

Antioxidant and UV-Blocking Functionalized Poly(Butylene Succinate) Films

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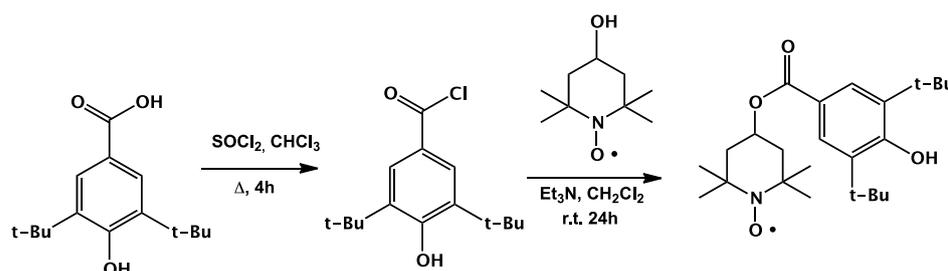
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Synthesis of 3,5-di-tert-butyl-4-hydroxybenzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (BHB-TEMPO)

In this study, 3,5-di-tert-butyl-4-hydroxybenzoic acid (4.00 g, 0.016 mol) and thionyl chloride (4.76 g, 0.04 mol) were added to a flask containing chloroform (40 mL). The solution was stirred under reflux for 4 h. At the end of the reaction, the solvent and the excess of thionyl chloride were removed under vacuum and the crude 3,5-di-tert-butyl-4-hydroxybenzoyl chloride was dissolved in 40 mL of dichloromethane. Then, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (2.76 g, 0.016 mol) and triethylamine (2.45 mL, 0.017 mol) were added at room temperature. The resulting solution was stirred at room temperature for 24 h. Crude mixture was hydrolyzed with water (50 mL) and extracted with dichloromethane (3 × 50 mL). BHB-TEMPO was purified by column chromatography by using dichloromethane/ethyl acetate (95/5) as an eluting mixture. Yield 50%. MS (CI): *m/z*: 427 [M + 23], 405 [M + 1], and 404 [M]; FT-IR (KBr): $\nu = 3548, 2957, 1712, 1599, 1462, 1434, 1365, 1313, 1228, 1131, \text{ and } 986, 771 \text{ cm}^{-1}$. C₂₄H₃₈NO₄ Calculated C, 71.25; H, 9.47; N, 3.46. Found: C, 71.40; H, 9.50; N, 3.49. Melting point: 170 °C.



Scheme 1. Synthesis of BHB-TEMPO.

UV-Vis calibration curve for FD determination of functionalized PBS samples

The UV-Vis calibration curve was developed by measuring the absorbance of CHCl₃ dilute solutions of PBS/BHB-TEMPO mixtures at known composition, and then plotting the absorbance versus BHB-TEMPO concentration. A PBS solution was obtained by dissolving 100 mg of the polymer in 10 mL of CHCl₃; a 6 × 10⁻⁴ M solution of BHB-TEMPO in CHCl₃ was also prepared. Then, exact volumes of the BHB-TEMPO solution (5 μL, 10 μL, 20 μL, 30 μL, 25 μL, 35 μL, 45 μL, 35 μL, and 55 μL) were added into the PBS solution (2.5 mL). The UV-Vis absorbance at 263 nm (which is a characteristic absorption band of BHB-TEMPO) of these diluted solutions was recorded and plotted versus the BHB-TEMPO

concentration (Fig. S1). By a linear fitting of the data, a curve was obtained which was a straight line in the range of selected concentrations (the absorbance of the calibration samples was < 1).

$$y = 6.32 \times 10^{-5}x - 6.62 \times 10^{-6} \quad (1)$$

The FD of the PBS-g-(BHB-T) 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 a known amount of polymer in CHCl_3 . The functionalization degree was determined by interpolating the absorbance value at 263 nm of the functionalized samples (corrected for the absorbance at 450 nm).

