

Accelerated Hydrolysis Method for Producing Partially Degraded Polyester Microplastic Fiber Reference Materials

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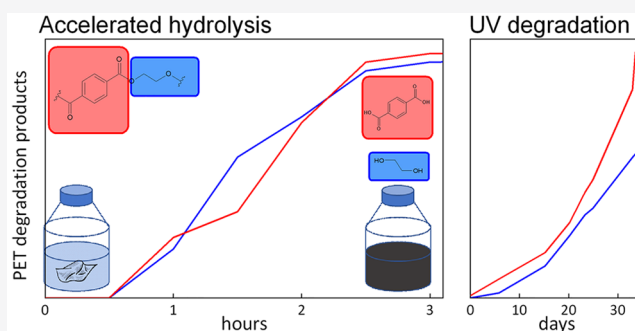


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ABSTRACT: Microplastic fibers (MPFs) from textiles significantly contribute to the microplastic (MP) load in many environmental matrices and have been shown to negatively impact the organisms therein. Most fate and effect studies to date rely on pristine reference MP materials that have limited relevance compared with the partially degraded MP particles and fibers typically present in the natural environment. The current study aimed to develop and validate a rapid method to generate environmentally relevant polyester (PET) MPF reference material with controllable levels of degradation. Importantly, the method produced the same degradation products (terephthalic acid (TA) and ethylene glycol (EG)) as those generated during natural UV (sunlight) exposure of PET. Alkaline hydrolysis provided linearly increasing degrees of degraded PET MPFs over just a few hours, with full decomposition into molecular fragments occurring after 3 h. The extent of physical degradation was determined by scanning electron microscopy, whereas chemical degradation was quantified by measuring the production of TA and EG degradation products. The proposed accelerated hydrolysis degradation method is relevant for producing partially degraded PET MPF reference materials for use in fate and effect studies.



INTRODUCTION

Microplastic fibers (MPFs) derived from synthetic textiles and other sources represent a significant proportion of the microplastic (MP) load in many environmental matrices^{1–3} and have been shown to have negative impacts on aquatic organisms.^{4,5} However, the majority of studies investigating the fate and effects of MP particles have employed commercially available pristine spherical reference materials, limiting the relevance of the data produced.^{6,7} As a result, some recent studies have explored ways to produce more environmentally relevant MP reference materials.^{1–3,8} For example, marine litter can be cryomilled to produce irregular shaped fragments with complex surface morphologies and chemistries.⁸ Because cryomilling of MPFs results in a loss of the fiber shape, techniques such as manual cutting (fibers >1 mm) or microtome (fibers <1 mm) are necessary.⁹ However, this still produces reference materials that do not reflect the partially degraded nature of MPs and MPFs in the natural environment. This is important when trying to assess the risks associated with MP pollution, as degradation processes alter both the physical and chemical properties of plastic materials and may influence their environment fate and potential bioavailability and effects on organisms.

UV-induced oxidation (photodegradation) is the most effective degradation mechanism for many plastic materials

released into the natural environment,^{10,11} resulting in the formation of hydroxy, carbonyl, and carboxy groups on the particle surface as well as cracking and fragmentation.^{11–15} These physicochemical changes are important when trying to assess the risks associated with MP pollution, as they may influence the MPF environment fate, bioavailability, and effects on organisms.^{6,16–18} However, the photodegradation of polymers is still very slow under typical environmental conditions.^{10,19–21} Accelerated degradation using artificial UV exposure in the laboratory, which is a widely accepted approach, can thus take weeks to months for significant degradation to occur, is costly to operate, and is not necessarily able to accurately reproduce the natural UV degradation process.¹⁹ There is therefore a need for accelerated degradation methods that allow the rapid and controlled simulation of environmental degradation mechanisms for the production of partially degraded MP and MPF reference materials.^{6,22} These need to be quick, cost-effective, reproducible

