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Photocontrolled Degradation of Stimuli-Responsive Poly(ethyl glyoxylate): Differentiating Features and Traceless Ambient Depolymerization

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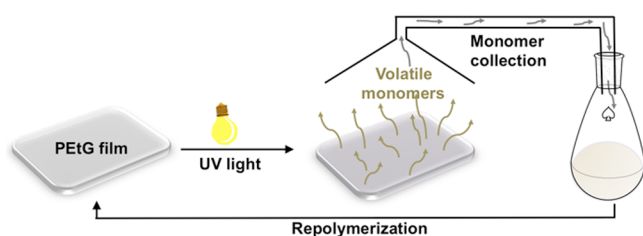
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Bo Fan, John F. Trant, Rebecca E. Yardley, Andrew J. Pickering, François Lagurné-Labarthet and Elizabeth R. Gillies*



Abstract

The depolymerization of coatings prepared from a 6-nitroveratryl carbonate end-capped poly(ethyl glyoxylate) (PEtG) self-immolative polymer was studied. This polymer undergoes end-to-end depolymerization following cleavage of the end-cap by UV light. Several important fundamental differences between this class of polymers and conventional degradable polymers were revealed. For example, polymer backbone cleavage and depolymerization exhibited different dependencies on pH, emphasizing the decoupling of these processes. Probing of the coating erosion mechanism illustrated an interesting combination of features from surface erosion and bulk degradation mechanisms that arise from the end-to-end depolymerization mechanism and further differentiate these polymers from conventional degradable polymers. It was also demonstrated that unlike backbone cleavage, PEtG depolymerization did not exhibit a dependence on water, and that PEtG could depolymerize back to the volatile monomer ethyl glyoxylate at ambient temperature and pressure. This unusual feature was utilized to perform facile polymer reprogramming/recycling via an irradiation-trapping-repolymerization sequence as well as polymer patterning by a simple irradiation-evaporation sequence.

Introduction

In recent years, there has been increasing interest in the development of degradable polymers for a wide range of applications from packaging to biomedical devices.¹⁻³ At present, polyesters are widely used, as they can be broken down to nontoxic products.^{4,5} However, their degradation cannot be easily controlled, as random backbone scission occurs gradually in a wide range of environments, and cannot be turned on or off as desired for a given application. To address this limitation, significant efforts have been directed towards the development of stimuli-responsive

polymers. Polymers responsive to light,^{6,7} heat,⁸ changes in pH⁹ and many other stimuli have been developed.^{10,11} These polymers require many stimuli-mediated events to completely degrade the polymer backbones. While they perform well in the laboratory, where large changes in conditions can easily be introduced, the gradient of conditions and the concentrations of stimuli in real environments are typically much smaller, presenting a challenge.

To address the above limitations, molecules that depolymerize from end-to-end in response to the cleavage of stimuli-responsive end-caps from the polymer termini, were developed.^{12,13} These polymers, often referred to as “self-immolative polymers” (SIPs), afford amplification of stimuli-mediated events as an entire polymer chain can degrade in response to a single end-cap cleavage. In addition, because of their end-to-end depolymerization mechanism, they exhibit predictable depolymerization times that are dependent on their length and backbone composition.¹⁴ Backbones including polycarbamates,¹⁵⁻¹⁸ polycarbonates,¹⁹ polyethers,²⁰ polyphthalaldehydes,^{21,22} and polyglyoxylates²³ have been synthesized and studied over the last several years and end-caps responsive to stimuli including light,²⁴ heat,²⁵ fluoride ions,²⁶ redox change,^{16,27} enzymes,²⁸ and mechanical force²⁹ have been reported. The unique features of these polymers have made them attractive for potential applications in molecular sensors,^{15,30} responsive films,^{31,32} micropumps,²⁶ drug delivery systems,^{17,24} and microcapsules.^{33,34}