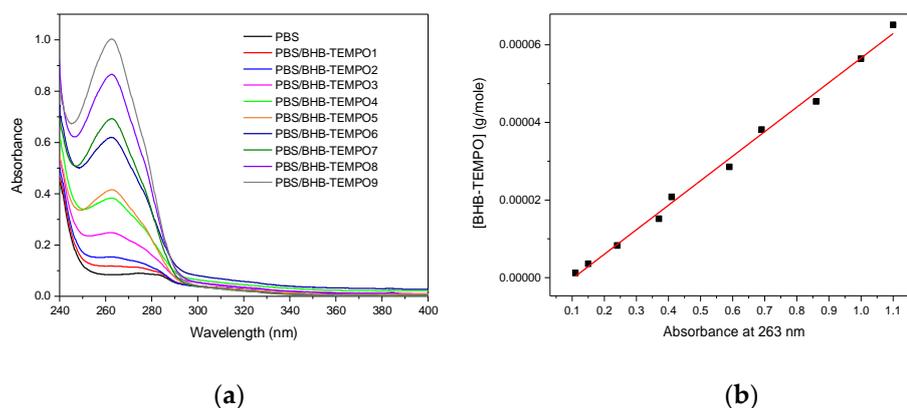
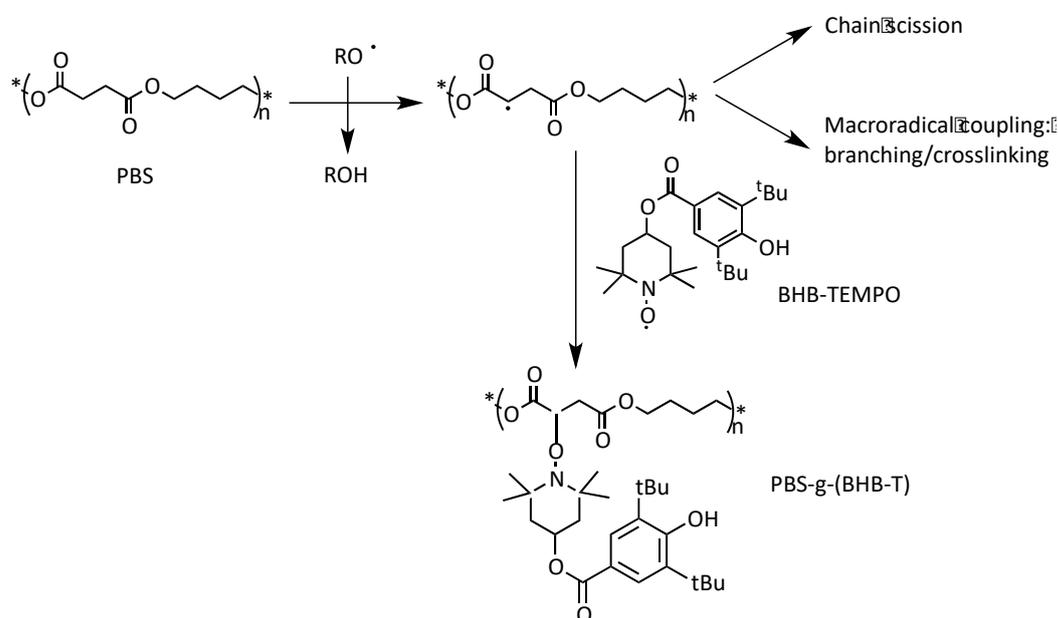


Figure S1. UV-Vis spectra of PBS/BHB-TEMPO solutions in chloroform at known concentration (a). Calibration curve (b).

