

Sunlight Converts Polystyrene to Carbon Dioxide and Dissolved Organic Carbon

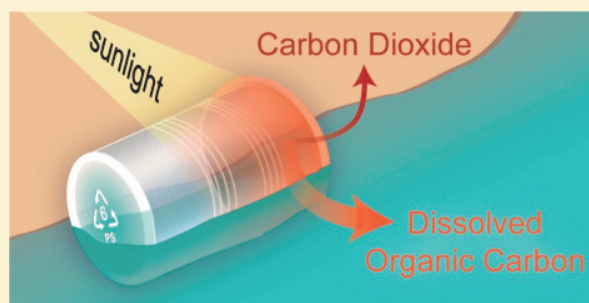
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S Supporting Information

ABSTRACT: Numerous international governmental agencies that steer policy assume that polystyrene persists in the environment for millennia. Here, we show that polystyrene is completely photochemically oxidized to carbon dioxide and partially photochemically oxidized to dissolved organic carbon. Lifetimes of complete and partial photochemical oxidation are estimated to occur on centennial and decadal time scales, respectively. These lifetimes are orders of magnitude faster than biological respiration of polystyrene and thus challenge the prevailing assumption that polystyrene persists in the environment for millennia. Additives disproportionately altered the relative susceptibility to complete and partial photochemical oxidation of polystyrene and accelerated breakdown by shifting light absorbance and reactivity to longer wavelengths. Polystyrene photochemical oxidation increased approximately 25% with a 10 °C increase in temperature, indicating that temperature is unlikely to be a primary driver of photochemical oxidation rates. Collectively, sunlight exposure appears to be a governing control of the environmental persistence of polystyrene, and thus, photochemical loss terms need to be included in mass balance studies on the environmental fate of polystyrene. The experimental framework presented herein should be applied to a diverse array of polymers and formulations to establish how general these results are for other plastics in the environment.



INTRODUCTION

Polystyrene (PS) was the first synthetic polymer detected in the euphotic zone of the ocean in the 1970s,¹ and it is routinely detected in the environment today.^{2,3} Tens of millions of tonnes are produced per year, accounting for 6% of the current global plastic market share.⁴ PS is used in a variety of consumer and industrial products, including food containers, protective packaging, and building materials. Despite widespread use of PS-based goods and detection of PS in the environment, environmental lifetimes of PS are poorly constrained.

The common assumption by leading international governmental agencies that guide policy is that polystyrene persists in the environment for millennia.^{4–8} For example, a 2018 United Nations Environment Programme report states that PS “can take up to thousands of years to decompose”.⁷ Presumably, the scientific basis for the stated lifespan is the resistance of PS to microbial respiration.⁷ Recalcitrance of PS to microbial respiration is due largely to its energetically unfavorable aromatic backbone (75% aromatic carbon by mass) and high molecular weight (tens to hundreds of thousands of Daltons).^{9–11} For example, in one study that used the most sensitive approach available (i.e., ¹⁴C-labeled PS), microbial

respiration of PS was too slow to quantify throughout month-long incubations, leading the authors to conclude that “numerous heterogeneous microbial communities failed to affect biodegradation of the plastic tested”.⁶

While the aromatic backbone of PS hinders microbial attack, it absorbs natural sunlight, resulting in a suite of photochemical oxidation pathways.^{12–21} Previous work has focused on changes to the physical properties of PS, demonstrating that sunlight exposure promotes fragmentation into smaller particles.^{12–18} Others have reported that sunlight partially oxidizes PS, yielding oxygenated breakdown products that are distinct from parent compounds.^{12,13,16–21} However, the rates and controls of partial photo-oxidation of PS are poorly characterized. Although complete photochemical oxidation of organic carbon to carbon dioxide (CO₂) is a well-documented pathway,^{22,23} most reports assume that only microbes are capable of completely oxidizing PS to CO₂,^{4–8} and the

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susceptibility of PS in sunlit environments to conversion to CO₂ is unknown.

