index calculated as the quotient of crystalline area and total area. Crystalline and amorphous areas in the X-ray diffraction pattern were quantified using PeakFit v4.12 software.
Figure S4. DSC traces of the first heating run of $^{SSM}PB_{92}Th_{18}T$ copolyester as a function of the residence time in the melt, with indication of their degrees of randomness $R$.

Figure S5. Log-log plot of PBT, $^{MP}PB_{96}Th_{4}T$, $^{MP}PB_{91}Th_{9}T$, $^{SSM}PB_{96}Th_{4}T$ and $^{SSM}PB_{91}Th_{9}T$ isothermally crystallized at 200 ºC.
Figure S6. SEM micrographs of PBT (a), $^{MP}$PB$_{62}$Thx$_{18}$T (b), $^{SSS}$PB$_{62}$Thx$_{18}$T (c) and PThxT (d): Initial sample (left) and after incubation at pH 2.0 at 80 °C for 6 weeks (right).
Figure S7. Compared $^1$H NMR spectra in CDCl$_3$/TFA of $^{MPB_8}_{2}{Thx_{18}T}$ after incubation at pH 2.0 at 80 ºC for 6 weeks (top) and initial sample (bottom).

Figure S8. Compared $^1$H NMR spectra in CDCl$_3$/TFA of $^{SSM}_{PB_8}_{2}{Thx_{18}T}$ after incubation at pH 2.0 at 80 ºC for 6 weeks (top) and initial sample (bottom).
**Figure S9.** Compared $^1$H NMR spectra in CDCl$_3$/TFA of PBT after incubation at pH 2.0 at 80 ºC for 6 weeks (top) and initial sample (bottom).

**Figure S10.** Compared $^1$H NMR spectra in D$_2$O of 2,3-$O$-methylene-$L$-threitol after incubation for 6 weeks at pH 2.0 (a), 7.4 (b) and 10.5 (c).