Polyglyoxylates are an attractive class of polymers that can undergo depolymerization upon end-cap cleavage due to their low ceiling temperatures (T_c).²³ Glyoxylate monomers such as ethyl glyoxylate (EtG) are commercially available or can be prepared from readily available starting materials such as maleic or fumaric acid.²³ In addition, they ultimately degrade to glyoxylic acid,³⁵⁻³⁷ a metabolite found in some mammalian biochemical pathways³⁸ and an intermediate in the glyoxylate cycle, an anaerobic variant of the tricarboxylic acid cycle that

occurs in plants, bacteria, protists, and fungi.³⁷ Here we explore in detail the degradation of end-capped self-immolative poly(ethyl glyoxylate) (PEtG). In particular, the solid-state degradation of PEtG demonstrates several important novel and unusual aspects of the end-to-end depolymerization and also reveals that upon end-cap cleavage, PEtG undergoes depolymerization under ambient conditions to afford volatile products. This offers new opportunities for one-step traceless patterning and for simple polymer recycling or reprogramming.

Experimental section

General procedures and materials. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Et₃N and CH₂Cl₂ were distilled from calcium hydride before use. 6-Nitroveratryl carbonate end-capped PEtG (PEtG-NVOC) and benzyl carbonate end-capped PEtG were prepared as previously reported.²³ PEtG-NVOC used in the current studies had a number average molar mass (M_n) of 35 kg/mol and a dispersity (D) of 1.4. The benzyl carbonate end-capped PEtG had an M_n of 42 kg/mol and a D of 1.4. Characterization data for these specific batches are included in Figures S1-S6. The soil was standard potting soil from Premier Tech (Rivière-du-Loup, Canada). Nylon bags were made from a nylon 6/6 woven mesh sheet with 80 μ m mesh size purchased from Small Parts, Inc. (Logansport, IN, USA). The size exclusion chromatography (SEC) instrument was equipped with a Viscotek GPC Max VE2001 solvent module (Malvern Instruments Ltd., Malvern, UK). Samples were analyzed using the Viscotek VE3580 RI detector operating at 30 °C. The separation technique employed two Agilent Polypore (300 x 7.5mm) columns connected in series and to a Polypore guard column (50 x 7.5mm) (Agilent Technologies, Santa Clara, CA, USA).

Samples were dissolved in tetrahydrofuran (THF) (glass distilled grade) at a concentration of approximately 5 mg/mL and filtered through 0.22 μm syringe filters, then injected using a 100 μL loop. The THF eluent was filtered and eluted at 1 mL/min for a total of 30 minutes. A calibration curve was obtained from poly(methyl methacrylate) standards with molar masses from 1540-1126000 g/mol (Agilent Technologies, Santa Clara, CA, USA). ^1H NMR spectra were obtained at 600 MHz on a Varian Inova instrument (Varian, Palo Alto, CA, USA). The scanning electron microscopy (SEM) images of polymer films were taken on a Hitachi S-3400N instrument at a voltage of 2 kV (Hitachi, Tokyo, Japan). The samples were mounted on carbon-taped aluminum stubs and sputtered with gold at a rate of 5 nm/min for 4 minutes (Hummer-6 sputtering system, Anatech, Union City, CA, USA).

Preparation of PEtG coatings. PEtG was dissolved in CH_2Cl_2 at a concentration of 90 mg/mL. This solution was drop-cast onto glass microscope slides and the solvent was evaporated *in vacuo* for 48 h to afford coatings. The coating thickness was measured using a caliper. 330 μL cast over 2 cm^2 afforded a thickness of ~ 150 μm . For thinner coatings, 1 mL of 30 mg/mL polymer solution cast over 6 cm^2 afforded ~ 50 μm , or 2 mL of 15 mg/mL polymer solution cast over 12 cm^2 afforded ~ 25 μm . Each coating had a total mass of ~ 30 mg.

