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Photochemical Transformation of Poly(butylene adipate-*co*-terephthalate) and Its Effects on Enzymatic Hydrolyzability

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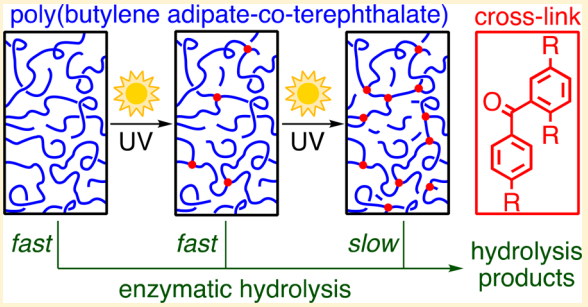
Supporting Information

ABSTRACT: Biodegradable polyesters are being increasingly used to replace conventional, nondegradable polymers in agricultural applications such as plastic film for mulching. For many of these applications, poly(butylene adipate-*co*-terephthalate) (PBAT) is a promising biodegradable material. However, PBAT is also susceptible to photochemical transformations. To better understand how photochemistry affects the biodegradability of PBAT, we irradiated blown, nonstabilized, transparent PBAT films and studied their enzymatic hydrolysis, which is considered the rate-limiting step in polyester biodegradation. In parallel, we characterized the irradiated PBAT films by dynamic mechanical thermal analysis. The rate of enzymatic PBAT hydrolysis decreased when the density of light-induced cross-links within PBAT exceeded a certain threshold. Mass-spectrometric analysis of the enzymatic hydrolysis products of irradiated PBAT films provided evidence for radical-based cross-linking of two terephthalate units that resulted in the formation of benzophenone-like molecules. In a proof-of-principle experiment, we demonstrated that the addition of photostabilizers to PBAT films mitigated the negative effect of UV irradiation on the enzymatic hydrolyzability of PBAT. This work advances the understanding of light-induced changes on the enzyme-mediated hydrolysis of aliphatic-aromatic polyesters and will therefore have important implications for the development of biodegradable plastics.



INTRODUCTION

Modern agriculture heavily relies on the use of synthetic polymers in various applications. For example, approximately two million metric tons of plastic mulch films are used annually around the world.[1] As most of these plastic materials are not biodegradable, these agricultural applications of plastics—also referred to as plasticulture—facilitate entry of nondegradable polymer materials into environmental systems and thus contribute to the accumulation of plastics in the environment.[2] Substituting nondegradable plastics with biodegradable alternatives is a promising strategy to mitigate the growing problem of plastic accumulation.[3−6] Polyesters are an important class of plastics because they can exhibit high performance while offering the potential for biodegradability. Ester bond hydrolysis, which can be catalyzed by extracellular microbial esterases,[7] is considered the rate-limiting step in the overall biodegradation of polyester materials in receiving environments; subsequent microbial uptake and utilization of oligomers and monomers formed during hydrolysis are comparatively fast.[8,9]

Among biodegradable polyesters, the aliphatic-aromatic copolyester poly(butylene adipate-*co*-terephthalate) (PBAT) is a commercially important material used extensively for plastic mulch film.[5] Several studies have shown that the ester bonds in PBAT can be hydrolyzed by extracellular carboxylesterases from microorganisms that are commonly found in terrestrial systems.[10−12] Cutinases, one particular class of extracellular carboxylesterases which hydrolyze cutin on plant surfaces, were particularly effective in hydrolyzing PBAT as well as other polyesters containing aromatic units.[13−17] We previously demonstrated that carbon from all monomeric units in PBAT (i.e., butanediol, adipate, and terephthalate) was microbially utilized and converted to carbon dioxide and microbial biomass during incubation of PBAT films in an agricultural soil.[9]

During application, mulch films encounter various weathering processes that alter the physicochemical properties of the product. Photochemical weathering of mulch films is particularly important due to the high rate of photoexposure

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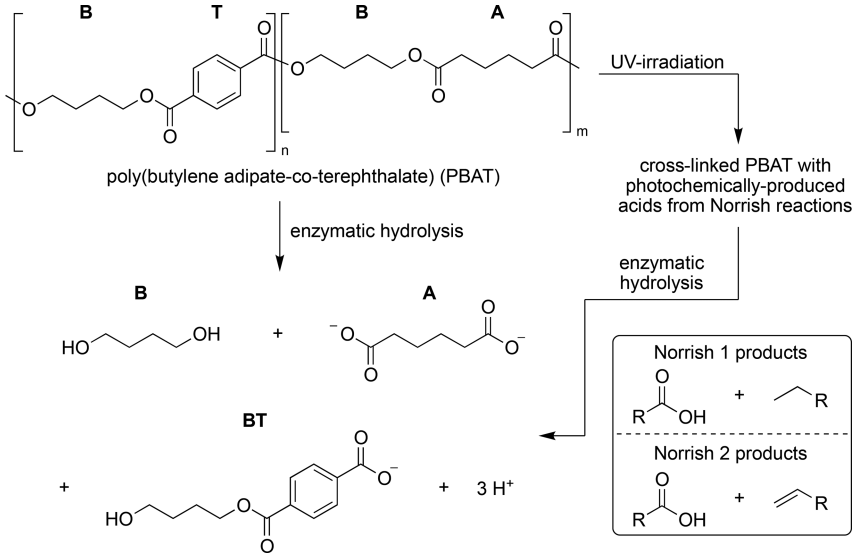
Scheme 1. Photochemical and Enzymatic Cleavage of Chemical Bonds in Poly(butylene adipate-*co*-terephthalate) (PBAT)



in the field; for this reason, industrial polymer films often contain additives that mitigate photochemical weathering (i.e., photostabilizers). While nonirradiated PBAT has been shown to be enzymatically hydrolyzable and to undergo biodegradation in soils, the effect of photochemical transformations resulting from sunlight exposure on the enzymatic hydrolysis of PBAT films remains unclear. Light irradiation of PBAT films, including photostabilized films, causes simultaneous cross-linking and cleavage of PBAT chains; these chemical reactions therefore result in the formation of both an insoluble polyester network and low molar mass PBAT chain fragments within the network.[18−21] Furthermore, light-induced cross-linking decreased the extent to which PBAT films were microbially utilized (i.e., biodegraded) during a 45 day incubation in manure compost.[20]

