# Supporting Information

## Heterogeneous Oxidative Upcycling of Polystyrene Plastics to Benzoic Acid under Air Conditions

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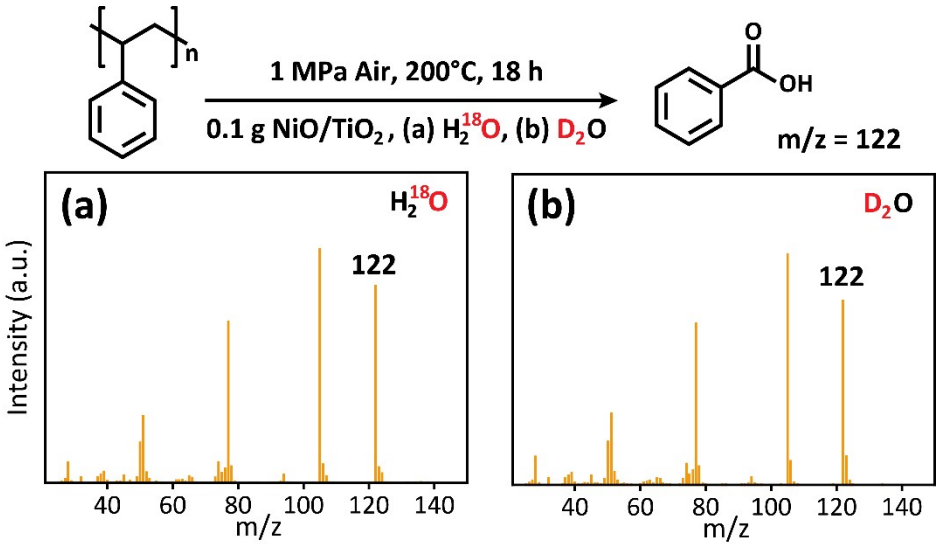


**Fig. S1.** Mass spectra of benzoic acid after isotopic experiments using (a) $H_2{}^{18}O$ and (b) $D_2O$. Reaction conditions: 0.2 g PS, 0.1 g $NiO/TiO_2$, 5 g $H_2{}^{18}O$ or $D_2O$, 1 MPa Air, 200°C, 18 h.

