

## Electronic Supplementary Information

### **Biodegradable all polyester-based multiblock copolymer elastomers with controlled properties**

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## EXPERIMENTAL SECTION

**Materials.** Adipic acid (99.6%, Tangshan Zhonghao Chemical Industry Co. Ltd.), ethylene glycol (EG) (99.5%, Sinopharm Chemical Reagent Co. Ltd.), tetrabutyl titanate (98%, Sinopharm Chemical Reagent Co. Ltd.), cyclic oligo(butylene terephthalate)s (COBTs) (Starbetter (Shanghai) Chemical Materials Co. Ltd.), Lipase PS (*Burkholderia cepacia*,  $\geq 23,000$  U/g, pH 7.0, 50 °C, Aladdin Industrial Co. Ltd.), potassium phosphate buffer (pH 7.4, Aladdin Industrial Co. Ltd.) were used as received.

### **Instrumentation.**

The apparent number-average molar mass ( $M_n$ , GPC) and polydispersity ( $D$ ) of various copolymers were measured by TOSOH HLC-8320 gel permeation chromatography (GPC) using three TSK gel Super Multipore HZ-M columns at 40 °C. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.35 mL/min, and the samples were calibrated with PS standard samples. The samples were dissolved in THF with a concentration of 1.0 mg/mL.

Nuclear magnetic resonance (NMR) spectra were recorded on an Agilent Direct-Drive II 600 MHz NMR instrument using  $(\text{CF}_3)_2\text{CDOD}/\text{CDCl}_3$  (1:10 in volume) as the solvent and tetramethylsilane (TMS) as the internal standard, with the solution concentration of 10 mg/mL at 25 °C. During the acquisition periods of both 1D and 2D-NMR experiments,  $^{13}\text{C}$  were decoupled by WURST-40. The  $^1\text{H}$  quantitative NMR spectra were collected with a 1.50 s acquisition time, 20 s relaxation delay, 9.6 kHz spectral window, 32 transients, and 8.4  $\mu\text{s}$  90° pulse width. The  $^1\text{H}$ - $^1\text{H}$  gCOSY (gradient correlation spectroscopy) experiments were performed with the standard Agilent sequence. This was done with a 9.6 kHz spectral width, 0.15 s acquisition time, 1 s relaxation delay, and 10.25  $\mu\text{s}$  90° pulse width; a total of 8 transients were averaged for 256 increments using the States method of Orthogonal detection in f1. Processing was done with shifted sine bell weighting functions in both dimensions and zero-filling to a 2048  $\times$  2048 data matrix prior to Fourier transformation.

Differential scanning calorimetry (DSC) was carried out from 0 °C to 280 °C on a TA Q100 instrument under a nitrogen atmosphere at a scanning rate of 10 °C/min for about 3-5 mg samples. The first cooling and second heating scans were used to determine the melting and crystallization peaks.  $T_m$  was taken from the peak temperature of the melting endotherm.

Dynamic mechanical analysis (DMA) was conducted on a TA Instrument Q800. Rectangular samples with size of 30 mm × 5 mm were clamped in multi-frequency-strain mode using tension: film ramp. The frequency was 1 Hz, while the furnace heated at 3 °C/min from -110 °C to the temperature above which the storage modulus of the sample was too low to be measured by the instrument.  $T_g$  measurements were recorded using the maximum in  $\tan \delta$  peak. All DMA test strips were dried overnight at 80 °C under vacuum to remove residual water. The measurement was replicated up to 5 times for each sample.

The copolyesters were dried at 50 °C under vacuum for 24 h to remove residual water prior to compression molding. Films (0.5 mm thick) were pressed between two PTFE sheets at 220 °C and 10 MPa for 4 min before immediately quenching in a cold press at room temperature under a pressure of 10 MPa. Tensile tests were performed at an Instron model 5966 universal material testing system, which maintained under the same conditions and operated at an extension rate of 10 mm/min. Dumbbell-shaped tensile-test specimens (central portion, 2.96 mm width × 0.5 mm thick; gauge length 18 mm) were cut from the sheets and conditioned at room temperature for 24 h.

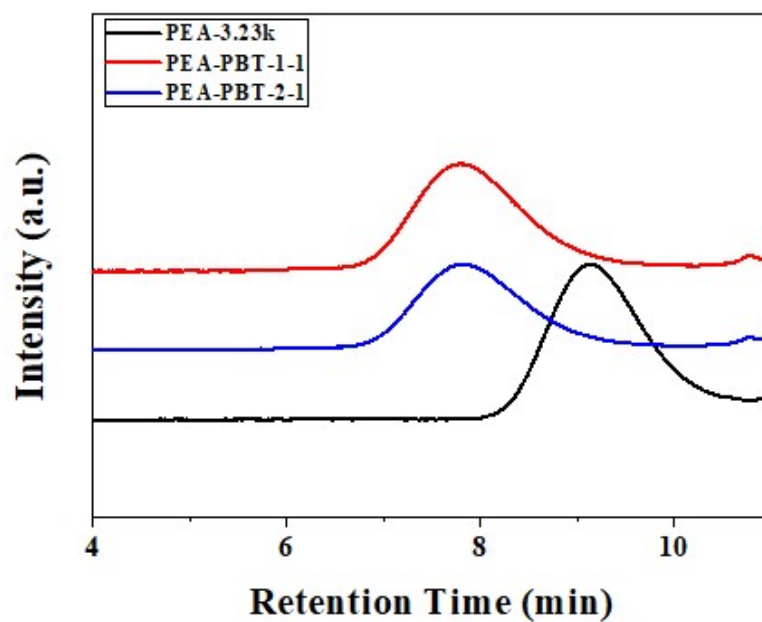
Copolyester films (disc-shape with  $d = 0.2$  mm) were incubated in shaking table at  $37 \pm 0.1$  °C, 120 rpm/min, in duplicate, in sample bottles containing potassium phosphate buffer (pH = 7.4, the ratio is 10 mg sample to 1 mL buffer), in the presence of lipase PS (1 mg/mL). Reference sample were in same sample bottles containing potassium phosphate buffer without lipase PS. The solution was changed every 3 days. At each time point, samples were removed from the solution and washed with distilled water several times, and dried at 35 °C under vacuum for 12 h. Finally, the degradation products were weighted.

The biodegradability was investigated by the weight ratio  $m/m_0$ , where  $m_0$  and  $m$  were initial weight and the weight after degradation.

Table S1 The peak integration value from  $^1\text{H}$  quantitative NMR spectra of  $(\text{PBT-}b\text{-PEA-}b\text{-PBT})_n$  multiblock copolyesters.

Sample	$I_a$	$I_b$	$I_c$	$I_d$	$I_e$	$I_f$	$I_g$	$I_h$	$I_i$	$I_j$	$I_k$	$I_l$
PEA-PBT-2-1	40.0	1.9	11.9	29.5	9.8	1.2	73.7	9.2	4.8	0.1	0.9	102.1
PEA-PBT-1-1	40.0	3.5	9.7	27.9	9.1	0.5	26.8	8.9	4.4	0.1	0.4	51.0
PEA-PBT-1-2	40.0	6.1	6.3	25.2	8.8	0.2	6.2	8.6	3.9	0.1	0.3	23.2

Supporting Figure:



**Fig. S1.** The GPC curves of macroinitiator PEA diol, and PEA-PBT-1-1 and PEA-PBT-2-1 copolyesters.

Eluent: THF, concentration: 1.0 mg/mL.