Here, we determined how the optical properties, relative susceptibility to complete and partial photo-oxidation, and wavelength and temperature dependence of photo-oxidation vary for five PS samples. Our results demonstrate that sunlight can completely oxidize PS to CO₂ and partially oxidize PS to dissolved organic carbon (DOC). Time scales of these photo-oxidation pathways are orders of magnitude faster (decadal to centennial) than microbial respiration (millennia), indicating that sunlight exposure is likely a governing factor for the environmental fate of PS.

MATERIALS AND METHODS

Five PS samples were used in this study: Goodfellow, Sigma 35 K, Sigma 192 K, Trycite 8001, and Trycite 8003 (Table S1). All samples are commercially available, vary in their physical and chemical properties (e.g., morphology, thickness, additive content), and are described in detail in the Supporting Information, Section 1.1.

Experimental Approach. Ultraviolet and visible light absorbance by the PS samples was measured using a PerkinElmer Lambda 650s spectrophotometer equipped with a 150 mm integrating sphere (Supporting Information, Section 1.2). Complete and partial photochemical oxidation of PS was quantified following previously described approaches (Supporting Information, Section 1.3).^{24–26} Briefly, all experiments were conducted in an Atlas XLS+ solar simulator equipped with a long-arc Xe lamp and a daylight filter (Ametek Inc.). Irradiance was quantified using a NIST-calibrated spectral radiometer (StellarNet, Inc.). On average, simulated sunlight was 3- to 10-fold greater than natural sunlight at 0° and 50° N, respectively. These latitudes were chosen for reference because they encompass the mouths of the 10 rivers that are currently estimated to export 90% of the plastic waste to the oceans (Figure S1, Table S2).²⁷

Analysis. Photochemical CO₂ production was quantified as the light minus dark difference in dissolved inorganic carbon concentration (AS-C3 DIC analyzer; Apollo SciTech, Inc.). Oxygen consumption was quantified as the dark minus light difference in dissolved oxygen concentration using membrane inlet mass spectrometry (Bay Instruments, Inc.). DOC was operationally defined as organic carbon that passes through a precombusted GF/F filter (nominal 0.7 μm pore size, Whatman) and quantified as CO₂ after high-temperature combustion using a Shimadzu 5000A TOC analyzer.²⁸ Calculations for half-lives of complete and partial photo-oxidation are described in the Supporting Information, Section 1.4. For simplicity, half-lives are referred to as lifetimes or lifespans. Natural abundance ¹⁴C and ¹³C measurements were conducted at the National Ocean Sciences Accelerator Mass Spectrometry facility (NOSAMS; Supporting Information, Section 1.5). Wavelength dependence was determined using a Xe-KiloArc system equipped with a monochromator for waveband tuning (Horiba Scientific, Inc.; Supporting Information, Section 1.6). Elemental analysis for C, H, N, O, and S of PS was conducted by Midwest Laboratories (Supporting Information, Section 1.7). Uncertainty of all measurements is described in the figure captions.

RESULTS AND DISCUSSION

Light Absorption by Polystyrene. Three PS samples (Goodfellow, Sigma 192 K, and Trycite 8001) shared absorption spectra characteristics of "pure" PS;²⁹ light absorption decayed exponentially across the UV-B and UV-A region and was undetectable in the visible region (Figure 1A). Sigma 35 K, a product marketed as a "pure" material, had a distinct UV-B absorbance profile indicating that it contains an additive (Figure 1A). The composition and concentration of the additive is unknown, but it is common for commercially