The goal of this study was to systematically assess the effect of UV-light irradiation on the enzymatic hydrolyzability of PBAT. To this end, we first irradiated PBAT films under controlled laboratory conditions for variable times. To directly assess photochemical changes in native PBAT, we chose films without commonly applied photostabilizers. After photoexposure, we monitored the enzymatic hydrolysis of the irradiated PBAT films by a cutinase from *Fusarium solani* (FsC), using both a pH-stat titration approach and an approach based on the quantification of released hydrolysis products by total organic carbon (TOC) analysis. In parallel, we characterized the irradiated PBAT films using dynamic mechanical thermal analysis (DMTA), gel fraction measurements, differential scanning calorimetry (DSC), and wide-angle X-ray scattering (WAXS). We then related the irradiation-induced changes of PBAT films to their enzymatic hydrolyzability. In a next step, we analyzed the products from the enzymatic hydrolysis of PBAT by high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC-HRMS) and found mechanistic support for the light-induced cross-linking of PBAT chains. Finally, we repeated selected experiments with PBAT films containing a photostabilizer to assess the extent to which photostabilization mitigates irradiation-induced changes in PBAT hydrolyzability.

MATERIALS AND METHODS

Poly(butylene adipate-*co*-terephthalate) (PBAT). Blown films of PBAT with a thickness of 25 μm were provided by BASF SE. The chemical structure of PBAT is shown in Scheme 1. The key physicochemical properties of the films include a number-average molar mass M_n = 37 kg/mol, a dispersity $Đ$ = 2.2, a melting transition between 40 and 150 °C, and a glass transition temperature T_g = −30 °C, as determined by size exclusion chromatography (SEC) and differential scanning calorimetry (DSC), respectively (Figures S1 and S2; experimental details in Section S1). The molar ratio of terephthalate (T) to adipate (A) of the PBAT was 0.936 $mol_T \cdot (mol_A)^{-1}$, as determined by ^{1}H NMR spectroscopy in $CDCl_3$ (Figure S3; spectrometer details in Section S1).

Enzyme. *Fusarium solani* cutinase (FsC, molecular weight: 20.8 kDa, isoelectric point: 8.4; both calculated from the RCSB Protein Data Base (PDB) entry 1AGY[22] with the pI/MW compute tool from expasy[23]) was obtained from ChiralVision as a solution (concentration of FsC of 4.2 mM, as determined from solution absorbance at 280 nm and the molar extinction coefficient of FsC of 13610 $M^{-1} \cdot cm^{-1}$).[24] We prepared a stock solution of FsC (4.1 $mg_{FsC} \cdot (mL)^{-1}$) in a pH 7 buffered solution (3 mM phosphate) and stored the aliquots at −20 °C until used.

Solutions. All solutions were prepared in Milli-Q water (resistivity = 18.2 MΩ cm; Barnstead Nanopure Diamond).

UV-light Irradiation of PBAT Films. PBAT films were cut into rectangular pieces (dimensions: 7 cm × 4 cm) and fixed to cardboard. The cardboard pieces were mounted on the outside of a carousel sample holder (diameter: 13 cm) of a Rayonet merry-go-round photoreactor. The films were subsequently irradiated with UV light from eight 300 nm bulbs (Rayonet, U.S.A.; lamp spectrum is shown in Figure S4) while the sample holder was continuously rotating. We confirmed that the lightbulbs in the photoreactor did not heat the samples enough to expect any thermally induced physicochemical changes in the films (the temperature was ≤36 °C). After the irradiation, the films were stored in 15 mL plastic tubes in the dark until subsequent analyses. In addition to the irradiation experiments performed in the Rayonet photoreactor, we performed

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complementary irradiation experiments with natural sunlight (see Figure S21 and experimental details in Section S1).

Hydrolysis of PBAT. The hydrolyzability of untreated and irradiated PBAT films by FsC was determined by pH-stat titration using an assay adapted from Marten et al.[25] In brief, circular pieces (diameter: 2.3 cm) were punched out of the PBAT films and placed into a thermo-jacketed beaker (40 °C) containing 10 mL of a 10 mM KCl solution. The pH of the solution was maintained at a constant pH of 7.0 by automated pH-stat titration with a Titrando 907 (Metrohm) that delivered a KOH solution (15 mM, diluted from a precise Titrisol solution; Merck: 1.09918.0001). Following the addition of the circular PBAT pieces into the solution, the system was allowed to equilibrate for 24 h prior to the addition of FsC from the stock solution (200 μL; final concentration: 82 $\mu g_{FsC} \cdot mL^{-1}$). Given that the hydrolysis of ester bonds at pH 7 releases an equimolar amount of H^+ into solution, the number of ester bonds in PBAT that were hydrolyzed by FsC was determined from the number of hydroxide ions added to maintain a constant pH. The division of the number of hydrolyzed ester bonds by the total number of ester bonds present in the added amount of PBAT yields the percentage of ester bonds cleaved during enzymatic hydrolysis (i.e., OH^- added/ester bonds in PBAT (%)). At the end of the experiment, the solution was collected and stored at −20 °C.