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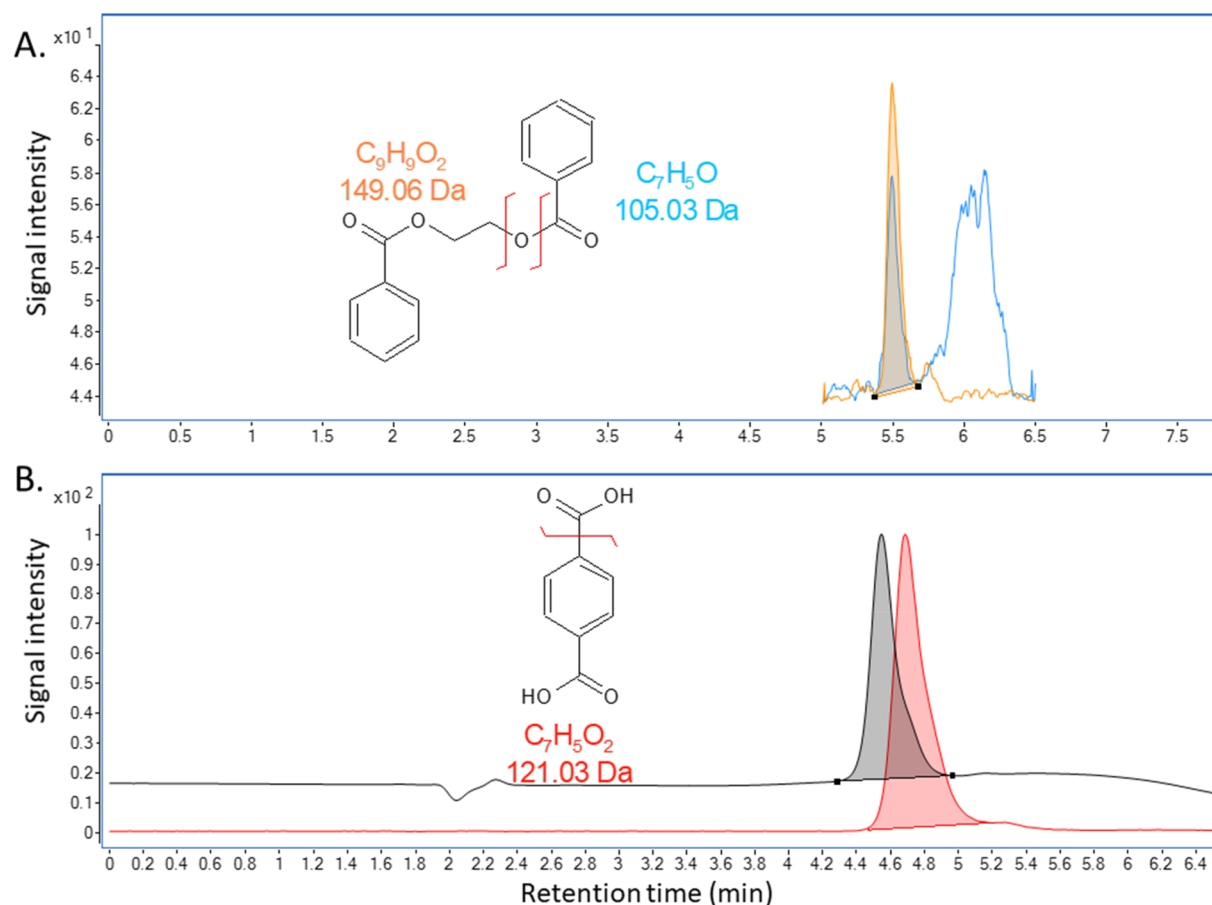


Figure 1. Analysis of terephthalic acid and ethylene glycol derivative. (A) LC-MS/MS chromatogram of the dibenzoyl derivate of EG and benzoyl chloride. The two peaks correspond to mass transitions from the proposed cleavages of the same color shown in the chemical diagram. (B) LC-UV-MS/MS chromatogram of TA. The black and red chromatograms correspond to the signals from the UV and MS/MS detectors, respectively, and the proposed cleavage is shown.

cible and have an acceptable degree of environmental relevance in terms of the degradation process and degradation products.

