

## Supporting Information

### HytreL-Like Copolymers Based on Furan Polyester: The Effect of Poly(Butylene Furanoate) Segment on Microstructure and Mechanical/Elastic Performance

Magdalena Kwiatkowska<sup>1,\*</sup>, Inez Kowalczyk<sup>1</sup>, Zbigniew Rozwadowski<sup>2</sup>, Elżbieta Piesowicz<sup>1</sup> and Anna Szymczyk<sup>3,\*</sup>

<sup>1</sup> Department of Materials Technology, West Pomeranian University of Technology in Szczecin, Piastow Av. 19, 70-310 Szczecin, Poland

<sup>2</sup> Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology in Szczecin, Piastow Av. 42, 71-065 Szczecin, Poland

<sup>3</sup> Department of Physics, West Pomeranian University of Technology in Szczecin, Piastow Av. 17, 70-310 Szczecin, Poland

\* Correspondence: magdalena.kwiatkowska@zut.edu.pl (M.K.); anna.szymczyk@zut.edu.pl (A.S.); Tel.: +48-91-449-45-89 (M.K.); +48-91-449-41-73 (A.S.)

Figure S1

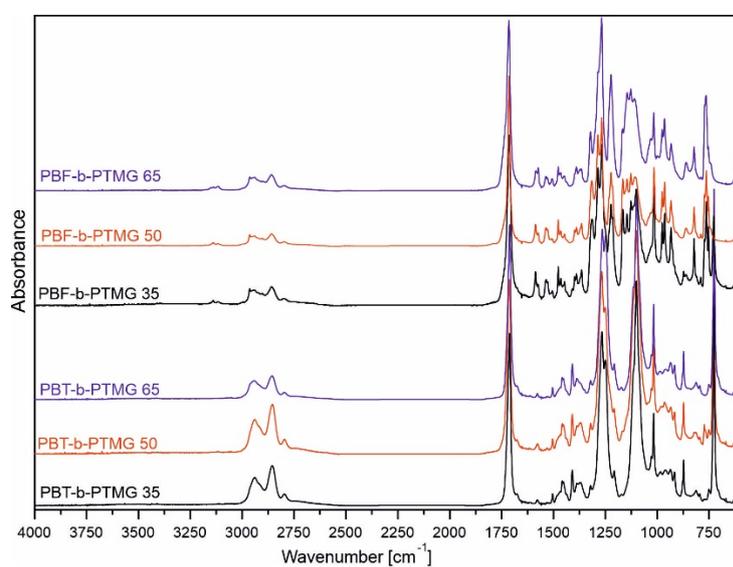


FIGURE S1. FTIR spectra of all investigated copolymers

Figure S2

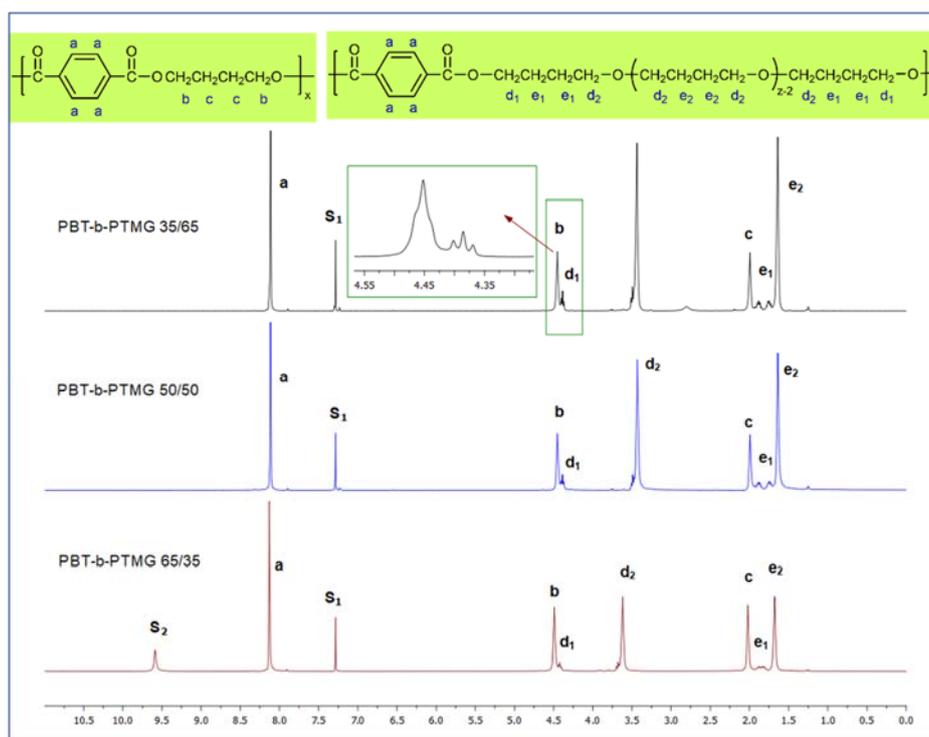


FIGURE S2.  $^1\text{H-NMR}$  spectra of PBT-*b*-PTMG copolymers in  $\text{CDCl}_3$  ( $s_1$ ) + drops of  $\text{CF}_3\text{COOD}$  ( $s_2$ ).

The chemical composition of PBT-*b*-PTMG copolyesters was confirmed by  $^1\text{H-NMR}$  spectroscopy (Figure 2S). The peaks at position of 3.62 ppm (peak  $d_2$ ,  $-\text{OCH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{O}-$ ) and 1.64 ppm (peak  $e_2$ ,  $-\text{OCH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{O}$ ) are assigned to the protons from PTMG flexible blocks, while the peaks at 8.11 ppm (peak  $a$ , aromatic protons), 4.45 ppm (peak  $b$ ,  $-\text{COO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OOC-}$ ) and 