

## Supporting Information

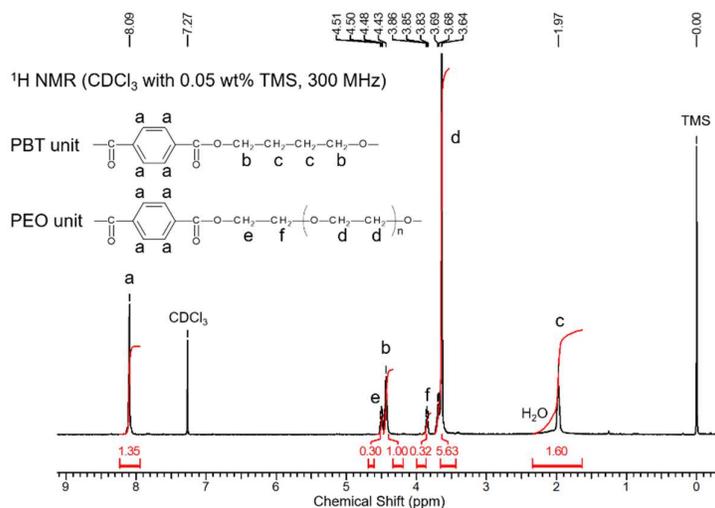
### Spin-trapping Analysis and Characterization of Thermal Degradation of Thermoplastic

#### Poly(ether-ester) Elastomer

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#### S1. Characterization of Molecular Structure and Composition of PBT-*co*-PEO Copolymer

The molecular structures of the synthesized PBT-*co*-PEO copolymer samples, TPEE-60, TPEE-70, and TPEE-80, were confirmed by  $^1\text{H}$  NMR spectroscopy.<sup>S1</sup> **Figure S1** shows an example  $^1\text{H}$  NMR spectrum of TPEE-60. Similar spectra were obtained for TPEE-70 and TPEE-80, too. The signal at 8.10 ppm corresponds to the aromatic proton of the terephthalate units (peak **a**; 4H). Two signals at 4.43 ppm and at 1.97 ppm are the protons at the  $\alpha$  and  $\beta$  positions for the methylene group of PBT, respectively (peak **b**; 4H,  $-\text{O}-\underline{\text{CH}_2}-\text{CH}_2-\text{CH}_2-\underline{\text{CH}_2}-\text{O}-$  and peak **c**; 4H,  $-\text{CH}_2-\underline{\text{CH}_2}-\underline{\text{CH}_2}-\text{CH}_2-$ ). The proton signal on the carbon of PEO repeating unit appears at 3.64 ppm (peak **d**;  $-\text{O}-\underline{\text{CH}_2}-\underline{\text{CH}_2}-\text{O}-$ ). Two small triplets at 4.50 ppm and at 3.85 ppm are the protons at the  $\alpha$  and  $\beta$  positions on the carbon atoms for PEO repeating units connected with terephthalic acid (peak **e**;  $-\phi-\text{CO}-\text{O}-\underline{\text{CH}_2}-\text{CH}_2-\text{O}-$  and peak **f**;  $-\phi-\text{CO}-\text{O}-\text{CH}_2-\underline{\text{CH}_2}-\text{O}-$ ). The existence of signal **d** indicates that a block part of PEO unit is incorporated in the copolymer from PEG 1000. The weight and mole fractions of the PEO flexible segments and PBT rigid segments in the PBT-*co*-PEO samples were calculated from the  $^1\text{H}$  NMR spectra based on the peak intensities at peak **b** for the PBT unit and at peaks **d** and **f** for the PEO unit. These numerical values are summarized in **Table S1** here and **Table 1** in the text. As shown in **Table 1**, the determined content of the flexible PEO segment is lower than that theoretically calculated from the mixed amounts of raw materials, as the mixed amount of PEG 1000 was higher. This is attributed to the incomplete incorporation of PEG 1000 in the copolymer chain and its subsequent extraction during purification.



**Figure S1.**  $^1\text{H}$  NMR spectrum of TPEE-60 in  $\text{CDCl}_3$ . Peaks **a–f** were assigned to protons on the PBT-*co*-PEO molecule, as shown in the insets showing the molecular structures of PBT and PEO units.