Dynamic Mechanical Thermal Analysis. Dynamic mechanical thermal analysis (DMTA) was performed using a TA Instruments RSA-G2 analyzer (tensile mode). A sinusoidal, oscillatory strain (constant frequency) is applied to a sample, and the resultant axial force is monitored as a function of temperature. This force is converted to a complex modulus (i.e., a measure of the sample's rigidity) by dividing by the cross-sectional area and the applied strain. Ultimately, the complex modulus is deconvoluted into the storage modulus E' (in-phase with the oscillatory strain, elastic solid-like behavior) and the loss modulus E'' (out-of-phase with the oscillatory strain, viscous liquid-like behavior). DMTA therefore gives insight into the viscoelastic behavior of polymeric materials as a function of temperature; furthermore, the elasticity (i.e., storage modulus) of a cross-linked polymer (above T_g and T_m) is directly related to its cross-link density ν_e, and therefore, this technique can be used to quantify the extent of cross-linking in the polymer. The cross-link density can be expressed in terms of the average molar mass between cross-links M_x as shown by eq 1, where ρ denotes the density of PBAT (1.25 $g \cdot cm^{-3}$), R is the ideal gas constant, and T is the temperature in Kelvin[26]

$$E' = 3RT\nu_e = \frac{3\rho RT}{M_x} \quad (1)$$

The calculated M_x from this equation can reflect the cross-link density corresponding to covalent cross-links, physical cross-links (e.g., chain entanglements), or both. Each DMTA measurement was performed using rectangular PBAT specimens [0.025 mm (T) x ca. 4 mm (W) x ca. 25 mm (L) with a gauge length of ca. 6 mm] which were cut out using a razor blade. Due to the thinness of the samples, a specialized method (described in the Supporting Information) was developed to obtain data in the range of −80 to 200 °C without breaking the films.

Gel Fraction Measurements. Extractions of sol fractions were performed using $CHCl_3$ as the swelling solvent. These experiments reveal the mass fraction that is actually incorporated into an insoluble polymer network. Although measuring the gel fraction is convenient and common,[18,27,28] it is a relatively crude way to evaluate the extent of cross-linking present in the sample (as shown below). For each swell test, a small amount of sample (ca. 35−40 mg) was placed in a 20 mL vial, which was subsequently filled with solvent. The solvent was decanted after 48 h, and the swollen sample was then dried under reduced pressure—first at 200 mTorr for 48 h and then at 20 mTorr for 48 h—to ensure no solvent remained when the final mass was measured. The gel fraction was calculated by taking the ratio of the final mass of the polymer sample to the initial mass. The sol fraction was also dried at 20 mTorr for 48 h to confirm closed mass balances.

Identification of PBAT Hydrolysis Products by HPLC-HRMS. To identify the predominant enzymatic hydrolysis products from PBAT films, we analyzed the solutions from the pH-stat titration experiments by high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC-HRMS). Centrifuged aliquots (20 μL) were separated by gradient elution and reversed phase chromatography (Hypersil Gold aQ, 150 × 4.6 mm, 5 μm particles, flow rate = 1 $mL \cdot min^{-1}$, thermostated to 50 °C). The mobile phase consisted of water (aqueous) and methanol (organic), both containing 0.1% (v/v) formic acid. The initial solvent mixing ratio was 85% aqueous to 15% organic and was held constant for 1 min after sample injection. The ratio was subsequently decreased linearly to 5% aqueous and 95% organic over 35 min, after which it was held constant for 5 min. Finally, to prepare for the next sample injection, the solvent ratio was readjusted to the initial conditions for 7 min. The eluent from the HPLC column was split postcolumn prior to introduction into the heated electrospray ionization (ESI) source of an Orbitrap Exactive high resolution mass spectrometer (Thermo Scientific) and into the UV/vis detector, respectively. Positive and negative polarity, high-resolution (R = 25 k fwhm at m/z 200, automatic gain control target = 10^6, injection time = 100 ms, m/z range: 100−2000) mass spectra (HRMS) were acquired in full-scan and all-ion higher-energy collisional dissociation (HCD, collision energy = 30 eV) modes throughout the chromatographic separation. UV/vis spectra were acquired concurrently with a diode array detector.

RESULTS AND DISCUSSION

Irradiation of PBAT films. To study the effect of light-induced photochemical changes in PBAT films on their enzymatic hydrolyzability, we irradiated both sides of blown, nonphotostabilized, transparent PBAT films with UV light for varying times between 6 and 24 h per side. We performed actinometry experiments with 4-nitroanisole solutions to verify constant light intensity in the photoreactor.[29] We found that the photodegradation of 4-nitroanisole followed the same kinetics before and after the PBAT irradiation experiments (Figure S5; experimental details in Section S1), demonstrating that the light in the photoreactor had a constant intensity over the course of the film irradiations.

Titration Experiments of PBAT Films. We assessed the hydrolyzability of untreated and irradiated PBAT films by pH-stat titration. Titration experiments were conducted in duplicate and showed high reproducibility (Figures S6 and S7). Figure 1a,b shows the titration results for one of the two replicates for the different irradiation times. The addition of untreated PBAT films to an enzyme-free solution at pH 7 did not result in the decrease of the pH of the solution (Figure 1a). Conversely, when adding irradiated films to an enzyme-free