In this study, we demonstrate a fast and cheap hydrolytic degradation method for producing environmentally relevant, partially degraded polyester (PET) MPFs reference materials for use in fate and effects studies. The temperature and pH were systematically varied to identify conditions resulting in the near-complete degradation of the polyester MPFs within 3 h. The degree of degradation was quantitatively determined by measuring the PET degradation products terephthalic acid (TA) and ethylene glycol (EG), allowing specific levels of degradation to be achieved. Scanning electron microscopy (SEM) imaging was used to visualize the degree of physical modification resulting from the degradation process. Finally, the environmental relevance of the accelerated hydrolysis method was verified by comparing the hydrolyzed PET and degradation products to PET MPFs exposed to UV irradiation in seawater.

MATERIALS AND METHODS

Materials and Chemicals. PET fleece material used to produce consumer clothing products was supplied by a commercial garment producer (Helly Hansen, Norway). All chemicals were purchased from Merck or Sigma-Aldrich. MPFs were carefully removed from the textile using a scalpel and stored in glass vials prior to use. Deionized water was of MilliPore Milli-Q quality. Natural seawater was collected from

90 m depth in Trondheimsfjorden, Norway (63°26'N, 10°24'E), filtered to remove coarse particles, and subjected to sterile filtration (0.22 μ m Sterivex) prior to use in the experiments. (See the SI for more details.)

Accelerated Hydrolytic Degradation Method Development. Two prestudies investigated the influence of temperature (60–90 °C) and pH (1–14) on the hydrolysis process. The hydrolysis of the PET MPFs was determined gravimetrically in the prestudies, and the method is described in the Supporting Information (SI). For all exposures, 200 mg of PET MPFs was introduced in glass bottles containing 25 mL of aqueous solution of NaOH (10% NaOH; pH 14.4), and hydrolysis was conducted at 90 °C using an oil bath. Samples were collected and subjected to analysis after 0, 0.5, 1, 1.5, 2, 2.5, 3, 6, and 24 h. A full overview of the experimental matrix is presented in Table S1. Upon sampling, the hydrolysis reaction was quenched by transferring the bottles immediately to an ice water bath, as studies showed that the reaction rate is significantly reduced at low temperatures (Figure S1). To isolate the fibers for SEM imaging, the samples were filtered using a paper filter with a pore size of 20–25 μ m (Whatman). After the filtration, the fiber samples were left on the filter, rinsed with deionized water, and dried overnight at 80 °C. Samples were stored at –20 °C until analysis.

UV Degradation Validation. UV degradation of PET fibers was performed using a Suntest CPS+ apparatus (Atlas Material Testing Solutions) equipped with a xenon UV lamp