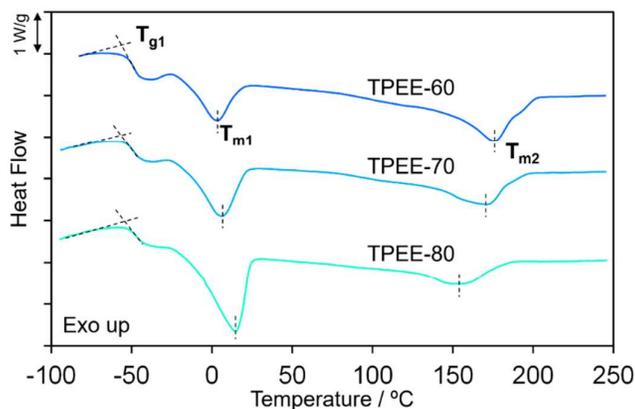
**Table S1.** The composition of PBT and PEO units in synthesized PBT-*co*-PEO copolymers determined by  $^1\text{H}$  NMR measurement.

Sample	PBT segment		PEO segment	
	mol%	wt%	mol%	wt%
TPEE-60	79.2	42.3	20.8	57.7
TPEE-70	76.1	38.0	23.9	62.0
TPEE-80	71.1	32.0	28.9	68.0

## S2. DSC Measurement of PBT-*co*-PEO

DSC thermograms of the PBT-*co*-PEO copolymers were measured to determine the thermophysical properties of PBT-*co*-PEO, the glass transition temperature  $T_g$ , and the melting point  $T_m$ , as shown in

**Figure S2** here and **Figure 3** in the text.



**Figure S2.** DSC thermograms of PBT-*co*-PEO copolymers with different wt% contents of PBT and PEO segments at 10 °C/min of heating rate.

Three phase transitions were observed for all copolymers:  $T_{g1}$ ,  $T_{m1}$ , and  $T_{m2}$ . The first  $T_{g1}$  was between  $-57.3$  and  $-53.8$  °C, determined as the onset points of the change in heat capacity. Deschamps et al. synthesized a series of PBT-*co*-PEO copolymers with components similar to those in our samples, using similar materials and synthesis methods.<sup>S2</sup> They determined  $T_g$  for samples of PBT/PEO = 0.30/0.70 and 0.39/0.71 using the midpoint of the heat-capacity change measured by DSC, obtaining  $T_g$  of  $-50$  °C for both samples. We also measured PEG 1000 by DSC and obtained a  $T_g$  of  $-68.1$  °C. Therefore, although our values are somewhat lower than those reported by Deschamps et al., the transitions around  $-55$  °C are assigned to the glass transition  $T_{g1}$  of the PEO block segments incorporated in the PBT-*co*-PEO chain.

**Table S2.** Thermophysical properties of PBT-*co*-PEO copolymers,  $T_g$ ,  $T_m$ ,  $\Delta H_m$ ,  $x_c^h$ , and  $x_c^h$ .

Sample	PEO segment					PBT segment				
	$T_{g1}$ °C	$T_{m1}$ °C	$\Delta H_m$ J/g	$x_{c1}$ %	$x_{c1}^h$ %	$T_{g2}$ °C	$T_{m2}$ °C	$\Delta H_m$ J/g	$x_{c2}$ %	$x_{c2}^h$ %
TPEE-60	-57.3	3.4	9.8	8.0	13.9	NA	175.9	30.5	21.1	49.9
TPEE-70	-55.5	6.1	15.5	12.7	20.4	NA	170.6	23.4	16.2	42.6
TPEE-80	-53.8	14.6	24.6	20.1	29.6	NA	153.1	16.2	11.2	35.1

$T_g$  is the glass transition temperature,  $T_m$  is the melting point,  $\Delta H_m$  is the heat of fusion at melting,  $x_c$  is degree of crystallinity relative to a whole sample, and  $x_c^h$  is degree of crystallinity for each component. The subscript numbers 1 and 2 indicate the PBT and PEO components, respectively.