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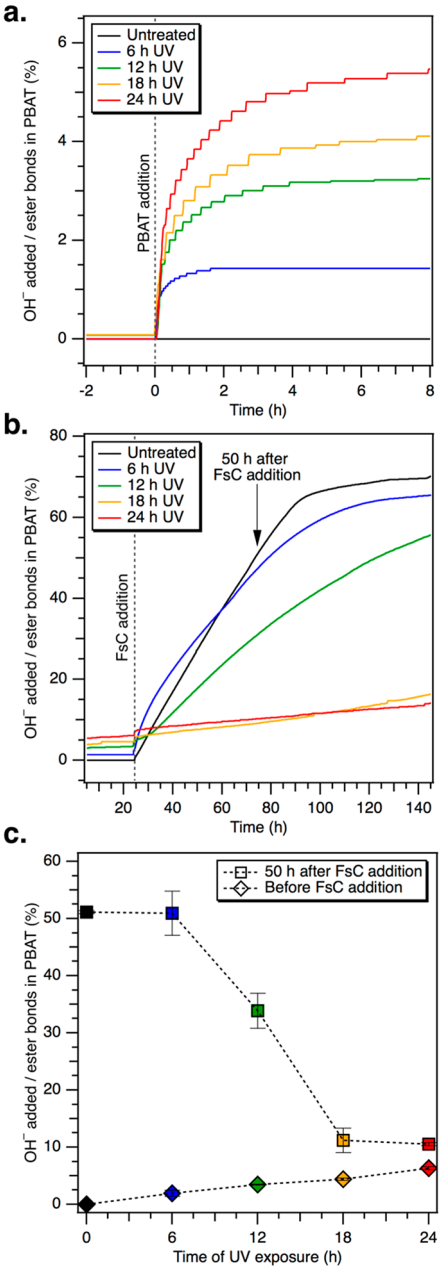

Figure 1. Results of pH-stat titration experiments at pH 7 and 40 °C on untreated and UV-irradiated films of poly(butylene adipate-*co*-terephthalate) (PBAT). Both sides of the films were irradiated with UV light for the time indicated in the legend (panels a and b) and on the *x*-axis (panel c). In all panels, the *y*-axis represents the cumulative amount of OH^- added relative to the number of ester bonds in the PBAT film; this includes titration of carboxylic acids produced by photochemical transformations and by enzymatic hydrolysis. (a) Initial portion of the pH-stat titration experiments with only PBAT film present in the solution. (b) The rest of the pH-stat titration experiments, with PBAT and *Fusarium solani* cutinase (FsC) present in the solution. (c) The amount of OH^- added before and 50 h after the addition of FsC (indicated by the arrow at 74 h in panel b). Error bars represent ranges of independent duplicates from their means.

solution, protons were released from the films, as evidenced from the KOH that was titrated to maintain a constant pH. We attributed the release of protons from irradiated PBAT films to carboxylic acid moieties produced by Norrish-type photochemical reaction mechanisms (Scheme 1) that have previously been reported for polyesters containing aromatic moieties.[20,30,31] For all irradiated films, titration rates were highest immediately after the film addition and subsequently slowed down and reached a plateau. The cumulative amounts of added KOH, and thus the amount of acidity generated by UV-irradiation, increased linearly with increasing irradiation time (Figure 1c). For films irradiated for the longest time studied here (24 h per side), the plateau of released protons corresponded to approximately 6% of the ester bonds in the added PBAT.

When the release of protons from photochemically produced acids reached a plateau (i.e., approximately 24 h after addition of PBAT films), we added *Fusarium solani* cutinase (FsC) to the solution. This enzyme addition resulted in the immediate rapid hydrolysis of ester bonds and the subsequent release of protons into the solution (Figures 1b and S7). For untreated PBAT films, the cumulative number of cleaved ester bonds increased linearly for approximately 70 h before reaching a plateau at values corresponding to approximately 70% of the ester bonds in the added PBAT films. Consistent with this high extent of ester bond cleavage, the film had disappeared, which provided a visual indication of the transformation of untreated PBAT into soluble hydrolysis products. Although enzymatic hydrolysis of the untreated PBAT films was extensive, approximately 30% of the ester bonds were not cleaved. This incomplete hydrolysis was not due to FsC inactivation: readdition of new FsC solution to the titration solution did not result in a significant increase in the cumulative number of hydrolyzed ester bonds (Figure S8). Taken together, these findings suggest that FsC did not cleave some specific ester bonds in the soluble hydrolysis products during the experiment.

To identify incompletely hydrolyzed products, we analyzed the solution that remained after the pH-stat titration experiments by HPLC-HRMS (Figure S9). Furthermore, we employed liquid–liquid extraction to isolate the hydrolysis products and quantified them using ^{1}H NMR spectroscopy (Figure S10; experimental details in Section S1). Both analyses consistently showed the formation of three predominant hydrolysis products: butanediol (B), adipate (A), and 4-hydroxylbutyl terephthalate (butanediol-terephthalate dyad; BT) (Scheme 1). The identification of BT as the major terephthalate-containing hydrolysis product explained the incomplete hydrolysis of ester bonds in PBAT observed by pH-stat titration. Furthermore, BT accumulation implies that the rate of FsC-mediated ester hydrolysis of a B-T-B sequence is rapid for the first aryl ester bond and then is strongly decreased for the second aryl ester bond.

The PBAT films that were irradiated with UV light for 6 h per side were hydrolyzed by FsC on similar time scales as the untreated films (Figures 1b,c and S7). However, the enzymatic hydrolysis curves of the 6 h UV-irradiated and the untreated PBAT films had slightly different shapes. While the hydrolysis rate of untreated films was constant for the first 70 h after FsC addition, the hydrolysis rate for the 6 h UV-irradiated films was initially higher but subsequently decreased to rates smaller than that for the untreated films. We speculate that the high initial rate is a result of the photochemical cleavage of some PBAT chains, which produced smaller and thus more hydrolyzable fragments.[32] We ascribe the subsequent regime with slower hydrolysis to photochemical cross-linking of PBAT chains that decreases their flexibility and hence their enzymatic hydrolyzability. This explanation is consistent with previous

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studies in which chain flexibility was used to explain polyester hydrolysis rates.[12,33−35] Films that were UV-irradiated for 12 h and longer per side were hydrolyzed considerably slower than the untreated films. Less than 5% of ester bonds were enzymatically hydrolyzed in films that were exposed to UV light for 24 h per side during incubation with FsC for 50 h.