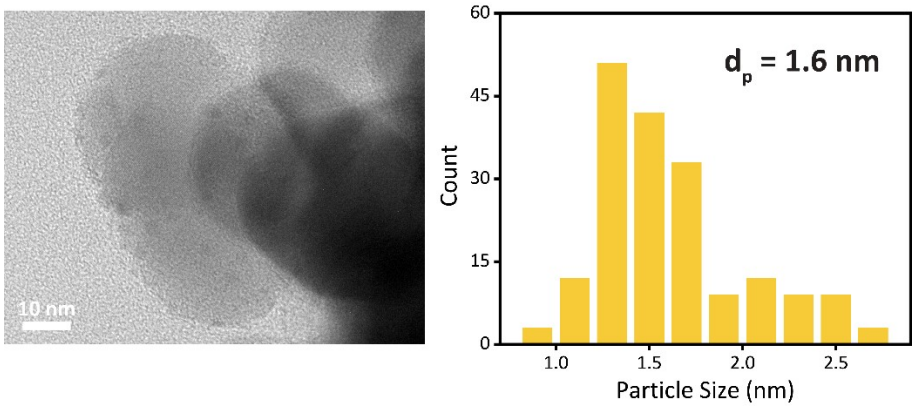


**Fig. S2.** TEM image and particle size distributions of $2NiO/TiO_2$.

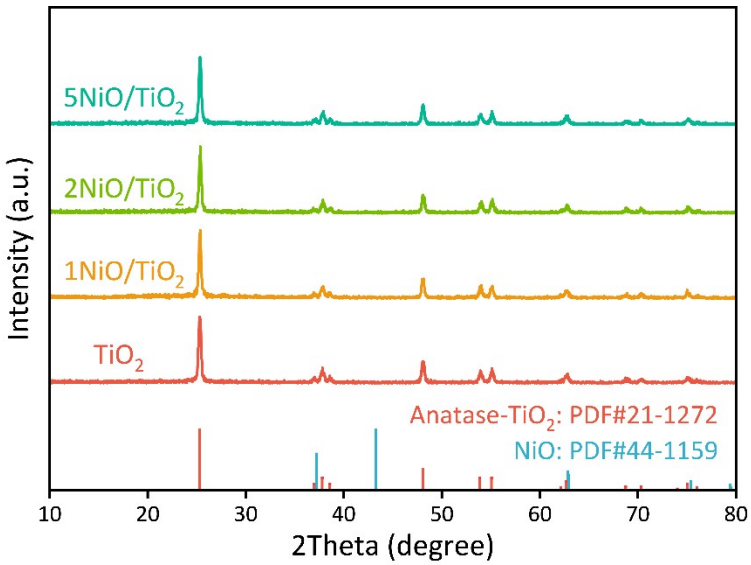


**Fig. S3.** XRD patterns of $TiO_2$, $1NiO/TiO_2$, $2NiO/TiO_2$ and $5NiO/TiO_2$ catalysts.

In the XRD patterns of three $NiO/TiO_2$ catalysts, no diffraction peaks of NiO can be observed, indicating NiO species were well dispersed on $TiO_2$ support.