1.99 ppm (peak  $c$ ,  $-\text{COO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OOC-}$ ) to the protons from PBT rigid segments, respectively. At 4.39 ppm (peak  $d_1$ ) and at 1.88 ppm (peak  $e_1$ ). The peaks at 4.39 ppm ( $d_1$ ) is and at 1.88 ppm ( $e_1$ ) corresponds to the flexible PTMG blocks ends connected with terephthalate unit of the PBT segment.

The real fractions of the PTMG segments (Table S1) in copolymers were calculated based on the characteristic peaks' integral intensities, according to Equation (S1):

$$W_{PTMG}(\text{wt}\%) = \frac{\left(\frac{I_{e1}}{4} \times 88\right) + \left(\frac{I_{e2}}{4} \times 72\right)}{\left(\frac{I_a}{4} \times 220\right) + \left(\frac{I_{e2}}{4} \times 72\right)} 100\% \quad (\text{S1})$$

where:  $I_a$ ,  $I_{e1}$ , and  $I_{e2}$  are the integral intensities of  $a$ ,  $e_1$  and  $e_2$  resonances on  $^1\text{H-NMR}$  spectra, whilst 220, 72, and 88 are the molecular weights of repeating units in PBT and PTMG blocks, respectively.

Table S1. The chemical composition and molecular weights of PBT-*b*-PTMG copolymers.

Sample	In feed			$^1\text{H-NMR}$								
	DP <sub>x</sub> mol	W <sub>PBT</sub> wt %	W <sub>PTMG</sub> wt %	I <sub>a</sub>	I <sub>b</sub>	I <sub>c</sub>	I <sub>d1</sub>	I <sub>d2</sub>	I <sub>e1</sub>	I <sub>e2</sub>	W <sub>PBT</sub> wt %	W <sub>PTMG</sub> wt %
PBT- <i>b</i> -PTMG 65	9.54	65	35	1.00	1.00	0.97	0.11	1.21	0.26	1.12	65.56	34.44
PBT- <i>b</i> -PTMG 50	5.14	50	50	1.00	0.92	0.90	0.21	2.38	0.23	2.57	49.59	50.41
PBT- <i>b</i> -PTMG 35	2.77	35	65	1.00	0.80	0.83	0.25	3.22	0.55	3.26	38.10	61.90

DP<sub>x</sub> – degree of polymerization of PBT block, W<sub>PTMG</sub> – weight content of flexible block, W<sub>PBT</sub> – weight content of rigid blocks