As a complementary approach to pH-stat titration, we assessed the enzymatic hydrolysis of these PBAT films in batch incubation reactors containing pH-buffered solutions; aliquots were removed at various times and their total organic carbon (TOC) content was measured to monitor the release of hydrolysis products over time (Figure S11; experimental details in Section S1). These independent experiments confirmed the results obtained with the pH-stat titration setup: PBAT films that were UV-irradiated for 12 h or more showed significantly decreased enzymatic hydrolysis rates. We also used the TOC-based approach to show that the rate of PBAT hydrolysis by FsC did not increase when we doubled the solution concentration of FsC (Figure S12). Thereby, we demonstrated that for all enzymatic hydrolyses presented herein (i.e., pH-stat titrations and incubations coupled to solution TOC analysis), the PBAT surfaces were saturated with FsC.

Characterization of Physicochemical Properties of Untreated and UV-Irradiated PBAT Films. First, we investigated the crystallinity of untreated and irradiated films, as crystallinity is an important parameter for polyester biodegradation.[36,37] For the UV-irradiated films, a quantitative analysis of the melting transition by DSC indicated that there was no substantial change in the % crystallinity as compared to untreated PBAT (Figure S13; experimental details in Section S1). We also employed WAXS as a complementary characterization technique; these data suggested that the crystal structure and the % crystallinity remain relatively unchanged by UV irradiation (Figures S14 and S15; experimental details in Section S1). On the basis of the DSC and WAXS results, we cannot ascribe the observed decrease in enzymatic hydrolyzability with increasing UV-irradiation to changes in PBAT crystallinity.

Second, we used the commonly employed technique of gel fraction measurements to assess the formation of cross-links in polymers. To this end, we determined the chloroform-soluble and chloroform-insoluble mass fractions of the untreated and the UV-irradiated PBAT films (Figures 2a and S16). These measurements showed that the soluble fraction of PBAT films strongly decreased from 1.0 for the untreated PBAT to less than 0.4 for films that were irradiated for 6 h per side. Additional irradiation further decreased the chloroform-soluble fraction—though less drastically—until it reached approximately 0.2 for samples that were irradiated for 24 h per side. Taken qualitatively, the swelling experiments confirmed that UV-irradiation induced cross-linking between chains in PBAT films. Furthermore, the monotonic decrease in the soluble fraction with increasing irradiation time suggested that more cross-links were formed with increasing UV exposure. As photochemical reactions are limited by the penetration depth of the light, we sought to demonstrate whether our procedure (i.e., irradiation on both sides) generated cross-links throughout the film. We therefore irradiated samples on one side for 24 h and compared their chloroform-insoluble (gel) fractions (ca. 0.41) to those of the 24 h samples shown in Figure 2a (ca. 0.84); the finding that one-sided irradiation resulted in gel fractions that were approximately half the value

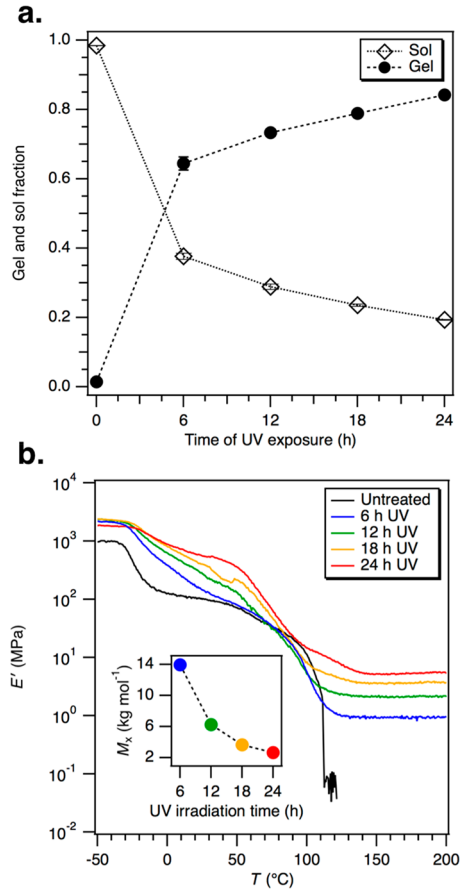

Figure 2. Characterization data for untreated and UV-irradiated poly(butylene adipate-*co*-terephthalate) (PBAT) films. (a) Chloroform-insoluble (gel) and chloroform-soluble (sol) fraction of PBAT as a function of UV-irradiation time; error bars represent ranges of independent duplicates from their means. (b) Representative dynamic mechanical thermal analysis curves showing storage modulus (E') as a function of temperature for untreated and irradiated films; the inset shows representative molar masses between cross-links (M_x) for the irradiated PBAT samples, which were calculated from the plateau storage modulus at 150 °C using eq 1.

measured for samples irradiated on both sides is consistent with our supposition that our procedure was successfully generating cross-links throughout the films. As these cross-linking events were expected to be accompanied by chain scission events, we analyzed the soluble fractions by size-exclusion chromatography (SEC); indeed, the SEC results demonstrated that increased irradiation time yielded smaller PBAT fragments in the soluble fractions (Figure S17, experimental details in Section S1).