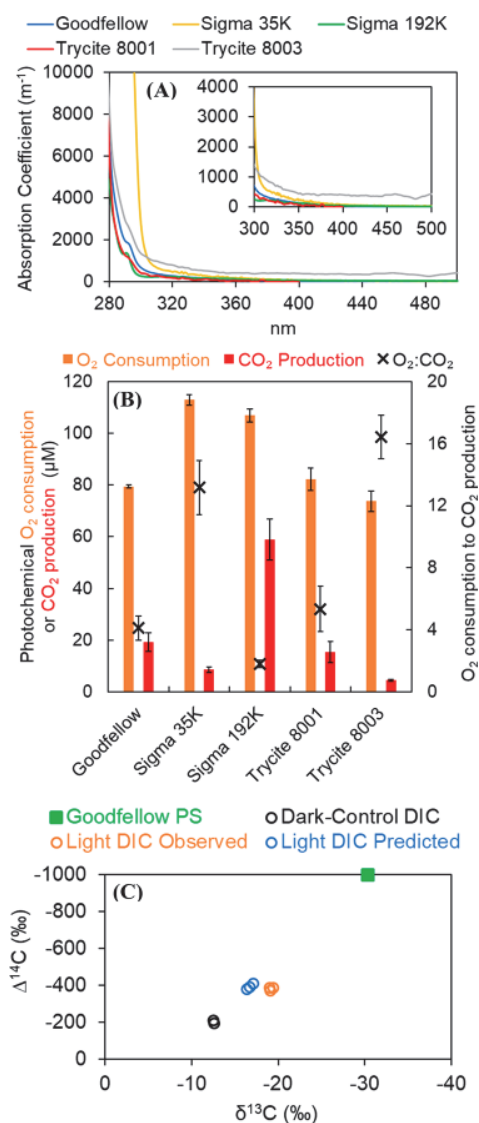


Figure 1. (A) UV–visible absorbance spectrum of five PS samples. Inset shows appreciable absorbance at visible wavelengths (>400 nm) by Trycite 8003, high-impact grade PS that contains black rubber additives. (B) Photochemical O₂ consumption and CO₂ production measurements for the five PS samples. The “x” symbol represents the ratio of O₂ consumption to CO₂ production. (C) Natural abundance radiocarbon (Δ¹⁴C) and stable carbon (δ¹³C) isotope composition of dissolved inorganic carbon (DIC) in dark-control and light-exposed treatments. Initial isotopic composition of PS is presented as filled green squares (N = 3). Predicted values were calculated using measured DIC photoproduction and the initial isotopic composition of PS.

available plastics to contain additives that can alter optical and photochemical properties.¹⁶ In contrast to Sigma 35 K, in which the additive was undisclosed, the distinct visible light absorption by Trycite 8003 is due to black rubber particles that are intentionally added to yield a more durable, high-impact grade PS (Figure 1A). The presence of black rubber additives is further evidenced by the 2-fold higher bulk sulfur content in Trycite 8003 relative to Trycite 8001, a difference likely attributed to the vulcanization process during rubber manufacturing (Table S3; Trycite 8003 = $0.6 \pm 0.1\%$ S; Trycite 8001 = $0.3 \pm 0.1\%$ S; ± 1 SE, $N = 3$; two-tailed, unpaired t test, $P = 0.02$). The impact of additives on the photochemical properties of PS, including susceptibility to complete and partial oxidation and wavelength and temperature dependence, is unknown and the subject of the following sections.

Complete Photochemical Oxidation of Polystyrene to CO₂. Complete photochemical oxidation of PS to CO₂ has previously been reported at 254 nm,³⁰ a waveband that does not reach Earth's surface due to attenuation by stratospheric ozone. In 1980, complete oxidation of PS by solar wavebands (i.e., greater than ~ 280 nm) was initially hypothesized.²⁰ In the current study, we report the first direct evidence of complete oxidation of PS to CO₂ by solar wavebands. All five PS samples were converted to CO₂ by sunlight (Figure 1B). For example, when exposing PS to increasing durations of simulated sunlight (up to 72 h), DIC increased (Figure S2), indicating that PS was completely photo-oxidized to CO₂.