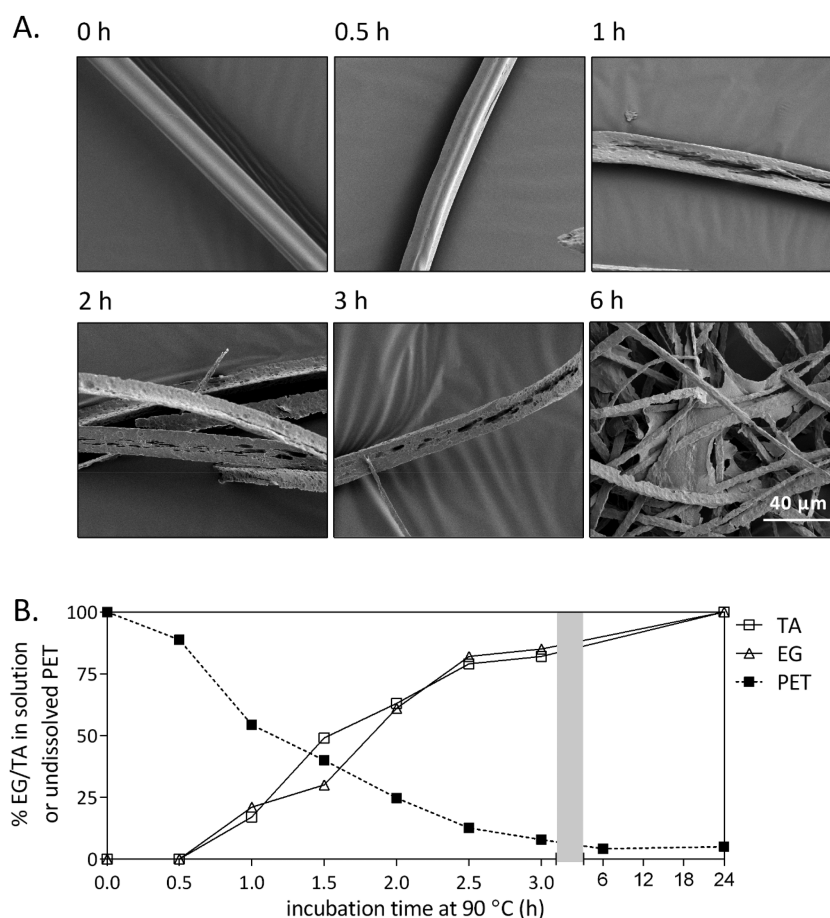


Figure 2. Accelerated hydrolysis fully degrades PET. (A) SEM images of PET subjected to accelerated hydrolysis (1000 \times magnification). (B) TA and EG measured by LC-UV-MS/MS plotted with undissolved PET determined gravimetrically during accelerated hydrolysis. The gray bar represents a change in the time increment on the x axis from 0.5 to 6 h.

(1500 W) and fitted with a natural daylight filter. PET fibers were mixed into Milli-Q or seawater at a concentration of 8 mg mL⁻¹ and placed into 35 mL quartz tubes with glass stoppers. Irradiation was conducted at 65 W/m², and the temperature in the exposure chamber was maintained at 24 \pm 3 $^{\circ}$ C. Sampling was performed approximately once per week for a period of 32 days, and 250 μ L aliquots were directly stored at -20 $^{\circ}$ C in the dark. The 32 day exposure period corresponded to \sim 304 days (10 months) of UV exposure based on mean European solar irradiance (details in the SI). Prior to sampling, the quartz tubes were shaken, after which 250 μ L was removed and filtered through a micropipette tip filter prior to analysis for EG and TA degradation products.

Determination of Ethylene Glycol and Terephthalic Acid by LC-UV-MS/MS. For the analysis, EG was derivatized with benzoyl chloride as previously described.²³ Derivatization was accomplished by adding 50 μ L of sample, 100 μ L of 4 M NaOH, and 50 μ L of benzoyl chloride to 250 μ L with deionized water. The reaction was vortexed and incubated at room temperature for 5 min. Next, the reaction was quenched by adding 50 μ L of 10% glycine and incubating for 3 min at room temperature. The dibenzoyl derivate was then extracted with 1 mL of pentane. Phase separation was accomplished by centrifugation at 10 000g for 5 min, and the organic phase was evaporated under nitrogen at 50 $^{\circ}$ C. The dried extract was dissolved in 800 μ L of 10 mM ammonium formate (pH 2.8) in 50% acetonitrile. Derivatized samples were diluted 500-fold

prior to analysis. TA was analyzed without derivatization by diluting samples 100-fold prior to analysis.