Figure S3

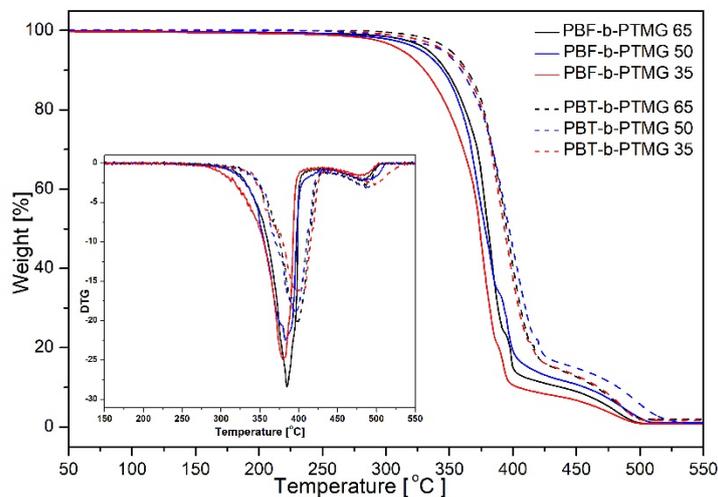


FIGURE S3. TGA thermograms of PBF and PBT copolymers received for samples subjected to thermo – oxidative atmosphere

Figure S4

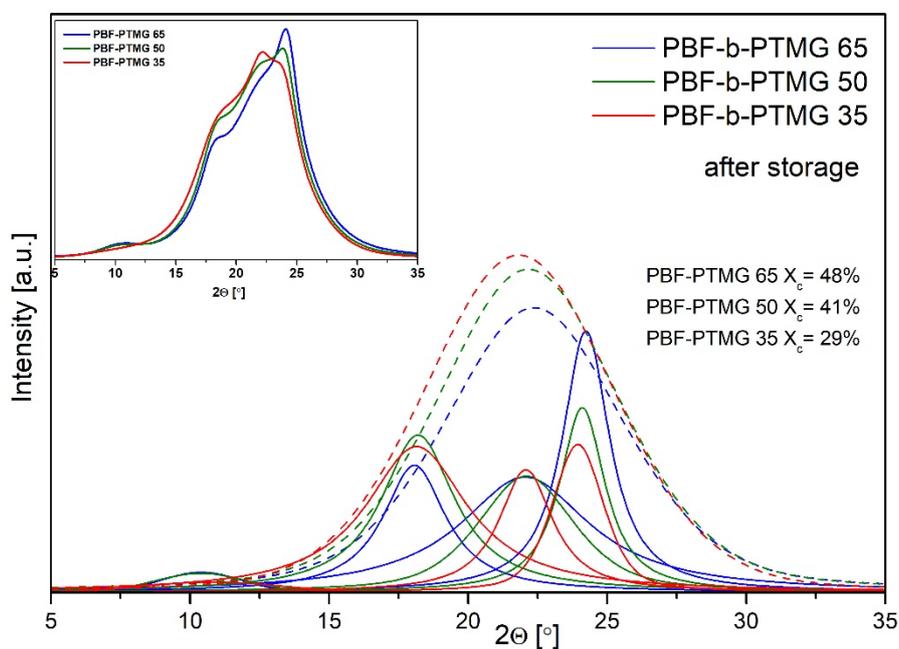


FIGURE S4. WAXS diffractograms of PBF-b-PTMG injected samples received after four weeks of storage with calculated crystallinity degrees.