Given that PS is produced using petroleum carbon (C) sources, complete oxidation of PS should shift the natural abundance ¹⁴C content of DIC toward a petroleum-C signature (e.g., $\Delta^{14}\text{C} = -1000\text{‰}$, $\delta^{13}\text{C} = -30$ to -20‰). We validated this hypothesis experimentally. Consistent with a petroleum-C source, PS had a $\Delta^{14}\text{C}$ of $-1000 \pm < 1\text{‰}$ and $\delta^{13}\text{C}$ of $-30.3 \pm < 0.1\text{‰}$ (Figure 1C; Table S4; ± 1 SE, $N = 3$). As expected, DIC in dark-controls equilibrated with laboratory air was more modern and enriched in ¹³C compared to PS (Figure 1C; Table S4; DIC $\Delta^{14}\text{C} = -202 \pm 8\text{‰}$, DIC $\delta^{13}\text{C} = -12.6 \pm < 0.1\text{‰}$, ± 1 SE, $N = 2$). Exposure to simulated sunlight increased DIC concentration by 32% and shifted DIC isotopic composition to values that were consistent with complete oxidation of PS (Figure 1C). Based on the measured DIC photoproduction and the isotopic composition of PS, we predicted the DIC $\Delta^{14}\text{C}$ in the light-exposed treatment to be $-394 \pm 10\text{‰}$, statistically similar to observed values of $-381 \pm 5\text{‰}$ (± 1 SE, $N = 3$, two-tailed, unpaired t test, $P = 0.29$). This result confirms that PS in sunlit surface waters is completely oxidized to CO₂.

Unlike DIC $\Delta^{14}\text{C}$, our predicted and observed DIC $\delta^{13}\text{C}$ values did not overlap (Figure 1C). We predicted a DIC $\delta^{13}\text{C}$ value of $-16.8 \pm 0.2\text{‰}$ but observed a significantly depleted value of $-19.2 \pm 0.1\text{‰}$ ($P = < 0.001$). There are two plausible explanations for this discrepancy. First, the differences between predicted and observed could result from kinetic fractionation of $\delta^{13}\text{C}$ during complete photo-oxidation. Such isotope effects have never been reported for any plastic but have been reported for other organic pollutants.^{31,32} The photochemical $\delta^{13}\text{C}$ isotope effect required to account for the difference between predicted and observed DIC $\delta^{13}\text{C}$ values in the light-exposed treatment is $-3.3 \pm 1.0\text{‰}$ (± 1 SE, $N = 3$). A second interpretation is that PS has different intramolecular ¹³C values. That is, the aromatic C in the PS backbone could be preferentially photo-oxidized to CO₂, and the $\delta^{13}\text{C}$ signature of

aromatic C could be more depleted compared to the $\delta^{13}\text{C}$ signature of aliphatic C in the PS backbone.³³ However, the reactants in the PS production mechanism, kinetic fractionation of C during production, and resulting isotopic homogeneity across C positions of PS is unknown. Irrespective of the precise cause, the photochemical production of depleted DIC $\delta^{13}\text{C}$ may explain field observations that "aged" plastics are more enriched in ¹³C compared to unweathered plastics.³⁴

Partial Photochemical Oxidation of Polystyrene. All five PS samples were partially oxidized by sunlight, an environmental process where oxygen is added to the C backbone to form distinct transformation products.^{24–26} In all cases, photochemical O₂ consumption exceeded CO₂ production, yielding O₂:CO₂ ratios greater than 1 (range 2–16; Figure 1B). Conservatively assuming 1 mol of O₂ is required per mol of CO₂ produced,^{25,26} the excess O₂ consumed is presumably chemically incorporated into PS. Given that oxygenation often increases aqueous solubility,^{35,36} we expected the DOC concentration to increase with irradiation of PS. Consistent with our hypothesis, DOC concentration nearly tripled after five days of simulated light exposure (Figure 2A). Similarly, previous studies have reported that irradiation of PS results in a complex array of lower molecular weight, water-soluble, partially photo-oxidized products.^{17,18}

The relative importance of complete and partial photo-oxidation is influenced by the presence of additives in the polymer formulation. The three presumably "pure" PS samples, as determined by optical spectroscopy (Figure 1A; Goodfellow, Sigma 192 K, and Trycite 8001), exhibited relatively low photochemical O₂:CO₂ molar ratios ranging from 2 to 5 (Figure 1B). In contrast, the additive-containing PS samples (Figure 1A; Sigma 35 K and Trycite 8003) had appreciably higher photochemical O₂:CO₂ ratios ranging from 13 to 16 (Figure 1B). This finding indicates that additives have disproportionate effects on photochemical oxidation pathways. That is, two products made from the same base polymer likely have considerably different photochemical fates depending on their formulations (Table S5), adding to the complexity of determining the fate of plastics in the environment.