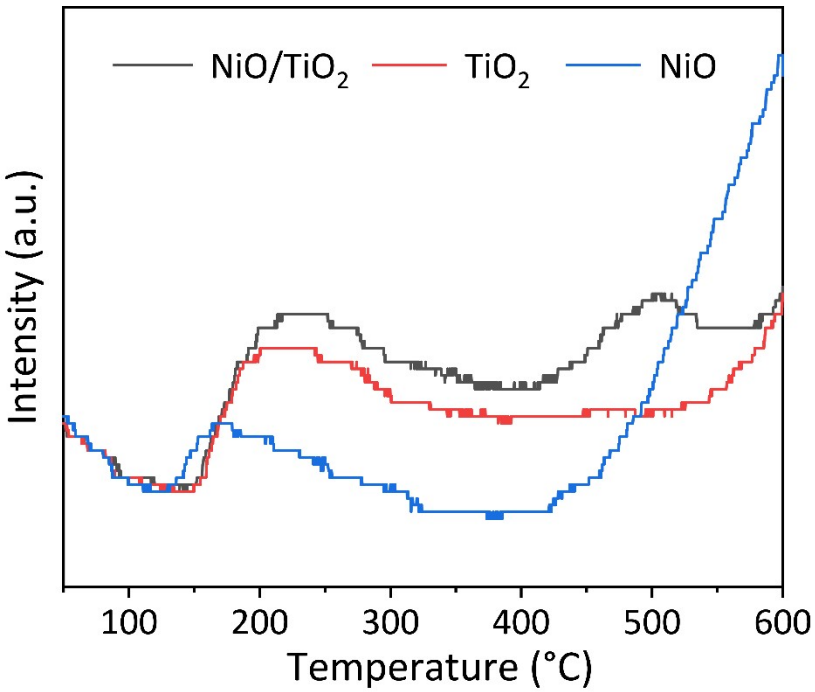


**Fig. S4.** $O_2$-TPD profiles of $NiO/TiO_2$, $TiO_2$ and NiO.

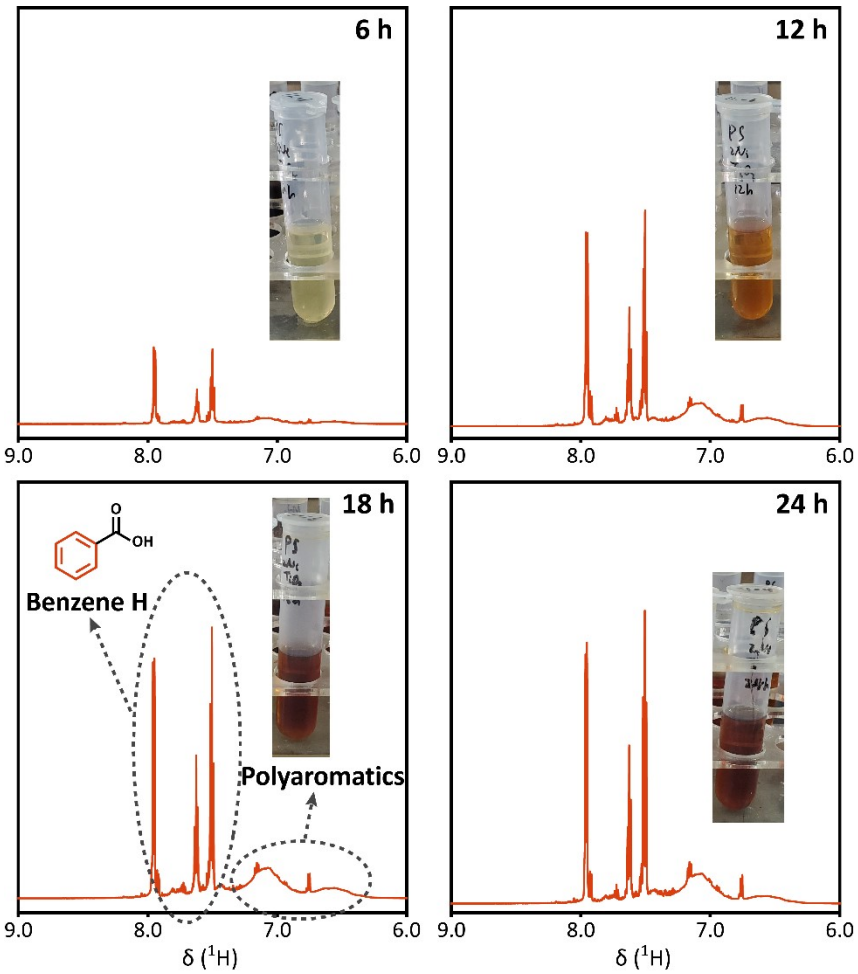


**Fig. S5.** Products analysis by $^{1}$H NMR (DMSO-D6 as solvent) of different reaction time, and the corresponding photo showing the color of products.

