Supporting Information

Water promoted the photo-oxidation and -mineralization of $^{14}$C-polystyrene nanoplastics

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**Synthesis of [β-¹⁴C]-styrene**

[β-¹⁴C]-malonic acid (1.5 × 10⁷ Bq, 2.1 × 10⁹ Bq mmol⁻¹, 99% radiochemical purity) was 50-fold diluted with non-labeled malonic acid (0.0362 g) and dissolved in pyridine (1 mL) in a 25 mL flask equipped with a magnetic stir bar and reflux condenser. Piperidine (177 µL) and benzaldehyde (0.1128 g, 1.065 mmol) were added to the flask. The mixture was heated at 105 °C for 14 h, acidified with 20 mL HCl (1 M), and extracted with ethyl acetate (9 times, each 15 mL). After drying over anhydrous Na₂SO₄ and rotary evaporation to 0.5 mL, the mixture was loaded onto a preparative thin layer chromatography (TLC) plate. TLC was performed on silica gel 60 plates with fluorescence indicator. Analytical (3 cm × 10 cm × 0.2 mm) and preparative (20 cm × 20 cm × 2 mm) plates (GF254; Qingdao Hailang Factory, Qingdao, China) were used. Preparative TLC plates were pre-treated by eluting the plates in ethyl acetate. The plates with loaded samples were developed in n-hexane: ethyl acetate: formic acid (100:100:1, by volume). An imaging scanner (Typhoon Trio⁺; GE Healthcare, Fairfield, USA) was used for autoradiography of the developed plates. The bands of cinnamic acid (Rᶠ = 0.67) were scraped from the plates and extracted with ethyl acetate (seven times, each 15 mL), resulting in [β-¹⁴C]-cinnamic acid (1.2 × 10⁷ Bq, 4.2 × 10⁷ Bq mmol⁻¹, 99.99% radiochemical purity) with a radiochemical yield of 82.8%.

The above [β-¹⁴C]-cinnamic acid was 10-fold diluted with non-labelled cinnamic acid and the total 3 mmol cinnamic acid was added to a 25-mL flask containing silver acetate (0.0096g, 0.6 mmol) and K₂CO₃ (0.0124 g, 0.9 mmol). After gentle flushing
the vessel with nitrogen gas to replace the headspace, degassed \(N,N\)-dimethylacetamide (DMAc) (4 mL) was dropwise added by syringe and the resulting mixture was stirred at 160 °C for 8 h. Then, it was allowed to cool down to room temperature, diluted with \(n\)-hexane (2 mL), poured into aqueous NaOH solution (1 M, 10 mL), and extracted repeatedly with \(n\)-hexane (5 times, each 4 mL). The organic extracts were combined and washed successively with aqueous NaHCO\(_3\) (50 g L\(^{-1}\), 4 mL) and saturated brine (4 mL), dried over anhydrous Na\(_2\)SO\(_4\), and rotary evaporated to 1 mL, resulting in [\(\beta\)-\(^{14}\)C]-styrene (4.2 \(\times\) 10\(^6\) Bq, 99.99% radiochemical purity) with 33.7% yield.

**Characterization of synthesized \(^{14}\)C-PS nanoplastics**

**Scan electron microscopy (SEM).** The morphological analysis was performed with a Field Emission Gun-SEM (Quanta 250 FEG, FEI, Oregon, USA). Samples were sputtering with gold before observation.

**Dynamic Light Scatter (DLS).** The hydrodynamic diameter and its distribution of nanoplastics were measured with a DLS (Zetasizer Nano ZS-90, Malvern Instruments, UK). The samples were suspend in deionized water and dispersed for 10 min by ultrasonic before measuring.

**Fourier-transform infrared spectroscopy (FT-IR).** Products were pretreated by tableting with KBr and measured in transmission mode on a Nexus 870 spectrometer (Nicolet, Massachusetts, USA). The spectra of PS samples were obtained with a 1 cm\(^{-1}\) resolution in the wavenumber range of 400–3600 cm\(^{-1}\).

**Nuclear Magnetic Resonance (NMR) spectroscopy.** The NMR was performed
on a DPX-500MHZ spectrometer (Bruker, Germany) with Tetramethylsilane (TMS) as internal standard and CDCl₃ as the solvent.

**Molecular weight determination.** The number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and polydispersity index ($PDI = M_w / M_n$) of molecules of nanoplastics were measured by gel permeation chromatography (GPC) (PL-GPC120; Agilent Technologies, USA) with a refractive index detector. Two tandem gel columns of polystyrene, PL-gel MIXED-B (10 μm, 300 mm × 7.5 mm) and PL-gel MIXED-C (5 μm, 300 mm × 7.5 mm), were used, with tetrahydrofuran as a mobile phase running at 1.0 mL min⁻¹ and 40 °C. The columns were calibrated using polystyrene standards (Polymer Source Inc., Dorval, Canada).
Fig. S1 The variation of leachates amount in the water washed $^{14}$C-PS nanoplastics from treatment of UV in air. In order to analyze the transformation products in treatment of UV in air, 10 mL nanopure water was added to wash the $^{14}$C-PS nanoplastics in air treatment. After shaking for 5 min, the $^{14}$C amount was detected and then sampling at 30 min, 60 min and 720 min respectively. No significant increase was observed after 5 min indicated that 5 min was enough to wash out all the products in $^{14}$C-PS nanoplastics.
**Fig. S2** Scanning electron microscope (SEM) image of synthesized $^{14}$C-PS (A) and the hydrodynamic diameter of synthesized $^{14}$C-PS in distilled water determined by DLS. The average size range was $250 \pm 88$ nm, with a PDI of 0.31.
Fig. S3 FTIR spectra of standard (A) and synthesized (B) PS. The indicated numbers are characteristic peaks of PS.
Fig. S4 $^1$H NMR spectra of standard (A) and synthesized (B) PS. Peak area was showed at the bottom of the peaks.
Fig. S5 $^{13}$C NMR spectra of standard (A) and synthesized (B) PS.
Fig. S6 FTIR spectra of $^{14}$C-PS nanoplastics before (black line) and after 48 h of UV irradiation in water (red line) and in air (blue line).
Fig. S7 UV spectra of leachates from $^{14}$C-PS nanoplastics after 48 h of UV irradiation in water (red line) and in air (blue line) as well as blank (black line). The absorption at 220 nm may be associated with carboxylic and aromatic chromophores.