# - Supporting Information -

# Thermoplastic polyester elastomers based on long-chain crystallizable aliphatic hard segments

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#### 1. Polymer thermal properties and molecular weights



**Figure S1.** DSC thermograms (second heating) of polyester-polyether copolymers based on PTMG<sub>1000</sub>.



**Figure S2.** DSC thermograms (second heating) of polyester-polyether copolymers based on PPDO<sub>2000</sub>



**Figure S3.** DSC thermograms (second heating) of polyester-polyether copolymers based on PPDO<sub>1000</sub>



**Figure S4.** DSC thermograms (second heating) of polyester-polyether copolymers based on  $C_{12}$  monomers

Entry		mol-% polyether diol of total diol	M <sub>n</sub> <sup>a</sup>	$M_w/M_n^a$	T <sub>m</sub> b	T <sub>c</sub> <sup>b</sup>
			[g mol <sup>-1</sup> ]		[°C]	[°C]
1	TPE-C <sub>12</sub> PTMG <sub>2000</sub> -62wt%	29% PTMG <sub>2000</sub>	5.5 x 10 <sup>4</sup>	1.9	17/66	1/45
2	TPE-C <sub>12</sub> PPDO <sub>2000</sub> -62wt%	29% PPDO <sub>2000</sub>	11.5 x 10 <sup>4</sup>	2.0	62	38

Table S1. Polyester-polyether copolymers based on dodecanedioic acid and dodecanediol.

<sup>a)</sup>Determined by GPC in THF at 50 °C *versus* polystyrene standards. <sup>b)</sup>Determined by DSC with a heating/cooling rate of 10 K min<sup>-1</sup>.

## 2. Tensile testing



Figure S5. Elongation at break of PTMG copolymers (crosshead speed of 50 mm min<sup>-1</sup>).



Figure S6. Elongation at break of PPDO copolymers (crosshead speed of 500 mm min<sup>-1</sup>).



Figure S7. Correlation of Young moduli and polymer composition.

**Table S2.** Mechanical properties of polyester-polyether copolymers based on dodecanedioic acid and dodecanediol.<sup>a</sup>

Entry		mol-% polyether diol of total diol	Young modulus <sup>b</sup>	ε <sub>b</sub> ¢	€b <sup>d</sup>	Permanent set <sup>e</sup>
			[MPa]	[%]	[%]	[%]
1	TPE-C <sub>12</sub> PTMG <sub>2000</sub> -62wt%	29% PTMG <sub>2000</sub>	42	880	-	25
2	TPE-C <sub>12</sub> PPDO <sub>2000</sub> -62wt%	29% PPDO <sub>2000</sub>	22	-	240	22

<sup>a)</sup> Tensile tests following ISO 527/1-2, specimen type 5A prepared by injection molding. <sup>b)</sup> Crosshead speed 1 mm/min. <sup>c)</sup> Crosshead speed 50 mm/min. <sup>d)</sup> Crosshead speed 500 mm/min <sup>e)</sup> determined from hysteresis experiments after 10 cycles at an elongation of 100%.



**Figure S8.** Stress-strain curves of polyester-polyether copolymer TPE-C<sub>23</sub>PTMG<sub>2000</sub>-65wt% (dashed line) and TPE-C<sub>12</sub>PTMG<sub>2000</sub>-62wt% (solid line).



**Figure S9.** Stress-strain curves of polyester-polyether copolymer TPE-C<sub>23</sub>PPDO<sub>2000</sub>-65wt% (dashed line) and TPE-C<sub>12</sub>PPDO<sub>2000</sub>-62wt% (solid line).

### 4. Cyclic hysteresis tests

For preliminary shape recovery tests rectangular specimens (length × width × thickness =  $60 \times 10 \times 1 \text{ mm}^3$ ) of polyester-polyether copolymer TPE-C<sub>23</sub>PTMG<sub>2000</sub>-65wt%, prepared via injection molding, were repeatedly exposed to a constant stress of about 5.6 MPa or extended to a defined elongation of ca. 80 % (c.f. **Figure S11**).



Figure S10. Shape recovery tests of polyester-polyether copolymer TPE- $C_{23}$ PTMG<sub>2000</sub>-65wt%.



Figure S11. Shape recovery tests on polyester-polyether copolymer TPE- $C_{23}$ PTMG<sub>2000</sub>-65wt% applying constant stress of about 5.6 MPa (left) and a constant elongation of ca. 80 % (right) (for clarity only every second cycle is displayed).

Cyclic hysteresis tests on dogbone-shaped sample bars ( $75 \times 12.5 \times 2 \text{ mm3}$ ; ISO 527-2, type 5A) of polyester-polyether copolymers were performed on a Zwick 1446 Retroline tC II instrument. The test specimens were repeatedly exposed to consecutive cycles of loading and unloading to a constant strain of 100 % with a constant crosshead speed of 50 mm min<sup>-1</sup>. The recovery was measured by observing the residual strain after 10 cycles.



Figure S12. Stress-strain curves from cyclic tensile tests with a constant strain of 100 % for polyester-polyether copolymer TPE-C<sub>23</sub>PTMG<sub>2000</sub>-65wt% (red) and TPE-C<sub>12</sub>PTMG<sub>2000</sub>-62wt% (green) (10 cycles are displayed).



Figure S13. Stress-strain curves from cyclic tensile tests with a constant strain of 100 % for polyester-polyether copolymer TPE-C<sub>23</sub>PPDO<sub>2000</sub>-65wt% (red) and TPE-C<sub>12</sub>PPDO<sub>2000</sub>-62wt% (green) (10 cycles are displayed).



**Figure S14.** Block lengths distributions expressed on  $C_{12}$ -basis for copolyester of  $C_{24}$  dicarboxylic acid with  $C_{24}$  diol and 25 mol% polyether (black) and for copolyester of  $C_{12}$  dicarboxylic acid with  $C_{12}$  diol and 14.3 mol% polyether (red), i.e. isolated acid repeat unit: n = 1 ( $C_{12}$ ) and n = 2 ( $C_{24}$ ); acid- aliph. diol-acid: n = 3 ( $C_{12}$ ) and n = 6 ( $C_{24}$ ) etc.





6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 fl (ppm)

Figure S15. <sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>2</sub>, 130°C) of TPE-C<sub>23</sub>PTMG<sub>2000</sub>-65wt%



Figure S16. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C) of TPE-C<sub>23</sub>PPDO<sub>2000</sub>-65wt%