Wavelength and Temperature Dependence of Polystyrene Photochemical Oxidation. Given that additives shifted the PS absorption spectrum beyond the UV and into the visible region (Figure 1A), we tested the hypothesis that the wavelength dependence of PS photochemical oxidation shifted. Consistent with our hypothesis, oxidation at 450 ± 26 nm was only detected for Trycite 8003 (Figure 2B; Trycite 8003 = $5.7 \pm 0.6 \mu\text{M O}_2$; Trycite 8001 = $0.1 \pm 0.4 \mu\text{M O}_2$; ± 1 SE, $N = 3$). This expansion of photochemical reactivity into the visible region has critical implications for photo-oxidation rates. Incident visible irradiance (400–700 nm) at Earth's surface is an order-of-magnitude higher than UV irradiance (280–400 nm). Furthermore, blue light at approximately 450 nm penetrates an order-of-magnitude deeper into the water column than UV light because it escapes absorption by chromophoric DOC. Together, additives will have disproportionate impacts on the rates of PS photo-oxidation at Earth's surface and at depth in the water column. This result suggests that environmental lifetimes of consumer and industrial plastics can be controlled by manipulating the additive content; a factor to be explored in the development of next-generation materials.

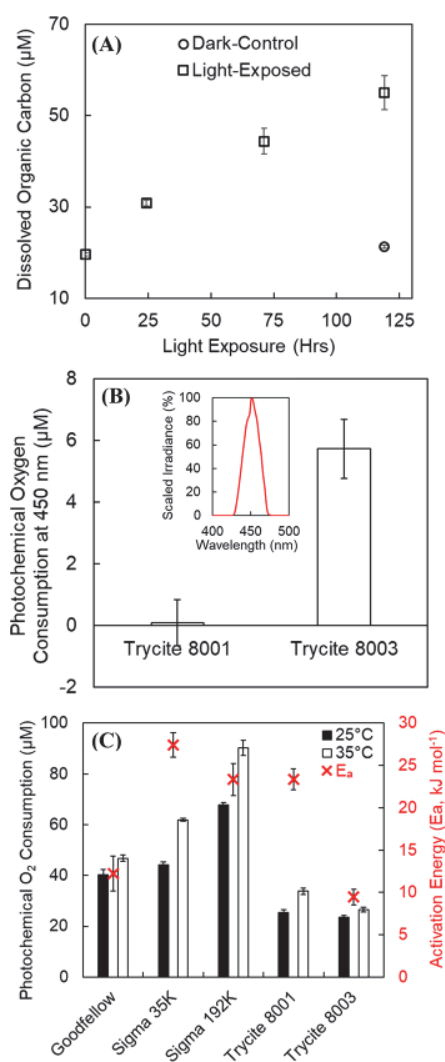


Figure 2. (A) Photochemical conversion of PS to operationally defined dissolved organic carbon (DOC). Error bars represent standard error from the mean ($N = 2$). (B) Photochemical O_2 consumption of PS at 450 ± 26 nm for Trycite 8001 versus Trycite 8003 ($\pm$ full width at half-maximum). Error bars represent standard error from the mean ($N = 3$). (C) Photochemical O_2 consumption at 25 and 35 $^{\circ}\text{C}$ under broadband light. Activation energy (kJ mol^{-1}) was calculated from the Arrhenius equation. Error bars represent one standard error from the mean ($N = 3$).

