Supplementary Material (ESI)

# Functionalization of aliphatic polyesters by nitroxide radical coupling

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## SEC

Figure S1 shows the SEC traces of PBS, PBS-120, and PBS samples functionalized at 120°C.



Fig. S1 Relative refractive index traces from SEC of PBS, PBS-120, and PBS samples functionalized at 120°C

#### MALDI TOF MS

In the MALDI TOF MS spectra of methanol residual fractions of PBS-BT2-BPO-120 and PBS-NfT2-BPO-120 (Fig. 2 and Fig. 3), ions terminated with carboxyl and hydroxyl end groups ( $m/z = 1589 + n \times 172$ ), with succinic acid ( $m/z = 1689 + n \times 172$ ) or butanediol ( $m/z = 1661 + n \times 172$ ) at both chain ends were present. Peaks due to cyclic oligomers bearing urethane units ( $m/z = 1657 + n \times 172$ ) as a consequence of the hexamethylene diisocyanate used in the synthetic procedure as a chain extender were detected as well. Less abundant ions at  $m/z = 1603 + n \times 172$  and  $m/z = 1703 + n \times 172$  were assigned to linear chains bearing methyl succinate ester groups originated reasonably from methanolysis during the purification procedure. Furthermore, signals at  $m/z = 1643 + n \times 172$  and  $m/z = 1659 + n \times 172$  were due to oligomers derived from thermal and thermo-oxidative degradation processes, respectively.

#### UV-Vis calibration curves for FD determination of functionalized PBS samples

Two different UV-Vis calibration curves were developed by measuring the absorbance of CHCl<sub>3</sub> dilute solutions of PBS/BZO-TEMPO and PBS/NfO-TEMPO blends having known composition, and then plotting the absorbance versus the TEMPO-derivative concentration. In the case of BZO-TEMPO, a PBS solution was obtained by dissolving 108 mg of the polymer in 10 mL of CHCl<sub>3</sub>; a 2.935 × 10<sup>-2</sup> M solution of BZO-TEMPO in CHCl<sub>3</sub> was also prepared. Then, exact volumes of the BZO-TEMPO solution (10  $\mu$ L, 30  $\mu$ L, 60  $\mu$ L, 100  $\mu$ L, 150  $\mu$ L, 210  $\mu$ L, 290  $\mu$ L, 390  $\mu$ L, 410  $\mu$ L, and 550  $\mu$ L) were added into the PBS solution (10 mL). The UV-Vis absorbance at 282 nm (which is a characteristic absorption band of BZO-TEMPO) of these dilute solutions was recorded and plotted versus the BZO-TEMPO concentration (Fig. S2). By a linear fitting of the data it was obtained a curve, which was a straight line in the range of selected concentrations (the absorbance of the calibration samples was < 1). The FD of the PBS-g-(BZO-TEMPO) samples (expressed as the moles of nitroxide moieties per 100 moles of monomeric units of polymer) was determined by measuring the UV-Vis absorbance of sample solutions prepared by dissolving in CHCl<sub>3</sub> a known amount of polymer.

Following the same procedure, the UV-Vis calibration curve for the samples functionalized with NfO-TEMPO was obtained preparing a PBS CHCl<sub>3</sub> solution (by dissolving 115 mg of the polymer in 10 mL of CHCl<sub>3</sub>) and a  $1.189 \times 10^{-2}$  M CHCl<sub>3</sub> solution of NfO-TEMPO. Then, exact volumes of the NfO-TEMPO solution (10 µL, 20 µL, 70 µL, 150 µL, and 250 µL) were added into the PBS solution (10 mL). For each blend the absorbance at 298 nm (which is a characteristic absorption band of NfO-TEMPO) versus the NfO-TEMPO concentration was plotted (Fig. S3). The linear fitting of the data allowed to obtain the calibration curve, which was used to evaluate the FD of the NfO-TEMPO functionalized PBS samples.