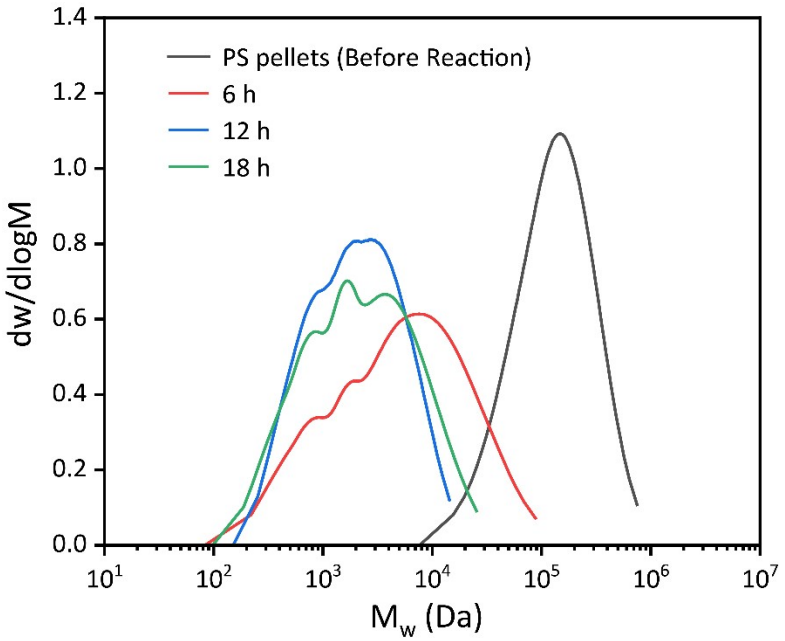


**Fig. S6.** Molecular weight distribution of polystyrene residues after different reaction time measured by GPC.

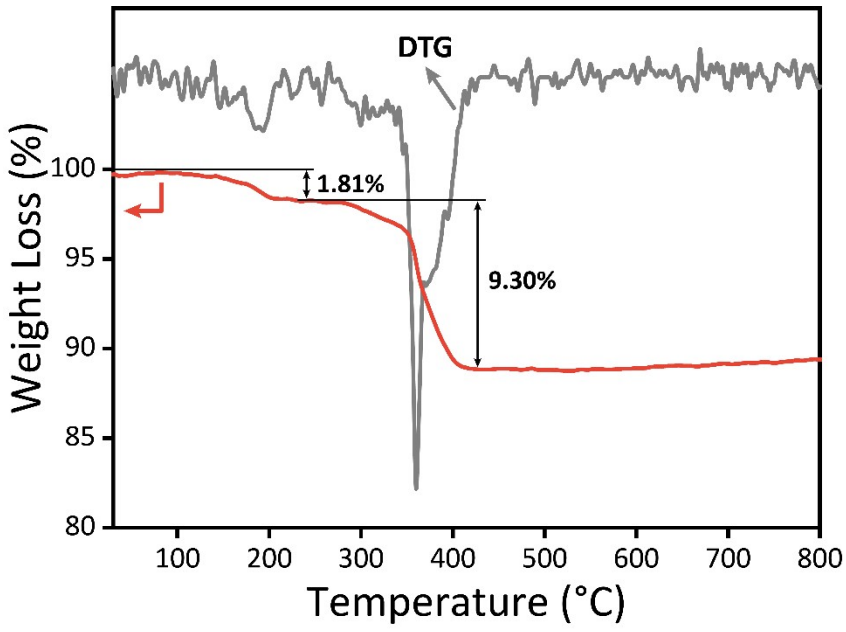


**Fig. S7.** TG and DTG profiles of spent $NiO/TiO_2$ catalyst.

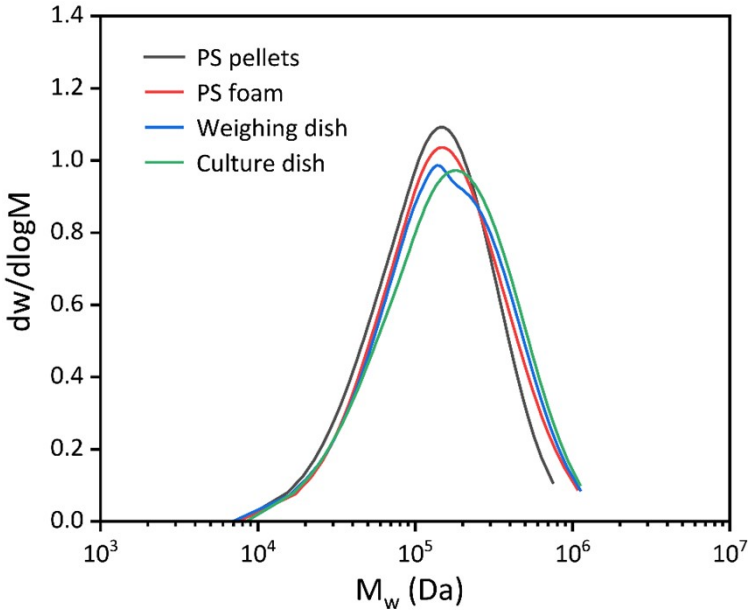


**Fig. S8.** Molecular weight distribution of the polystyrene samples measured by GPC.

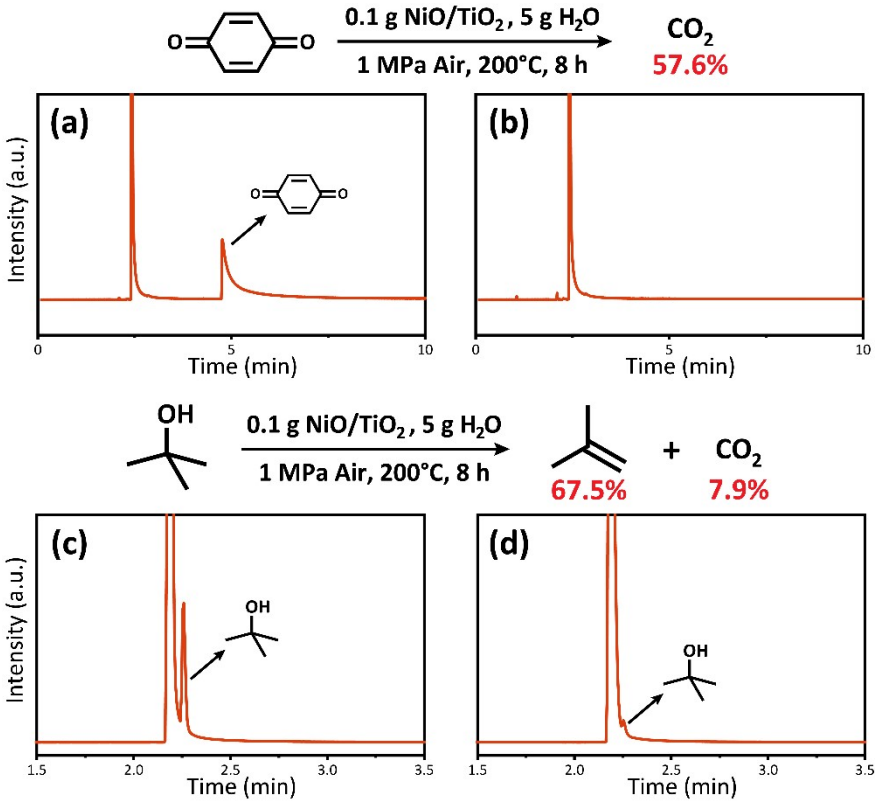


**Fig. S9.** GC/MS chromatograms and products indicating the consumption of radical quenchers: 1,4-benzoquinone (a) before reaction and (b) after 8 h oxidation, tert-butanol (c) before reaction and (d) after reaction. Reaction conditions: 0.1 g quencher, 0.1 g $NiO/TiO_2$, 5 g $H_2O$, 1 MPa Air, 200°C, 8 h.