The second transition was a large endothermic peak at 3.4–14.6 °C. Deschamps et al.<sup>S2</sup> reported that PEO melted at 6 °C and –1 °C for the same samples mentioned above. Therefore, our resulting endothermic peaks are also assigned to the melting of PEO segments in the PBT-*co*-PEO copolymers. Incidentally, our PEG 1000 showed a melting peak at 35.3 °C by DSC. Some reported values of  $T_m$  for PEG 1000 are similar to our results; 34 °C was reported by Fakirov et al.<sup>S3</sup>, 39 °C by Deschamps et al.<sup>S2</sup>, and 40.7 °C by Li et al.<sup>S4</sup> These  $T_m$  values are larger than those of the copolymers. This is because the crystallites of the PEO segments in the copolymer cannot grow sufficiently because of the PBT units; the melting point is lower than that of original PEG 1000 because of size effects, such as the Gibbs–Thomson effect. The crystalline growth of PEO was suppressed more as the PBT content increased and  $T_{m1}$  was decreased for copolymers with higher PBT contents.

The third transition is observed as broad endothermic peaks at ~153.1–175.9 °C. Deschamps et al.<sup>S2</sup> reported the melting points of PBT segments at 149 °C and 166 °C for the same copolymers mentioned above. Because these values are very close to our results, the endothermic peaks are also assigned to the melting of the PBT segment,  $T_{g2}$ , in our PBT-*co*-PEO copolymers. The original melting point of the PBT homopolymer is ~225–230 °C, which is much higher than the values observed for copolymers. This difference also arises from the size effect of PBT crystallites, as described above.<sup>S3</sup> The crystalline growth of PBT is suppressed more with increasing PEO content and  $T_{m2}$  is decreased for copolymers with higher PEO contents.

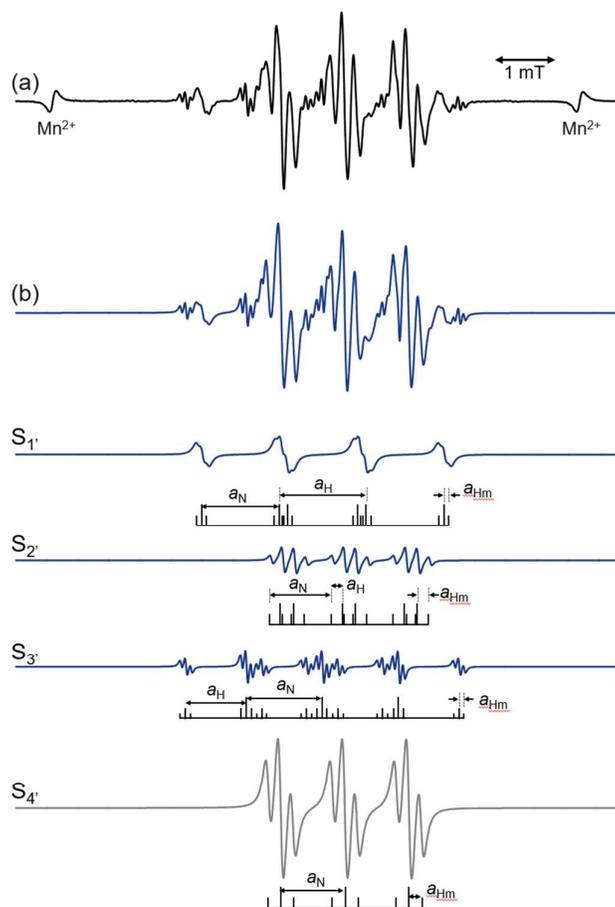
The glass transition temperature of PBT,  $T_{g2}$ , should also be observed as  $T_{g1}$  of the PEO unit was. However, no apparent phase transition appears in the DSC thermogram between  $T_{m1}$  and  $T_{m2}$  in **Figure S2**. For example, Deschamps also reported that  $T_g$  for homopolymeric PBT was observed at 54 °C by DSC, but it was not observed for the two copolymers mentioned above. According to another paper by Konishi et al.<sup>S5</sup>, who investigated the complexity of  $T_g$  and  $T_m$  of PBT in detail, the  $T_g$  of the amorphous region of PBT appears at 31 °C, but the height of the heat capacity change of  $T_g$  in their results is ~1/20 of the peak height of  $T_m$  at 225 °C. Therefore, the  $T_g$  of PBT units in our samples may appear at ~30 °C, but it may be very difficult to observe because of its low intensity.