Degradation studies of PEtG films in aqueous buffer solutions at varying pH and temperature. The initial masses of coatings were measured and recorded. Irradiated coatings were placed into an ACE Glass photochemistry cabinet containing a mercury light source (450 W bulb, 2.8 mW/cm^2 measured for UVA radiation at the sample position) for 5 h to cleave the NVOC end-cap. A coating of PEtG with a benzyl carbonate (non-photo-responsive end-cap) was

also irradiated to verify that the polymer backbone was stable to UV irradiation and that it was specifically the NVOC end-cap that was susceptible to cleavage by UV light (Figure S7). Non-irradiated coatings were stored in the dark. Next, all of the slides (3 per time point, per condition) were immersed into a 0.1 M aqueous buffer solution (citrate buffer for pH 5.0; phosphate buffer for pH 6.0, 7.0 and 8.0) at a given temperature. 10 °C was obtained by placing the samples into a refrigerator set to this temperature. 20 °C corresponded to ambient temperature of a temperature-controlled room. In this case, protection from light was afforded by storing the samples in a cabinet. 30 °C was obtained by placing samples into an oven set to this temperature. At selected times, 3 coatings from each treatment were removed from the buffer solution, rinsed with distilled water, dried under house vacuum for 48 h, and then weighed. The percent of initial mass of the coating at a given time point was calculated as $(\text{mass at time point}/\text{initial mass}) \times 100\%$. In each case, the error bars correspond to the standard deviation of the measurements of 3 different samples. At pH 7.0 and 20 °C, the samples were also analyzed by SEC, samples at $t = 0$ and $t = 5$ days were analyzed by SEM, and the residual coatings at selected time points were dissolved in CDCl_3 and ^1H NMR spectra were obtained (Figures S8-S11).

Degradation of PEtG coatings in soil with varying water content. The soil was autoclaved, dried in an oven (120 °C), and weighed. The soil was then used dry or rehydrated with 0.1 M pH 7.0 phosphate buffer to 10, 20, or 30 mass percent. The irradiated and non-irradiated coatings with a thickness of 150 μm were prepared as described above for the studies in buffer except that instead of immersing the coatings into buffer solution, they were placed into nylon bags, and immersed in soil (350 g dry soil per 30 slides). The box was sealed to prevent the evaporation of water. At different time points, the nylon bags were removed from the soil, and both the slides

and nylon bags were washed with CH_2Cl_2 , filtered and the solvent was evaporated. The remaining material was weighed to determine the mass of remaining polymer and the percent of initial mass of the coating was calculated as described above. Error bars correspond to the standard deviation of the measurements of 3 different samples.

Degradation of PETG coatings in air. Coatings were prepared and weighed as described above. Irradiated coatings were placed into the photochemistry cabinet described above for 4 h to remove the end-cap. During this time the non-irradiated coatings were stored in the dark. All coatings were then stored at either 20 °C (ambient, thermostat-controlled) or at 30 °C (oven). Protection from light was afforded by storing samples in either a cabinet or the oven. At selected time points, the masses of the slides were measured and then the slides were returned to their depolymerization conditions. The percent of initial mass of the coating was calculated as described above. Error bars correspond to the standard deviation on the measurements of 3 different samples.

Sunlight-triggered coating degradation. Coatings were prepared and weighed as described above. All coatings were then placed in a greenhouse, with half protected from sunlight with aluminum foil, and the other half exposed to sunlight through the greenhouse glass. The temperature of the environment varied over the experiment from approximately 9 to 37 °C over the day-night cycle in a Southwestern Ontario, Canada, Spring (May-June). At selected time points, the masses of the slides were measured and then they were returned to their depolymerization conditions. The percent of initial mass of the coating remaining was calculated

as described above. Error bars correspond to the standard deviation of on the measurements of 3 different samples.