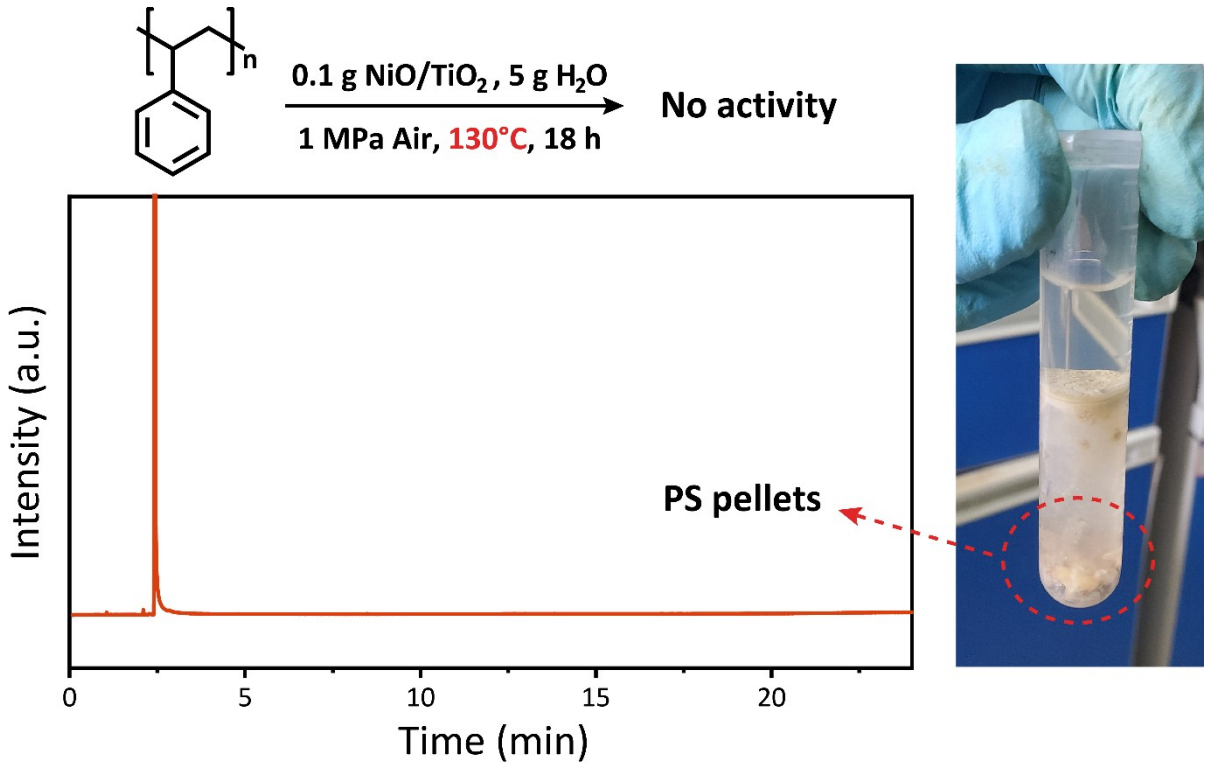


**Fig. S10.** GC/MS chromatogram of PS oxidative upcycling under lower temperature. Reaction conditions: 0.2 g PS, 0.1 g $NiO/TiO_2$, 5 g $H_2O$, 1 MPa Air, 130°C, 18 h.