Samples were analyzed on an Agilent 1260 HPLC system equipped with a variable wavelength detector coupled to a 4670 triple-quadrupole mass spectrometer equipped with an electrospray ion source (Agilent Technologies, Santa Clara, CA). The HPLC column (ZORBAX Eclipse Plus C18 2.1 \times 50 mm, 1.7 μ m particle size, Agilent Technologies) was kept at 25 $^{\circ}$ C, and the injection volume was 10 μ L. The mobile phase consisted of 10 mM ammonium formate pH 2.8 (A) and acetonitrile containing 0.1% formic acid (B). The 7.5 min HPLC program for EG was as follows: Start at 10% B, ramp to 90% B by 3 min, hold until 3.5 min, and ramp to 10% B by 3.6 min. The EG derivate was detected by MS using the following mass transitions in positive ionization mode: m/z 271.1 \rightarrow 149 (quantifier) and m/z 271 \rightarrow 105.1 (qualifier). The 6.5 min HPLC program for TA was as follows: Start at 10% B, ramp to 90% B by 2 min, hold until 2.5 min, and ramp to 10% B by 2.6 min. TA was detected by UV absorption at 254 nm, and the peak identity was confirmed by MS using the following mass transition in negative mode: m/z 165 \rightarrow 121.1.

Scanning Electron Microscopy. Prior to analysis, MPFs from both the accelerated hydrolysis studies and the UV exposure studies were mounted on double-sided tape and coated in a thin layer (5–10 nm) of evaporated gold to make them conductive. MPF imaging was performed (1000 \times magnification) using an FEI Nova Nano SEM 650 apparatus,

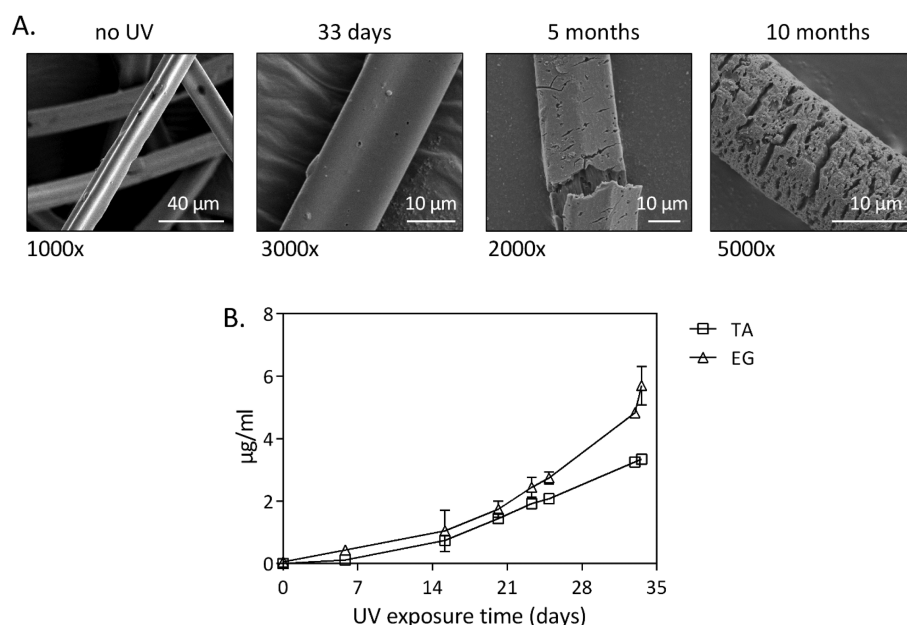


Figure 3. UV-irradiated PET releases terephthalic acid and ethylene glycol. (A) SEM images of nonirradiated and UV-irradiated PET fibers after 33 days, 5 months, and 10 months. (B) TA and EG measured by LC-UV-MS/MS.

operated in high-vacuum mode at accelerating voltages of 5 kV, with an emission current of 90 pA and at a working distance of 8 mm.