Collection of depolymerized ethyl glyoxylate monomer. 600 mg of PEtG-NVOC was dissolved in 5.0 mL of CH_2Cl_2 , then the CH_2Cl_2 was evaporated *in vacuo* to coat the walls of a round bottom flask (A). Then the polymer film was dried under high vacuum. Flask A was then placed in the photochemistry cabinet described above for 4 hours. It was then immersed in an oil bath at 50 °C, and connected to a vacuum (240 mTorr) and to Flask B, which was cooled in a liquid nitrogen bath to trap the volatile ethyl glyoxylate depolymerization product (Figure S13). The mass of flask B was measured every 1 or 2 hours over a period of 9 hours to determine the mass of collected ethyl glyoxylate. The identity of the collected product was determined by ^1H NMR spectroscopy to be ethyl glyoxylate, by comparison with the known spectrum of the commercial product (Figure S14). A control experiment was also performed under identical conditions but without UV irradiation. No conversion to liquid monomer was observed and no monomer transferred to the collection flask.

Repolymerization of collected monomer. The collected ethyl glyoxylate (0.5 g, 5 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (0.5 mL) and Et_3N (0.35 μL , 2.5 μmol , 0.0005 equiv.) was added. The solution was stirred for 1 h at -20 °C. 6-Nitrovertryloxycarbonyl chloride (NVOC-Cl) (22 mg, 73 μmol , 0.014 equiv.) and Et_3N (10 μL , 73 μmol , 0.014 equiv.) were then added at 0 °C to end-cap the polymer. The solution was stirred for 24 h at room temperature. Purification was achieved by dialysis against 1:1 acetone: methanol using a regenerated cellulose membrane with a molecular weight cut-off of 2000 g/mol. The yield was 12%. This is an unoptimized yield as

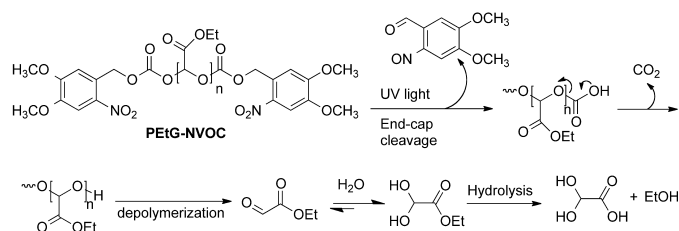
the aim of the experiment was to demonstrate proof of principle. It is likely low as the polymer has a low M_n , making the standard precipitation procedure impossible and much material was likely lost through the dialysis. It can likely be improved through optimization of the set-up (such as decreasing exposure of the ethyl glyoxylate to air during the weighing procedure that was used to generate Figure 3) and also certainly through distillation of the recycled ethyl glyoxylate if required (high purity is very important for achieving high degrees of polymerization). ^1H NMR (600 MHz, CDCl_3): δ 7.69-7.76 (m, 2H), 7.12-7.21 (m, 2H), 5.46-5.78 (m, 18H), 4.10-4.33 (m, 32H), 4.00-4.06 (m, 6H), 3.94-3.98 (m, 6H), 1.21-1.44 (m, 50H). SEC: $M_n = 1.7$ kg/mol, $M_w = 2.8$ kg/mol, $D = 1.6$.

Pattern fabrication. For Figure 4c, PEtG-NVOC (15 mg) was dissolved in CH_2Cl_2 (1 mL) and was drop-cast onto a glass slide over a surface area of 6.6 cm^2 to provide a $\sim 20\text{ }\mu\text{m}$ -thick film. For Figure 4d, PEtG-NVOC (100 mg) was dissolved in CH_2Cl_2 (4 mL) and 1 mL was spin-coated onto a glass slide over a surface area of 20 cm^2 to provide a $13\text{ }\mu\text{m}$ -thick film. After the solvent was evaporated *in vacuo* for 48 h, the coatings were covered with metal mask patterns shown in Fig. 3a and 3b, for the $20\text{ }\mu\text{m}$ and the $13\text{ }\mu\text{m}$ -thick coatings respectively. The mask with $500\text{ }\mu\text{m}$ diameter holes was a meshed aluminum grid while the mask with $20\text{ }\mu\text{m}$ diameter holes was a chromium mask engraved over a borosilicate glass. Irradiation through the masks was performed using a mask-aligner (Neutronix-Quintel NXQ 4006) to ensure spatial uniformity of the irradiation. The thinner film was irradiated during 0.5 hour while the thicker film was irradiated for 1 hour using an irradiance of 35 mW/cm^2 from a mercury light source. After the irradiation, the films were stored in the dark at ambient temperature ($\sim 20\text{ }^\circ\text{C}$) for 6 days. The

images of polymer patterns were taken on an optical microscope (Zeiss Axioskop2 MAT Microscope equipped with 1300 CCD Digital Camera) on the 6th day after irradiation.