Third, we sought to obtain a quantitative measure of the number of cross-links formed by UV-irradiation. To this end, we characterized untreated and UV-irradiated PBAT films using dynamic mechanical thermal analysis (DMTA). As we heated the untreated PBAT film through its melting transition (ca. 110 °C), the storage modulus E' dropped precipitously (Figures 2b and S18). In contrast, heating the irradiated PBAT films through their melting transitions resulted in a more gradual drop in E', which was afterward steady throughout the rest of each experiment (Figures 2b, S18, and S19). The relatively constant storage modulus above the melting transition for the UV-irradiated films confirmed that they were indeed cross-linked, which corroborated the qualitative

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conclusion drawn from the swelling experiments. The storage modulus in this regime can be related to the cross-link density in the PBAT films and thus the average molar mass between cross-links M_x, as shown by eq 1. As expected, increasing the irradiation time resulted in increasing storage moduli as the samples become more extensively cross-linked (Figures 2b, S18, and S19); the calculated M_x decreased with increasing irradiation time (Figures 2c and S20). The M_x for the sample irradiated for 6 h per side was 14 kg·mol^{-1}, and it decreased to 6.2, 3.7, and 2.7 kg·mol^{-1} for samples irradiated for 12, 18, and 24 h per side, respectively. Using an average monomer molar mass of 105 g·mol^{-1}, these M_x values correspond to an average number of monomers between cross-links of approximately 130, 60, 35, and 26, respectively.

Relating Enzymatic Hydrolyzability to Changes in the Physicochemical Properties of PBAT Films upon UV-Irradiation. In Figure 3a,b, we related the changes in the enzymatic hydrolyzability to changes in the physicochemical properties of the PBAT films determined by swelling experiments and DTMA, respectively.

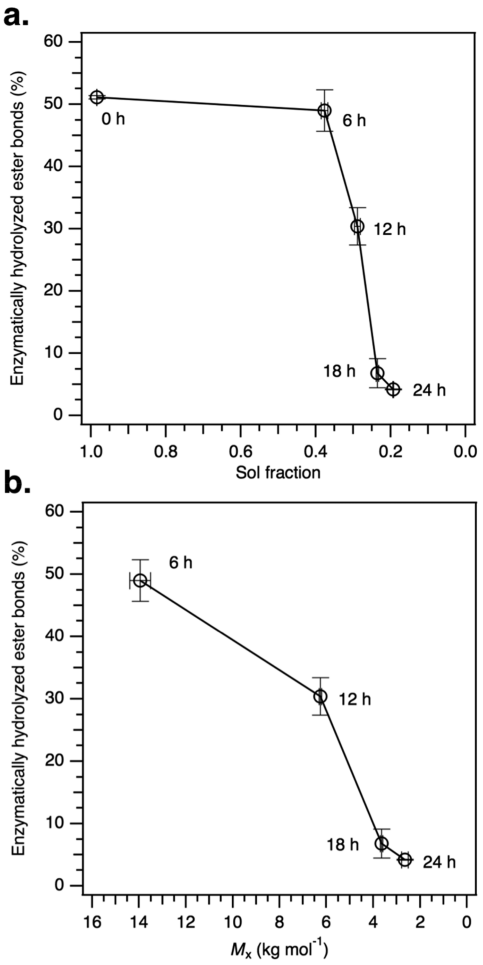

Figure 3. (a) Correlation between the chloroform-soluble fractions of untreated and irradiated PBAT with the percentage of enzymatically hydrolyzed ester bonds 50 h after *Fusarium solani* cutinase (FsC) addition. (b) Correlation between the average molar masses between cross-links (M_x) for irradiated PBAT with the percentage of enzymatically hydrolyzed ester bonds 50 h after FsC addition. In both panels, error bars represent ranges of independent duplicates from their means and the UV-irradiation time is specified next to each data point. The *y*-axes are distinct from those in Figure 1 because here, the contribution of the photochemically produced acids (i.e., titration before FsC addition) is intentionally not considered.

The decreases in enzymatic hydrolyzability were not well correlated with changes in the sol fraction (Figure 3a): although the extent of PBAT hydrolysis by FsC over 50 h was comparable for the untreated and the PBAT film UV-irradiated for 6 h per side, the 6 h of UV irradiation causes the soluble mass fraction to decrease from 1.0 to 0.4 (Figures 2a and 3a). This comparison demonstrated that the density of interchain cross-links formed within 6 h of UV-irradiation per side was sufficient to render the majority of the PBAT insoluble while not significantly impacting the enzymatic hydrolyzability; we propose that at this low cross-link density, the overall chain flexibility of PBAT remains largely unaffected on the length scales required to access the active site of the enzymes. Irradiation for more prolonged periods of time (>6 h per side) resulted in small decreases in the sol fraction yet quite substantial decreases in the extent of ester hydrolysis, which strongly suggests the change in sol fraction (i.e., gel content) is not a good indicator of the expected change in enzymatic hydrolyzability.

As compared to gel content, the decrease in enzymatic hydrolyzability of UV-irradiated PBAT correlated more closely with the average molar mass between cross-links determined by DMTA (Figure 3b). This linear relationship shows that substantial increases in the cross-link density (i.e., decreases in M_x) significantly reduce the enzymatic hydrolyzability of PBAT chains, likely due to the reduced probability that these chains will be able to readily enter the active site of FsC. Our findings agree well with the previously suggested concept that the enzymatic hydrolysis of polyesters is highly dependent on the flexibility of the polyester chains.[12,33−35]

The data in Figure 3b show that hydrolyzability of PBAT by FsC becomes impaired at cross-link densities corresponding to M_x values in the range of 14 to 6 kg·mol^{-1}. In the photoreactors used in this study, M_x values of approximately 6 kg·mol^{-1} were reached when films had been irradiated for 12 h per side. We estimated the corresponding irradiation time under natural sunlight conditions by performing sunlight irradiation experiments of PBAT films in Zurich, Switzerland (47° latitude, experimental details in Section S1). We collected irradiated film samples at various time points and determined the chloroform-insoluble mass fraction (i.e., gel fraction, Figure S21). We compared the initial rate of gel formation during sunlight and photoreactor irradiations; after accounting for the number of sunny days that occurred during the sunlight irradiation experiments (Figures S22 and S23), our analyses suggest that a 12 h irradiation in the photoreactor corresponds to approximately 26 sunny days in central Europe in early June.