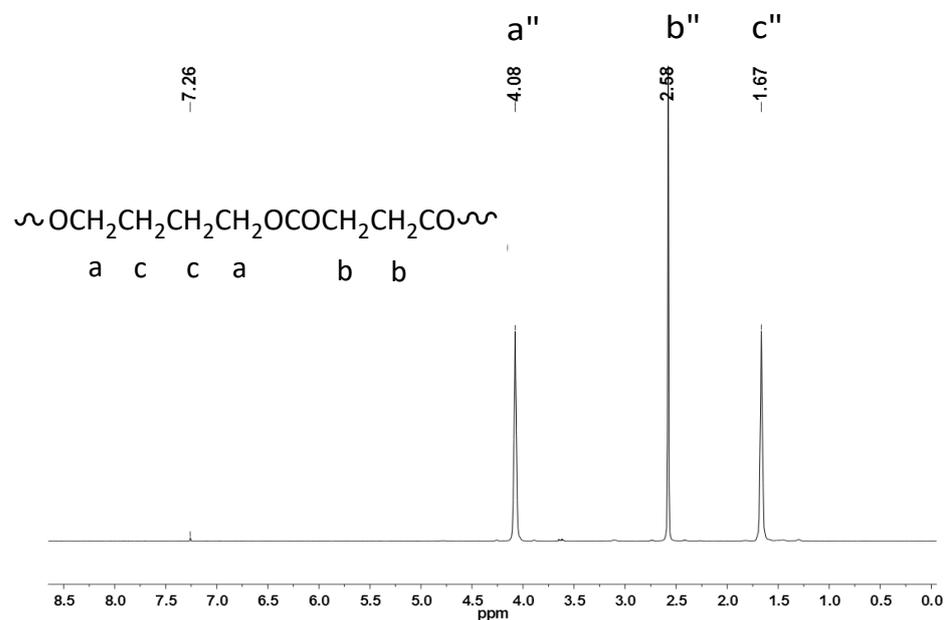


Scheme 2. Simplified mechanism of BHB-TEMPO radical grafting on PBS chains.

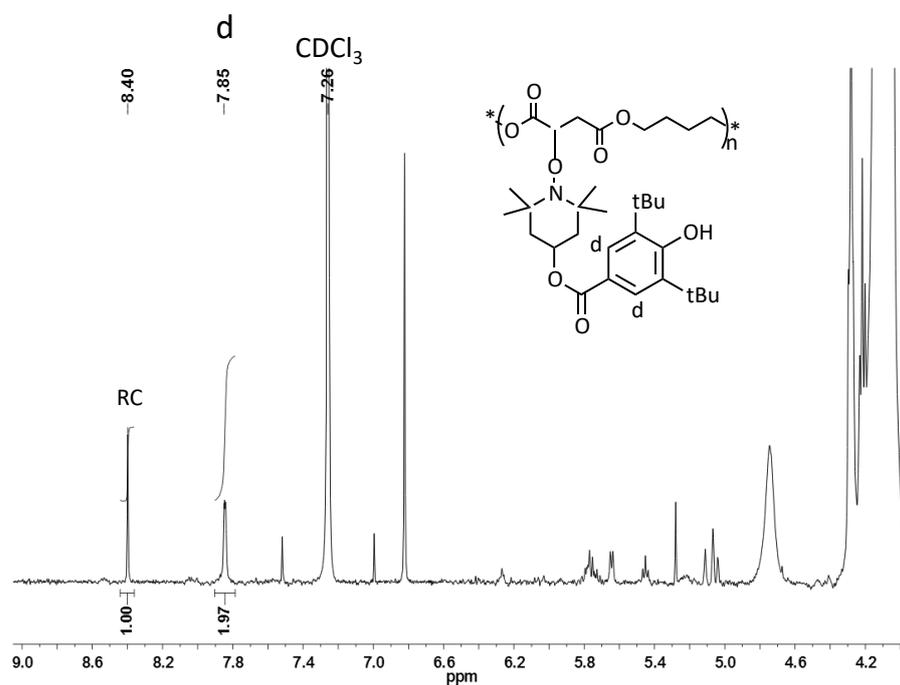
$^1\text{H-NMR}$ characterization of PBS-g-(BHB-T)3.

To corroborate the outcomes of the UV-Vis procedure, the FD of PBS-g-(BHB-T)3 was determined by $^1\text{H-NMR}$ spectroscopy. To obtain a complete attribution of polymer signals, the $^1\text{H-NMR}$ spectrum of the PBS was acquired first. The PBS spectrum showed typical signals of the polymer repeating unit at 4.08, 2.58, and 1.67 ppm (Ha, Hb, Hc), in agreement with the literature [27]. Besides the typical PBS signals, the spectrum of PBS-g-

(BHB-T)3 (Figure S2) highlighted a signal at 7.85 ppm which can be attributed to the two aromatic protons of BHB-TEMPO grafted onto the PBS chains (Hd, Figure S2) [22].