Temperature has previously been reported to be a determining factor in the photochemical degradation of plastics in the ocean, based on indirect lines of evidence.¹² This conclusion is surprising because photochemical reactions generally have weak temperature dependences, especially when compared to biological activity.³⁷ Therefore, we directly tested the temperature dependence of the five PS samples by quantifying photochemical O_2 consumption at 25 and 35 $^{\circ}\text{C}$. For all PS samples, photochemical O_2 consumption was significantly higher at 35 $^{\circ}\text{C}$ compared to 25 $^{\circ}\text{C}$ (two-tailed, paired t test, $P = <0.05$), with an average increase of $27\% \pm 5\%$ (Figure 2B; $\pm 1\text{SE}$, $N = 5$). The mechanism of this temperature dependence is unknown. It is plausible that the reaction of photochemically generated reactive oxygen species with PS is slightly dependent on temperature, as has been reported for dissolved organic carbon.^{38,39} Independent of the mechanism,

this weak temperature dependence is consistent with previous studies of organic carbon photochemical oxidation.^{37–39} Moreover, biodegradation rates of synthetic polymers have been reported to increase by greater than 100%–300% when increasing temperature by 10 $^{\circ}\text{C}$.⁴⁰ Consequently, temperature is unlikely to be a determining factor for the photochemical oxidation of PS; however, in cases where biological degradation is appreciable, temperature may be a determining factor.

Environmental Implications. When accounting for complete and partial photo-oxidation, the environmental lifetimes of PS are notably shorter than previously reported.^{4–8} Assuming first-order kinetics and accounting for differences between simulated and natural irradiance from 0 $^{\circ}$ to 50 $^{\circ}\text{N}$, average lifetimes of complete photochemical oxidation of Goodfellow and Trycite 8003 are on the order of centennial time scales (Table S5; Goodfellow $t_{1/2} = \sim 300$ years, Trycite 8003 $t_{1/2} = \sim 450$ years). Using the same approach, average lifetimes of partial photochemical oxidation of Goodfellow and Trycite 8003 are on the order of decadal time scales (Table S5; Goodfellow $t_{1/2} = \sim 50$ years, Trycite 8003 $t_{1/2} = \sim 10$ years). These decadal and centennial photochemical lifetimes challenge the commonly held assumption that PS persists in the environment for millennia,^{4–8} an assumption presumably based on the recalcitrance of PS to microbial attack.⁹ Consequently, sunlight exposure, rather than recalcitrance to microbial degradation, is the governing control of the environmental lifetime of PS.

Multiple variables are not considered in these lifetime calculations that could shift our estimates to be shorter or longer. For example, it is unknown how the light absorption properties of PS change with increasing time in the environment (e.g., yellowing or fouling by organics and biofilms) or how the residence time of PS in sunlight environments varies. Accounting for these variables presumably could lead to longer lifetimes. Alternatively, the amount of PS completely oxidized to CO_2 may be underestimated. Given that organic carbon must be dissolved to be respired by microbes,⁴¹ we hypothesize that the DOC produced from the partial photo-oxidation of PS is more labile to microbial respiration than unweathered PS. Such coupled photochemical and biological breakdown of PS has been reported to occur in terrestrial ecosystems,^{10,11} but the viability of this mineralization pathway in aquatic ecosystems is unknown.

Nevertheless, these initial environmental lifetime estimates suggest that PS does not persist in the environment for millennia, an assumption commonly made by leading international governmental agencies that steer policy.^{4–8} Future work should expand the experimental framework presented herein to a diverse array of polymer types^{17,42} and formulations to establish how general these results are for other plastics in the environment. Consequently, photochemical loss terms should be incorporated into global fate models, which we expect will (i) refine estimates of the environmental lifetime of plastics, (ii) improve our understanding of the amount of plastics on land and in the ocean,⁴³ (iii) inform assessments of the risks associated with plastic pollution, and (iv) help frame evidence-based policy.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.9b00532.

Descriptions of PS samples, optical properties of PS, characterization of the complete and partial photo-oxidation of PS, calculations of half-lives of complete and partial photo-oxidation, radiocarbon and stable carbon isotope experiments, wavelength dependence experiments, and elemental analysis of PS. Figures of incident irradiance and complete photo-oxidation time-series. Tables of complete and partial photo-oxidation of PS, incident irradiance, elemental composition of PS, ^{14}C and ^{13}C experimental results, and lifetime calculations. (PDF)

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Notes

The authors declare no competing financial interest.

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