For both the calibration curves the absorbance (Abs) of the pure PBS solution at the wavelength of absorption of the chromophore was evaluated. Moreover, the  $Abs_{Max}$  of the calibration blends was calculated by considering the value of the absorbance at 282 nm in the case of BzO-TEMPO and at 298 nm in the case of NfO-TEMPO, and subtracting to this value the absorbance at 450 nm (considered as the baseline).



Fig. S2 (A) UV-Vis spectra of PBS/BzO-TEMPO calibration solutions and (B) UV-Vis calibration curve at 282 nm



Fig. S3 (A) UV-Vis spectra of PBS/NfO-TEMPO calibration solutions and (B) UV-Vis calibration curve at 298 nm

# <sup>1</sup>H-NMR spectrum of PBS-120

The whole <sup>1</sup>H-NMR spectrum of PBS-120 reported in Fig. S4 shows typical signals due to the butylene succinate repeating unit at 4.08, 2.58 and 1.67 ppm, a large singlet at 4.79 ppm, which can be attributed to the proton bonded to the nitrogen of the urethane group, as well as signals at 3.11, 1.46 and 1.30 ppm, which are all due to the methylene groups of the 1,6-hexamethylene diurethane moiety. The signal at about 6.8 ppm is likely due to the proton bonded to the nitrogen of the urethane group deriving from the aromatic diisocyanate. The two multiplets at 3.62 and at 2.27 ppm can be attributed to the methylene protons in alpha position of alcoholic and carboxylic acid terminal groups, respectively.



Fig. S4 <sup>1</sup>H-NMR spectrum of PBS-120

## DFT quantum mechanical calculations

DFT calculations, referred to a segment of the PBS chain made of three monomeric units, have provided that the energy of H-abstraction from the polymer chain promoted by the benzoyl radical is lower on the C11 and C10 positions of the succinic acid unit (Fig. S5). This result is consistent with the calculated spin density surface of the radical formed by H-abstraction from the polymer chain (Fig. S6). Indeed, the map of the calculated electrostatic potential surfaces (Fig. S7) shows clearly that the hydrogen atoms of the two CH<sub>2</sub> groups of the succinic acid unit are the most probable sites of electrophilic attack of the benzoyl radical, being those with the maximum electrostatic potential values.



Fig. S5 A segment of the PBS chain showing a sequence of three monomeric units used as a model of the polymer and reaction parameters for the PBS/benzoyl radical system



**Fig. S6** DFT calculated Spin density (0.002 electron/au3) surface of the macroradical formed by H-abstraction from the polymer chain promoted by the benzoyl radical. Red: negative spin density; Green: positive.



Fig. S7 DFT calculated electrostatic potential surface of a segment of the PBS chain (the electrostatic potential decreases on going from blue to red).

Torque-time curve of PBS runs carried out at 150°C



Fig. S8 Torque curves of PBS-150, PBS-DTBPIB-150, and PBS-BT2-DTBPIB-150

# UV-Vis spectra of PBS sample functionalized with BzO-TEMPO at 150°C



Fig. S9 UV-Vis absorption spectra of PBS-150 and PBS-BT2-DTBPIB-150



Fig. S10 UV-Vis absorption spectra of PLA and PLA-NfT2-DTBPIB-180

## <sup>1</sup>H-NMR spectrum of PLA-NfT2-DTBPIB-180

The <sup>1</sup>H-NMR spectrum of PLA-NfT2-DTBPIB-180 was registered on a CDCl<sub>3</sub> solution obtained by solubilizing a known amount of both the functionalized polymer and the reference compound (1,4-dimethoxybenzene). Even if the signals of the naphtoic group between 8.9 and 7.9 ppm are in this case quite low and poorly resolved, due to their low concentration, it is possible to calculate the integrals. The comparison between the area of the signal at 6.83 ppm of the reference compound with those of the naphtalene protons allowed the evaluation of the FD<sub>NMR</sub> (Tab. 2 in the main text), which resulted consistent with the FD<sub>UV</sub> value.



Fig. S11 <sup>1</sup>H-NMR spectrum of PLA-NfT2-DTBPIB-180