(a)



(b)

Figure S2. ¹H-NMR spectra of PBS (a) and PBS-g-(BHB-T)3 (b). The ¹H-NMR spectrum of PBS shows three signals (Ha, Hb, Hc) due to the aliphatic protons of the polymer repeating units (see molecule structure in Fig. S2a for attributions). The ¹H-NMR spectrum of PBS-g-(BHB-T)3 shows a signal (Hd) due to the aromatic protons of the grafted BHB-TEMPO unit (see molecule structure in Fig. S2b for attribution). The peak at about 8.4 ppm is due to the reference compound (RC) protons.

For the quantitative determination of the grafted groups, a known amount of a reference compound (1,4-dinitrobenzene, RC) was dissolved in a deuterated chloroform solution of the functionalized polymer at a known concentration. A comparison between the area of the peak of the R protons at 8.4 ppm with that of the aromatic protons of the grafted BHB-TEMPO unit allowed for evaluation of FD_{NMR} (Table 1). The value of FD is in excellent agreement with that determined by the UV method.

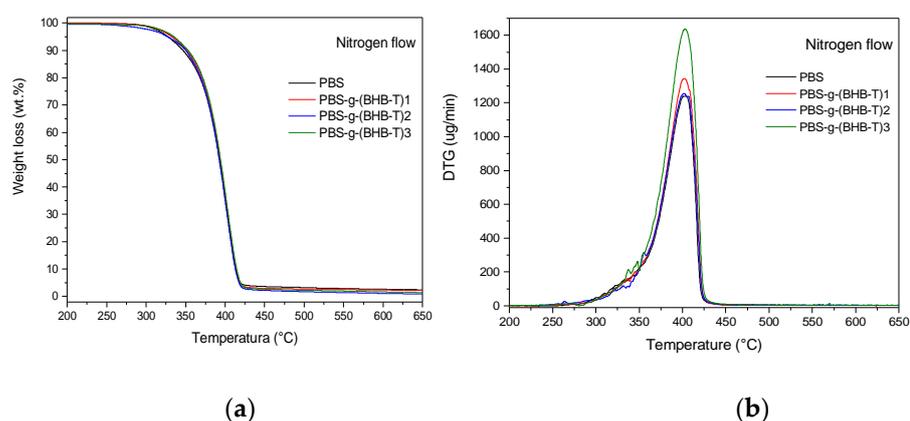


Figure S3. Representative TG (a) and DTG (b) curves of PBS, PBS-g-(BHB-T)1, PBS-g-(BHB-T)2, and PBS-g-(BHB-T)3 under nitrogen flow.