In summary, our experiments show that the decrease in enzymatic hydrolyzability of UV-irradiated PBAT correlates better to the increase in the cross-link density than to the decrease in the soluble PBAT mass fractions. Although swelling experiments provide insight as to the mass fraction that is present in a cross-linked state, they do not necessarily provide a correlation to how densely cross-linked—and thus how flexible—the polymer chains are in the network. For future studies assessing potential effects of photoirradiation of polymers on their enzymatic hydrolyzability, we therefore recommend quantifying the cross-link density by DMTA. Future research on PBAT-containing films may also assess whether light-induced changes in film surface properties or the

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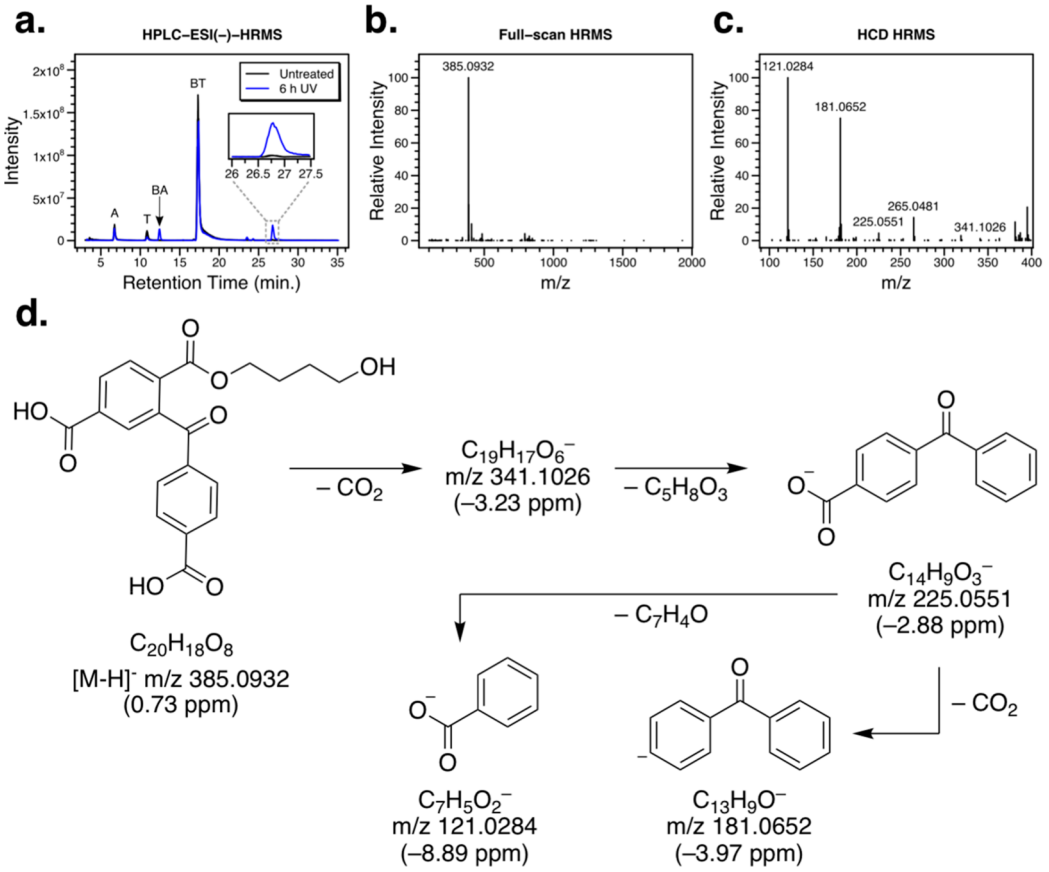
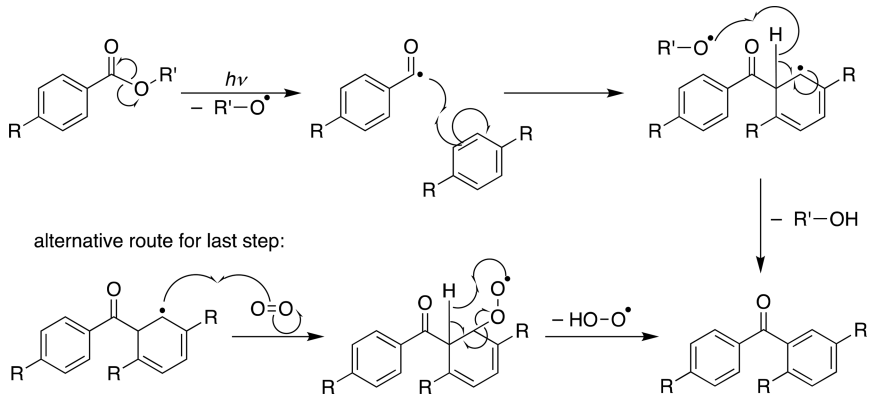


Figure 4. Analysis of the enzymatic hydrolysis products of poly(butylene adipate-*co*-terephthalate) (PBAT) by high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC-HRMS). (a) Base peak chromatograms for untreated and irradiated PBAT with peaks assigned to the hydrolysis products adipate (A), terephthalate (T), butanediol-adipate dyad (BA), and butanediol-terephthalate dyad (BT). (b, c) Full-scan HRMS (panel b) and higher-energy collisional dissociation (HCD) HRMS^2 (panel c) of the peak eluting at 26.6 min. (d) Proposed structures and fragmentation mechanisms for the observed ions in panels b and c.