RESULTS AND DISCUSSION

Terephthalic Acid and Ethylene Glycol Assay. PET degradation by alkaline hydrolysis leads to the formation of its constitutive components TA and EG (the latter in the form of disodium terephthalate salt).²⁴ Thus we established protocols to measure both by HPLC with a combination of UV and MS detection. EG detection is potentiated by derivatization using benzoyl chloride (Schotten–Baumann reaction) and extracted with pentane.^{23,25} Two mass transitions were used to detect and quantify EG, and the quantification limit (LoQ) for the assay was 2.5 pg (corresponding to 0.5 ng mL⁻¹, Figure 1A). UV detection was also achievable at 237 nm, but the sensitivity was three orders of magnitude lower, and an unidentified coeluting peak hindered accurate quantification. TA could be directly quantified (i.e., without extraction or derivatization) in the water phase. Our experiments were performed in seawater or water containing a high (3.5%) NaCl concentration, neither of which are amenable to electrospray mass spectrometry. We therefore used UV detection at 254 nm for TA quantification, using the MS to confirm the identity of the TA peak (Figure 1B). The LoQ for TA detection with UV was 250 pg (corresponding to 50 ng mL⁻¹). More sensitive MS detection can be used if samples are in Milli-Q or are desalted using, for example, solid-phase extraction columns. For both compounds, a stable-isotope-labeled internal standard can also be used to enable absolute quantification using mass spectrometry, especially when working with low concentrations.

Accelerated Hydrolytic Degradation Method Development. Alkaline hydrolysis is used as a softening process in the production of PET fabrics²⁶ and can also be used in the chemical recycling of PET to its synthetic components TA and EG.^{24,27} To optimize alkaline hydrolysis, we tested PET degradation at different pH values and temperatures. An aqueous solution at pH 14.4 (10% NaOH) was found to be

most effective at hydrolyzing the PET MPFs, with lower pH values not resulting in any significant hydrolysis. A temperature of 90 °C was observed to reduce the hydrolysis time significantly compared with 60 and 70 °C, with >90% degradation after 3 h (Figure S1) and complete degradation after 24 h.

Having established a method to rapidly fully degrade PET MPF (24 h), the PET fibers were subjected to alkaline hydrolysis over time to determine whether they were suitable for use as partially degraded MPF reference materials. Physical and chemical degradation was studied using a combination of SEM, gravimetry, and LC-UV-MS/MS (Figure 1, Figure S2). SEM analysis showed that superficial fiber degradation occurs after 30 min, with significant structural damage observable after 1 h. After 6 h, substantial structural degradation had occurred, and no material was detected after 24 h (Figure 2A). LC-MS/MS analysis of PET degradation products similarly showed a linear time-dependent increase in both TA and EG degradation products that plateaued after 2.5 to 3 h, increasing slightly at 24 h (Figure 2B). This was inversely mirrored when measuring undissolved PET gravimetrically (Figure 2B). We suggest that by 6 h, the fibers are largely degraded into a mixture of monomers (i.e., EG and TA) and short water-soluble polymers, although some heavily degraded PET fibers remain detectable by SEM at this point. Full hydrolysis of the water-soluble polymers into the final degradation products occurs by 24 h, and no fibers are visible by SEM imaging. Thus alkaline hydrolysis of PET fibers can be used to generate reference material of partially degraded MPF by attenuating hydrolysis time.

Comparison of Hydrolysis and UV Degradation. To determine the environmental relevance of the partially degraded PET MPF reference material, we confirmed whether PET degradation by alkaline hydrolysis resembles UV degradation that occurs in the environment. To this end, we exposed PET fibers in seawater to simulated sunlight and measured the generation of EG and TA, as described above. Small holes were observed in the fibers exposed to UV after

~33 days (Figure 3A), suggesting the onset of physical changes to the PET MPFs. In extended UV exposure studies, the PET fibers exhibited significant changes in their surface morphology after 5 months, which grew even more pronounced after 10 months of UV exposure (corresponding to 7.5 years under natural environmental conditions). These results are consistent with the findings in our recent study investigating the UV degradation of multiple synthetic fiber types.²⁸ Importantly, both the UV exposure and the accelerated hydrolysis approaches yield partially degraded PET fibers that exhibit many physical similarities, including a change from a smooth to an irregular surface and the formation of crack and holes along the fiber length.