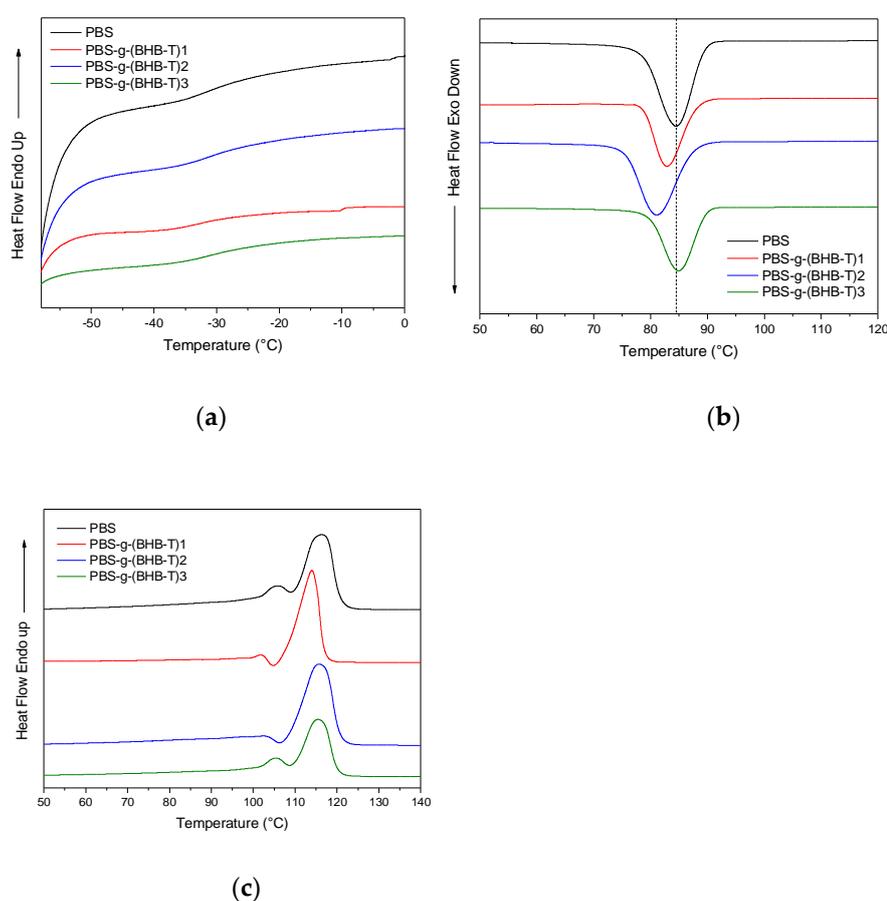
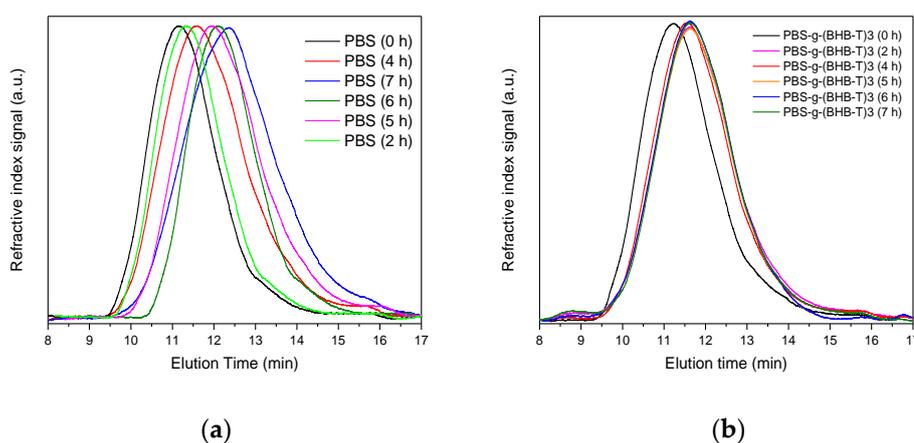


Figure S4. DSC curves of PBS, PBS-g-(BHB-T)1, PBS-g-(BHB-T)2, and PBS-g-(BHB-T)3: glass transition second heating (a); crystallization first cooling (b); melting second heating (c).

Table S1. Number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity (\mathcal{D}) vs of PBS and PBS-g-(BHB-T)3 vs the thermo-oxidative ageing time.

Sample	Ageing Time (h)	M_n (g/mol)	M_w (g/mol)	\mathcal{D}
PBS	0	75980	145210	1.8
	2	65320	127300	1.9
	4	44800	100390	2.2
	5	38760	96560	2.5
	6	20450	75670	3.7
	7	15940	60900	3.8
PBS-g-(BHB-T)3	0	65240	137600	2.1
	2	52130	105900	2.0
	4	50260	101340	2.0
	5	49270	100530	2.0
	6	48720	99730	2.0
	7	48420	97080	2.0

**Figure S5.** Overlay of SEC curves between 8 and 17 min of PBS (a) and PBS-g-(BHB-T)3 (b) after 0, 2, 4, 5, 6, and 7 h of oven ageing. All chromatograms were normalized.**Table S2.** Number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity (\mathcal{D}) of PBS and PBS-g-(BHB-T)3 vs the photo-oxidative ageing time.