Scheme 2. Proposed Molecular Mechanism for the Photochemical Formation of Cross-Links between Chains in Poly(butylene adipate-*co*-terephthalate) (PBAT)



formation of leachable phototransformation products impact enzymatic hydrolysis.

HPLC-HRMS Analysis of Cross-Linked Hydrolysis Products. Given the importance of cross-linking density on enzymatic hydrolyzability, we aimed to identify the chemical nature of the formed cross-links. To this end, we compared the enzymatic hydrolysis products of untreated PBAT films to those of films irradiated for 6 h per side. We found a chromatographic peak (retention time of 26.6 min) that was significantly larger among the hydrolysis products from UV-irradiated films than among those from untreated PBAT films (Figure 4a). Negative-ionization, full-scan HRMS at this elution time provided evidence for an $[M - H]^-$ ion of $C_{20}H_{18}O_8$ (*m/z*: exact 385.0929, found 385.0932) (Figure 4b).

Figure 4c,d depicts the associated higher-energy collisional dissociation (HCD) HRMS^2 and proposed structure annotations for the observed product. HCD HRMS^2 showed neutral losses of CO_2 suggestive of terminal carboxylate moieties. Furthermore, the neutral loss of $C_5H_8O_3$ to give $C_{19}H_{17}O_6^-$ (*m/z*: exact 341.1031, found 341.1026) was consistent with

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the cleavage of a butanediol benzoate ester. Finally, an intense fragment ion was observed with the sum formula $C_{13}H_9O^-$ (m/z: exact 181.0659, found 181.0652), which strongly supported the presence of a benzophenone substructure. To further support this assignment, we analyzed authentic 4-benzyolybenzoic acid by ESI(-)-HRMS, which gave the deprotonated pseudomolecular ion (m/z: exact 225.0557, found 225.0556) and was decarboxylated when treated with HCD to form the same benzophenone anion (m/z: exact 181.0659, found 181.0654, data not shown).

Taken together, these data provided strong evidence for the photochemical production of substituted benzophenone cross-links in PBAT films during their irradiation. This structure is also consistent with the findings of Kijchavengkul et al., who used Fourier-transform infrared (FTIR) spectroscopy to show that a signal corresponding to 1,2,4-trisubstituted benzene becomes increasingly prominent with increasing irradiation time of PBAT.[18] On the basis of our results, we propose that the cross-links between chains in PBAT are formed by the radical-based mechanism depicted in Scheme 2. A similar mechanism has been proposed for the formation of benzophenone cross-links in terephthalate-containing polymers.[38]

Photostabilization of PBAT Films. We have demonstrated that extensive photochemical cross-linking of nonphotostabilized PBAT films impairs their enzymatic hydrolyzability. We therefore assessed the extent to which photostabilizers added to the PBAT films prevent the decrease in enzymatic hydrolyzability. In a proof-of-principle experiment, we solvent-casted PBAT films both with and without 2% (w/w) of the photostabilizer 2-(2-benzotriazolyl)-4-methylphenol (BMP) and studied whether its presence decreased the effect of UV irradiation on the enzymatic hydrolysis of PBAT (Figure S24; experimental details in Section S1). BMP was chosen because it is a commonly used photostabilizer for polymeric materials.[39,40] We found that FsC-mediated hydrolysis after UV irradiation (24 h per side) was indeed faster for photostabilized films than for those without BMP. Furthermore, enzymatic hydrolysis rates of untreated films were not significantly different between photostabilized and nonphotostabilized films. These findings demonstrate that the addition of photostabilizers to PBAT films can mitigate photochemical transformations while maintaining the hydrolyzability of PBAT by extracellular enzymes that may be present in natural soil environments.

Implications. We have demonstrated that UV-irradiation of a nonphotostabilized, transparent film of PBAT, an aliphatic-aromatic copolyester, results in cross-links between polyester chains that can severely decrease the ability of the film to be enzymatically hydrolyzed, which is a key step in polyester biodegradation. Our results highlight the relevance of considering photochemical reactions in the study of the environmental fate of biodegradable polyesters and the importance of employing photostabilizing additives to biodegradable polyesters.[41,42] Such additives aid not only in maintaining the desired material properties (e.g., preventing embrittlement) during the application of the material but also in ensuring that it remains biodegradable after its functional lifetime.

On a molecular level, we demonstrated that the enzymatic hydrolyzability of irradiated films negatively correlated with the density of cross-links formed between polyester chains. We attribute this trend to the decreased flexibility of polyester chains in a densely cross-linked network and thus the lower probability of polyester chains at the sample surface readily accessing the active site of adsorbed esterases. Our findings extend the previously suggested hypothesis that enzymatic hydrolysis of polyesters is determined by the degree of flexibility of chains in the polyester: whereas previous work showed that crystalline regions in the polyesters have impaired chain flexibility and thus enzymatic hydrolyzability, we herein show that extensive cross-linking of polyester chains is a second characteristic that restrains chain flexibility and hence impairs enzymatic hydrolyzability.

Lastly, we showed that UV-irradiation results in the formation of benzophenone-containing structures in PBAT, suggesting that cross-links between PBAT chains are formed by a radical mechanism coupling two terephthalate units. We note that benzophenone moieties are well-known photosensitizers and such cross-links may accelerate photochemical changes during long-term UV exposure of these materials.[43,44] This mechanistic insight will help in assessing the performance of existing photostabilizers and guide the development of environmentally friendly photostabilizers for aliphatic-aromatic polyesters. In future work, the environmental fate of photostabilizers and the formation of coupling products under field conditions need to be assessed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b06458.

Information and data on chemicals and on NMR, pH-stat titration, TOC, gel fraction, DMTA, WAXS, SEC, and DSC experiments (PDF)

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Notes

The authors declare no competing financial interest.

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