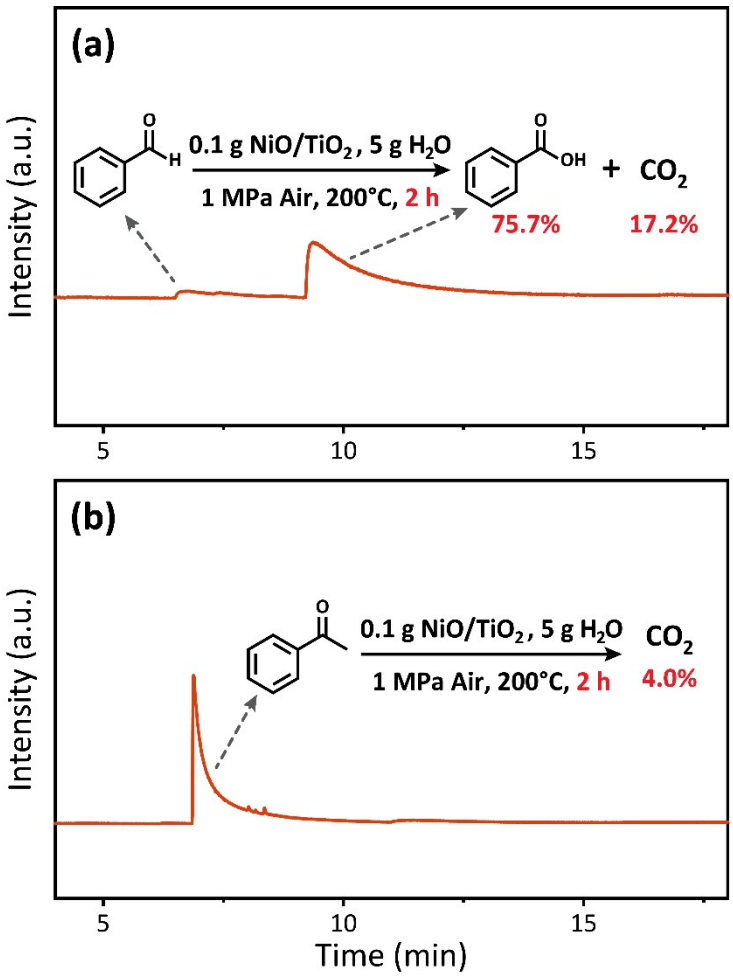


**Fig. S11.** GC/MS chromatograms and products of (a) benzaldehyde and (b) acetophenone after 2 h oxidation reaction. Reaction conditions: 0.2 g substrate, 0.1 g $NiO/TiO_2$, 5 g $H_2O$, 1 MPa Air, 200°C, 2 h.

**Table S1.** Summary of physical properties of $NiO/TiO_2$ catalysts.

| Entry | Catalyst | Surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (nm) | Ni content [a] (wt%) |
|---|---|---|---|---|---|
| 1 | $TiO_2$ | 43.3 | 0.27 | 15.4 | - |
| 2 | $1NiO/TiO_2$ | 36.0 | 0.26 | 17.5 | 1.6 |
| 3 | $2NiO/TiO_2$ | 34.4 | 0.25 | 18.3 | 3.0 |
| 4 | $5NiO/TiO_2$ | 31.6 | 0.24 | 18.6 | 6.0 |
| 5 | $2NiO/TiO_2$-spent | - | - | - | 2.4 |

[a] Determined by ICP-AES.

**Table S2.** Weight-average molecular weight ($M_w$) and polymer dispersity index (PDI) of polystyrene samples obtained by GPC measurements.

| Entry | Sample | $M_w$ (Da) | PDI |
|---|---|---|---|
| 1 | PS pellets | 177873 | 2.05 |
| 2 | PS-6 h | 11724 | 6.51 |
| 3 | PS-12 h | 4146 | 3.68 |
| 4 | PS-18 h | 3052 | 2.51 |

**Table S3.** Weight-average molecular weight ($M_w$) and polymer dispersity index (PDI) of polystyrene samples obtained by GPC measurements.

| Entry | Sample | $M_w$ (Da) | PDI |
|---|---|---|---|
| 1 | PS pellets | 177873 | 2.05 |
| 2 | Culture dish | 239342 | 2.35 |
| 3 | Weighing dish | 228416 | 2.35 |
| 4 | PS foam | 217162 | 2.22 |

**Table S4.** Elementary composition of PS samples determined by Elemental analyzer.

| Entry | Sample | C (wt%) | H (wt%) |
|---|---|---|---|
| 1 | PS-$C_8H_8$ (Theoretical) | 92.3 | 7.7 |
| 2 | PS pellets | 92.6 | 8.1 |
| 3 | Culture dish | 92.7 | 7.9 |
| 4 | Weighing dish | 88.6 | 7.9 |
| 5 | PS foam | 91.3 | 7.6 |