Figure S5

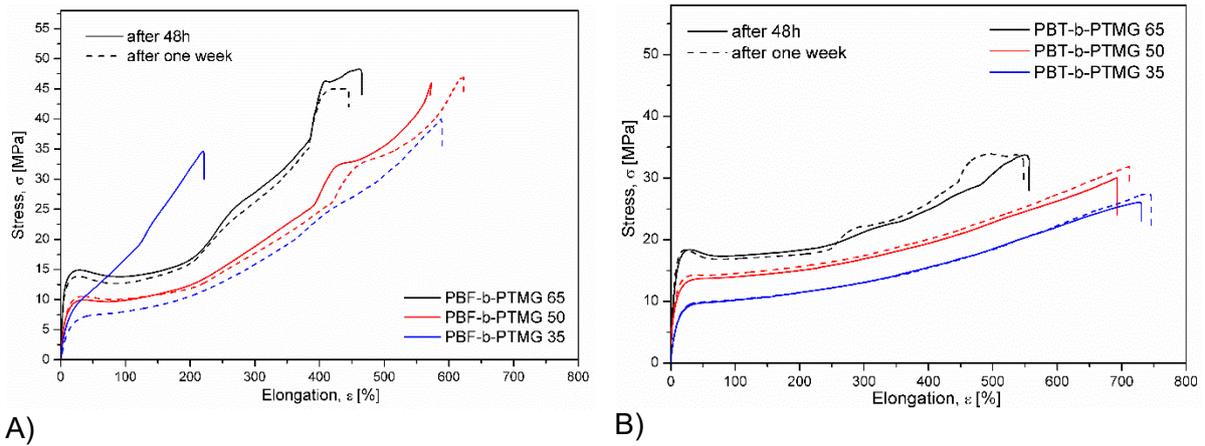
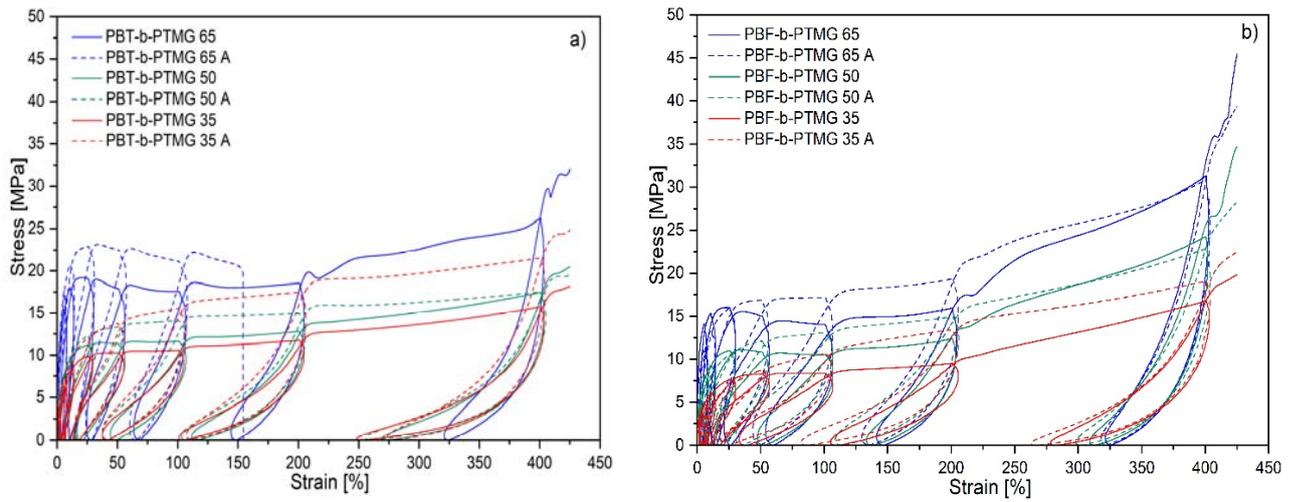


FIGURE S5. The representative uniaxial stress – strain plots of A) PBF and B) PBT copolymers tested in 48h and after one week from processing

Table S2. Mechanical parameters of PBF and PBT copolymers in 48h and one week after injection molding

Sample	After 48h				After one week			
	Rm [MPa]	$\epsilon_b$ [%]	E [MPa]	$\sigma_y$ [MPa]	Rm [MPa]	$\epsilon_b$ [%]	E [MPa]	$\sigma_y$ [MPa]
PBF-b-PTMG 65	48.1 ± 0.9	487 ± 46	217 ± 58	14.8 ± 0.1	44.7 ± 1.1	468 ± 48	143 ± 33	14.2 ± 0.4
PBF-b-PTMG 50	45.1 ± 5.0	576 ± 18	111 ± 25	9.9 ± 0.1	47.8 ± 3.5	645 ± 50	79 ± 12	10.5 ± 0.2
PBF-b-PTMG 35	34.7 ± 2.0	230 ± 24	103 ± 24	9.6 ± 0.3	41.1 ± 1.0	597 ± 59	86 ± 24	7.5 ± 0.1
PBT-b-PTMG 65	33.8 ± 0.3	556 ± 36	296 ± 64	18.3 ± 0.1	34.4 ± 0.9	560 ± 38	287 ± 50	18.6 ± 0.1
PBT-b-PTMG 50	31.3 ± 0.6	692 ± 34	171 ± 29	13.7 ± 0.1	32.3 ± 0.6	712 ± 33	135 ± 10	14.2 ± 0.1
PBT-b-PTMG 35	25.1 ± 2.7	669 ± 69	133 ± 25	9.7 ± 0.1	25.4 ± 2.6	713 ± 84	79 ± 6	9.3 ± 0.4

Figure S6



**FIGURE S6.** The cyclic stress – strain paths for PBT (a) and PBF (b) copolymers. Samples after one month of storage. Dash lines refer to annealed samples.