Sample	Ageing Time (h)	M_n (g/mol)	M_w (g/mol)	\mathcal{D}
PBS	0	59090	123330	2.1
	0.5	54330	110450	2.0
	6	34940	82790	2.4
PBS-g-(BHB-T)3	0	65240	137600	2.1
	0.5	56120	121810	2.2
	6	44070	112000	2.5

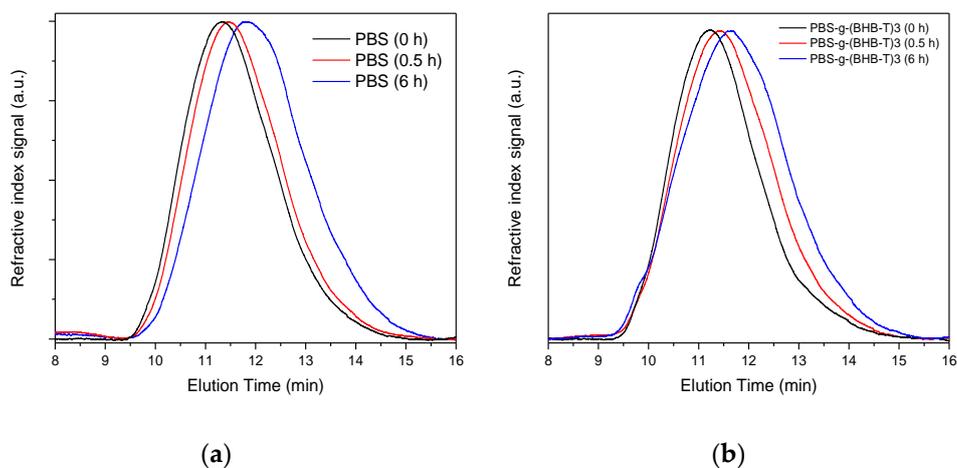


Figure S6. Overlay of SEC curves between 8 and 16 min of PBS (a) and PBS-g-(BHB-T)3 (b) after 0, 0.5, and 6 h of UV irradiation. All chromatograms were normalized.

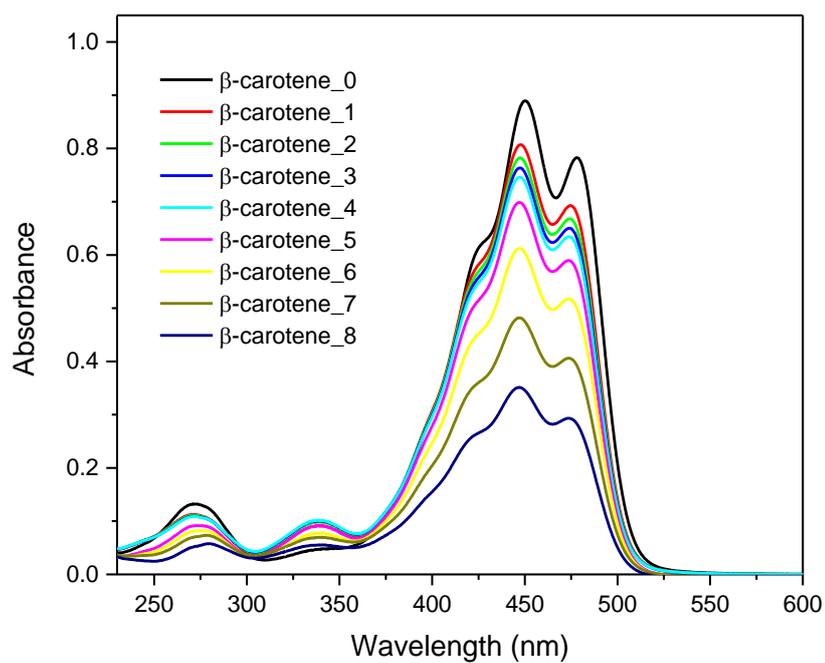


Figure S7. Overlay of UV-Vis spectra of β -carotene solution (10^{-5} M) per different irradiation time (0: 0 min; 1: 10 min; 2: 20 min; 3: 30 min; 4: 40 min; 5: 60 min; 6: 90 min; 7: 140 min; 8: 190 min).

