

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 ^1H NMR spectroscopy.^{S1} **Figure S1** shows an example ^1H 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 α and β positions for the methylene group of PBT, respectively (peak **b**; 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ and peak **c**; 4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$). The proton signal on the carbon of PEO repeating unit appears at 3.64 ppm (peak **d**; $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$). Two small triplets at 4.50 ppm and at 3.85 ppm are the protons at the α and β positions on the carbon atoms for PEO repeating units connected with terephthalic acid (peak **e**; $-\phi-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ and peak **f**; $-\phi-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$). 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 ^1H 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.

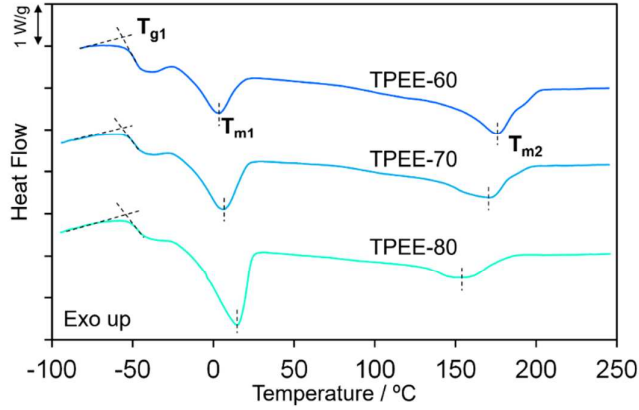


Figure S2. DSC thermograms of PBT-*co*-PEO copolymers with different wt% contents of PBT and PEO segments at 10 °C/min of heating rate.

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.^{S2} 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 , ΔH_m , x_c^h , and x_c^h .

Sample	PEO segment					PBT segment				
	T_{g1} °C	T_{m1} °C	ΔH_m J/g	x_{c1} %	x_{c1}^h %	T_{g2} °C	T_{m2} °C	ΔH_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, ΔH_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.^{S2} 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.^{S3}, 39 °C by Deschamps et al.^{S2}, and 40.7 °C by Li et al.^{S4} 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.^{S2} 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.^{S3} 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.^{S5}, 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^{S6} and $\Delta H_m = 144.5$ J/g for the PBT unit^{S2}, 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^h_c , was also calculated. As the amount of PEO increased, both x_{c1} and x^h_{c1} increased but both x_{c2} and x^h_{c2} 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.

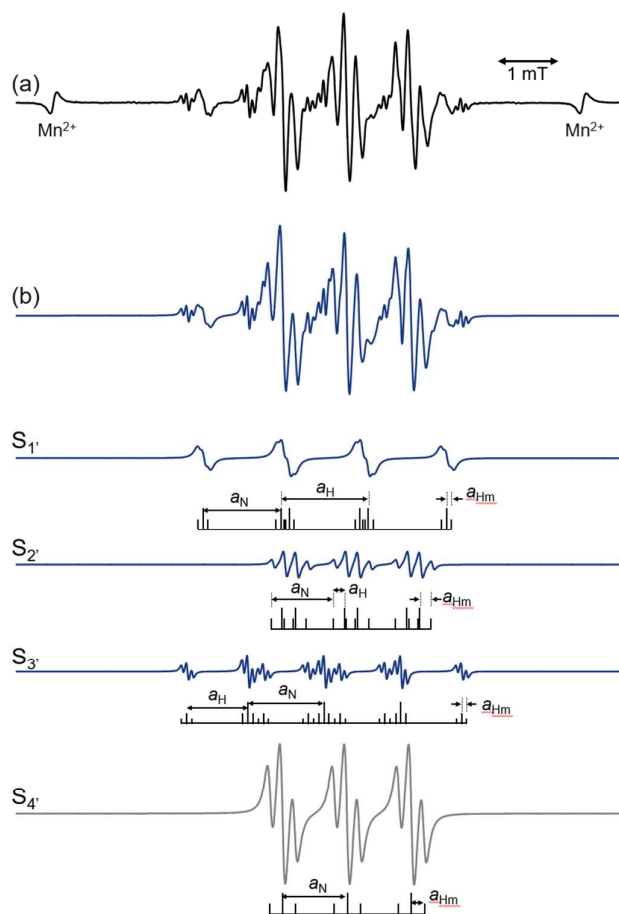


Figure S3. (a) ESR spectrum of DEE/TTBNB at 120 °C for 60 min. (b) Simulated spectrum using four radical adduct components, S'_1 , S'_2 , S'_3 , and S'_4 . Horizontal arrows indicate simulation parameters and the hyperfine coupling constant (*hfcc*) a_N , a_H , and a_{Hm} for each spin adduct spectrum.

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	$M_n/10^3$	$M_w/10^4$	M_w/M_n	gelation
	Time (min)				
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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