The degrees of crystallinity  $x_{c1}$  and  $x_{c2}$  for the PEO and PBT segments were determined using

reported values of heat of fusion,  $\Delta H_m = 122.4$  J/g for the PEG 1000 unit<sup>S6</sup> and  $\Delta H_m = 144.5$  J/g for the PBT unit<sup>S2</sup>, respectively. Because the DSC thermogram is not straight and decreases for more than 50 °C before the  $T_{m2}$  peak, it is difficult to determine the beginning of the melting region for  $T_{m2}$ . Thus, the fusion area was integrated from 75 °C for all samples. Moreover, the degree of crystallinity based on each level of PBT or PEG units in the copolymer,  $x_c^h$ , was also calculated. As the amount of PEO increased, both  $x_{c1}$  and  $x_{c1}^h$  increased but both  $x_{c2}$  and  $x_{c2}^h$  decreased. This may be because the higher PEO content suppressed the crystalline growth of the PBT unit.

### **S3. Spin-trapping ESR for Diethoxyethane (DEE)**

As a model compound for PEG 1000 segment in PBT-*co*-PEO, DEE was characterized by spin-trapping ESR spectroscopy. By spectral simulation, the ESR spectrum of DEE/TBNB after heating at 120 °C for 60 min consisted of four kinds of radical spin adduct components, **S'1**, **S'2**, **S'3**, and **S'4**, as shown in **Figure S3**. The parameters determined by simulation, *hfcc* and the g-value, are summarized in **Table S3**. These parameters are very close to those for the spin adducts of the PBT-*co*-PEO copolymers **S1**, **S2**, **S3**, and **S4**, as listed in **Table 4** in the text.



**Figure S3.** (a) ESR spectrum of DEE/TTBNB at 120 °C for 60 min. (b) Simulated spectrum using four radical adduct components,  $S'_1$ ,  $S'_2$ ,  $S'_3$ , and  $S'_4$ . Horizontal arrows indicate simulation parameters and the hyperfine coupling constant (*hfcc*)  $a_N$ ,  $a_H$ , and  $a_{Hm}$  for each spin adduct spectrum.

**Table S3.** Spectral parameters for spin adducts observed by spin-trapping method for model compound DEE heated at 120 °C for 60 min.

Spin Adduct	Trapped Radical	Adduct Type	Sample	$g$	<i>hfcc</i> /mT		
					$a_N$	$a_H$	$a_{Hm}$
$S'_1$	$-O-\dot{C}H-$	nitroxide	DEE	2.0058	1.30	1.40	0.08
$S'_2$	$-O-\dot{C}H-$	anilino	DEE	2.0031	1.02	0.20	0.19
$S'_3$	$\dot{C}H_2-$	nitroxide	DEE	2.0058	1.26	1.00	0.08
$S'_4$	$\dot{t}$ -butyl	anilino	DEE	2.0037	1.06	-	0.20

#### S4. The average molecular weights, $M_w$ and $M_n$

Molecular weight distributions after heating at 120 °C were investigated for the PBT-*co*-PEO samples by GPC measurement, as shown in **Figure 11a–c** in the text. The average molecular weights,  $M_w$  and  $M_n$ , were calculated from the GPC curves and summarized in **Table S4**. All samples were completely dissolved in the eluent chloroform before heating; however, TPEE-60 and TPEE-70 samples showed gelation after heating at 120 °C for more than 60 min and could not completely dissolve in chloroform. Thus, **Table S4** shows the average molecular weights from the solution parts of the samples after dissolution with chloroform.

**Table S4.** The average molecular weights,  $M_w$  and  $M_n$  of PBT-*co*-PEO copolymers, TPEE-x, and PEG 1000.

Sample	Heating at 120 °C Time (min)	$M_n/10^3$	$M_w/10^4$	$M_w/M_n$	gelation
TPEE-60	blank	9.55	3.37	3.53	–
	30	7.97	2.77	3.48	–
	60	5.35	2.06	3.86	+
	120	3.88	1.78	4.58	+
	300	2.50	1.37	5.30	+
TPEE-70	blank	9.69	3.38	3.49	–
	30	6.39	2.42	3.79	–
	60	5.37	2.28	4.24	+
	120	3.78	1.64	4.35	+
	300	2.38	1.11	4.65	+
TPEE-80	blank	8.12	2.81	3.46	–
	30	5.84	2.21	3.79	–
	60	5.03	2.17	4.32	–
	120	4.61	2.27	4.92	–
	300	3.00	1.40	4.65	–
PEG 1000	blank	1.27	1.46	1.15	–
	30	1.04	1.23	1.24	–
	60	0.93	1.26	1.35	–

## References

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