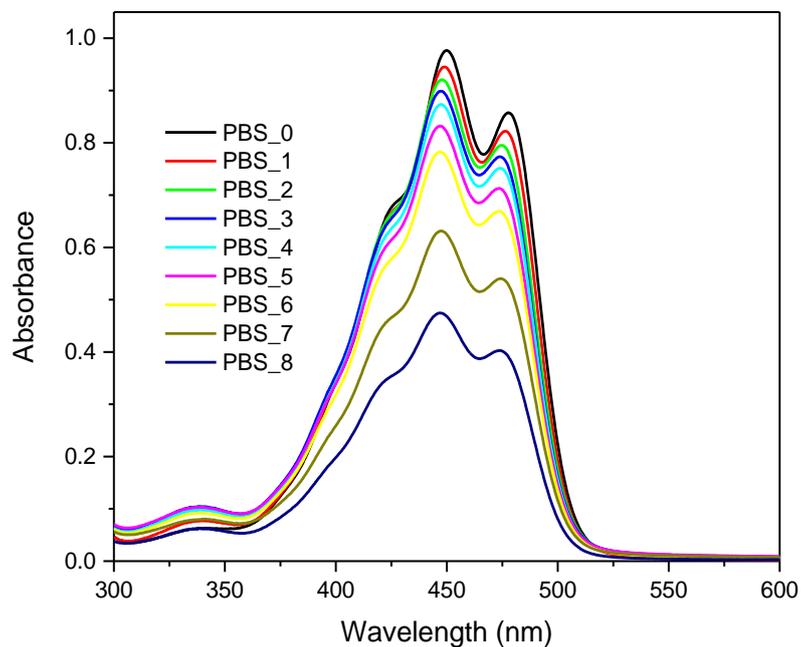


Figure S8. Overlay of UV-vis spectra of β -carotene solution (10^{-5} M) coated with PBS film per different irradiation time (0: 0 min; 1: 10 min; 2: 20 min; 3: 30 min; 4: 40 min; 5: 60 min; 6: 90 min; 7: 140 min; 8: 190 min).

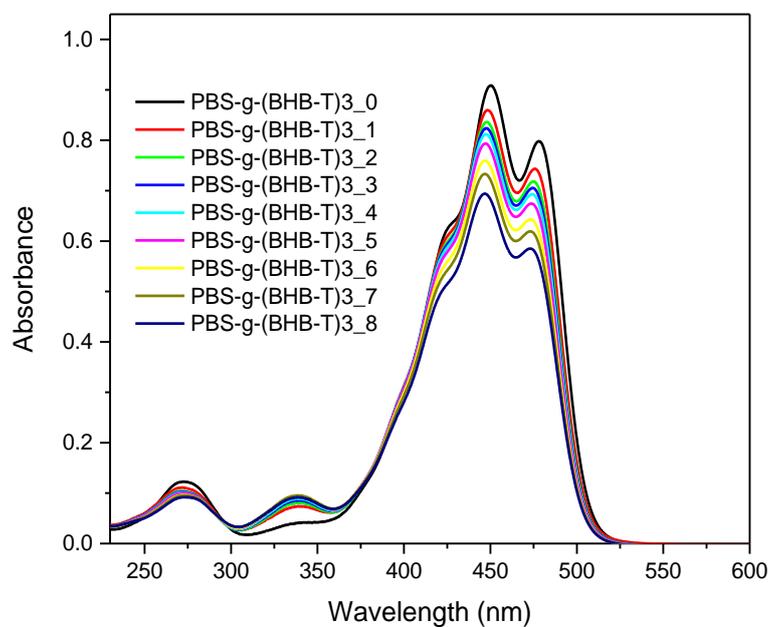


Figure S9. Overlay of UV-vis spectra of β -carotene solution (10^{-5} M) coated with PBS-g-(BHB-T)3 film per different irradiation time (0: 0 min; 1: 10 min; 2: 20 min; 3: 30 min; 4: 40 min; 5: 60 min; 6: 90 min; 7: 140 min; 8: 190 min).