Pristine, hydrolyzed, and UV-degraded PET MPFs were also analyzed by FTIR to investigate changes in the surface chemistry resulting from the two degradation mechanisms (Figure S3). After 3 h of hydrolysis, the PET MPFs were significantly modified physically, but the FTIR spectrum remained almost identical to that of the pristine material (Figure S3a). Similarly, PET MPFs subjected to 10 months of UV exposure also underwent physical changes, but no significant differences in surface chemistry were observed (Figure S3b). Although, it could be expected that UV degradation leads to increased oxidation of the fiber surface, the FTIR spectra do not support this. It is suggested that the UV degradation mechanism results in products that rapidly fragment from the main fiber or quickly dissolve into the surrounding aqueous media. The photodegradation of PET has been proposed to occur via chain scission leading to the generation of carboxyl end groups followed by the formation of mono- and dihydroxyterephthalates, carboxyl end groups, and aldehydes (Norrish type I reaction).^{29,30} The likely scenario occurring is that PET fibers are broken down into polymers or oligomers of different lengths with a variety of chemical end groups that can spontaneously degrade to soluble EG and TA. Although the ultimate degradation products of PET degraded by UV exposure will vary in composition, we propose that TA and EG can be used to estimate PET degradation. Both TA and EG were measured after only 6 days of *in vitro* UV exposure (corresponding to ~2.3 months of sunlight) and steadily increased throughout the experiment (Figure 3B). Controls incubated in the dark at room temperature over the same amount of time contained no measurable EG or TA.

Importantly, the extent and kinetics of the breakdown reaction from intact fibers to the different degradation products warrants further study to determine exactly which products are formed upon UV exposure. We observed a ratio of 0.5 and 3.5 EG moieties per TA for the alkaline hydrolysis and UV degradation experiments, respectively. The expected ratio for pure PET is 1, but it is possible that EG was supplemented with other glycols (e.g., polypropylene glycol) or that EG was degraded during alkaline hydrolysis. During the UV degradation, it is likely that hydroxyterephthalates and polymers are released from the fibers upon UV exposure, which would release EG but not generate a corresponding TA. These terephthalate intermediates would break down much more quickly during the alkaline hydrolysis reactions than during UV degradation experiments, explaining the larger EG-to-TA ratio. Thus the relationship between TA/EG formation, as well as that between alkaline hydrolysis and UV degradation, should be interpreted as a proportional relationship and not a direct correlation. Nevertheless, the generation of TA and EG by the UV exposure of PET confirms that (1) the two

compounds can be used as universal markers of PET degradation and (2) reference materials produced using alkaline hydrolysis can be used to approximate UV degradation. Although it is difficult to directly compare the accelerated hydrolysis of the PET fibers with the combination of degradation mechanisms occurring simultaneously under natural environmental conditions (e.g., UV, mechanical and microbial), the method appears to yield comparable physical changes to those caused by UV exposure.

The current study outlines a fast (<3 h), cheap, and reproducible method for producing partially degraded PET MPF reference materials for use in environmental fate studies. Importantly, the reference materials are similar in nature to partially degraded polyester microfibers generated through exposure to UV, and the degree of degradation can be accurately controlled depending on the required properties for the final materials. The ability to produce such reference materials is critical for improving our understanding of the fate and impacts of polyester microfibers in the natural environment and represents an important step away from studying pristine reference materials. We conclude that PET degradation can be measured by TA and EG and, by extension, that the degree of fiber degradation in our reference material is a valid benchmark for environmental fate studies. Because hydrolysis mainly occurs in polymers that have water-sensitive groups in the polymer backbone, such as polyesters (including polyethylene terephthalate), polyanhydrides, polyamides, polyethers, and polycarbonates, the method described above has potential application for producing a broad range of partially degraded plastic reference materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.0c01002>.

Summary of preliminary study, calculation of total UV irradiance exposure, gravimetric determination of PET dissolution, and photographic presentation of hydrolysis (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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