Results and discussion

PEtG with a UV light-sensitive 6-nitroveratryl carbonate end-cap (PEtG-NVOC) was synthesized as previously reported via the low temperature polymerization of EtG, following by end-capping with 6-nitroveratryl chloroformate.²³ Irradiation of PEtG-NVOC with UV light results in cleavage of the NVOC moiety from the polymer terminus (Scheme 1). This is followed by decarboxylation, revealing hemiacetal-terminated PEtG, which undergoes depolymerization. In the presence of water, the resulting ethyl glyoxylate (EtG) is rapidly converted to ethyl glyoxylate hydrate (EtGH), then gradually hydrolyzed to glyoxylic acid hydrate and ethanol.²³ It was previously demonstrated that the degradation of PEtG by backbone cleavage in the absence of UV light was much slower than UV-triggered depolymerization and that UV irradiation of PEtG with a non-responsive benzyl carbonate end-cap did not lead to degradation.²³ For the current study, unless otherwise indicated, coatings of PEtG-NVOC were prepared by drop-casting the polymer onto glass slides to provide coatings ~150 μm thick. Samples treated with UV light were irradiated with a mercury lamp having an intensity of ~2.8 mW/cm^2 in the UVA range. Control coatings were kept in the dark. The slides were then immersed in aqueous solution. At each time point, irradiated and control films were removed from the solution, rinsed, dried, and their masses were measured. As the polymers are insoluble in water beyond the oligomer form and the films remained intact and adhered to the glass slides until greater than 90% mass loss had occurred, this measurement provided a good indication of the extent of depolymerization that had occurred.



Scheme 1. Chemical structure of PEtG-NVOC and its UV light-initiated depolymerization. This is followed by hydrate formation and hydrolysis of the resulting ethyl glyoxylate in the presence of water.

To investigate the effect of pH, coatings were immersed in buffer solutions of pH 3 - 8 and stored at 20 °C. As shown in Figure 1a, at pH 6 - 8 the irradiated coatings behaved similarly, eroding to ~50% of their initial mass over 5 days. At pH 5, the erosion of the irradiated polymer was significantly slower, requiring more than 20 days to reach 50% mass loss. Then, at pH 3 – 4 the erosion again became more rapid, reaching a rate intermediate between that of pH 5 and pH 6 – 8. This highlights the first key difference between the end-to-end depolymerization and random backbone cleavage mechanism for polyglyoxylates. Random backbone cleavage of PEtG would involve the hydrolysis of an acetal linkage. This is well known to be an acid-catalyzed process, with a rate directly dependent on the concentration of H⁺ (Scheme S1).³⁹ Based on the stability of the non-irradiated control coatings, this reaction is very slow at 20 °C from pH 3-8. This can likely be attributed to the electron-withdrawing ester moiety, which would destabilize the adjacent carbocation intermediate involved in the hydrolysis mechanism. On the other hand, end-to-end depolymerization of the triggered PEtG involves the sequential breakdown of terminal hemiacetals. In aqueous solution, hemiacetal hydrolysis can be catalyzed by acid (Scheme S2) or base (Scheme S3).^{40,41} It has been reported that hemiacetal decomposition is generally faster

than acetal decomposition and that a rate minimum for hemiacetal cleavage occurs at mildly acidic pH.^{40,41} Both of these observations are consistent with the results of the current study, where more rapid mass loss was observed for the irradiated polymer coatings at all pHs, and a minimum rate of mass loss was observed at pH 5. Overall, these differences in mechanisms and rates between of the backbone cleavage and end-to-end depolymerization demonstrate an effective decoupling of these processes.

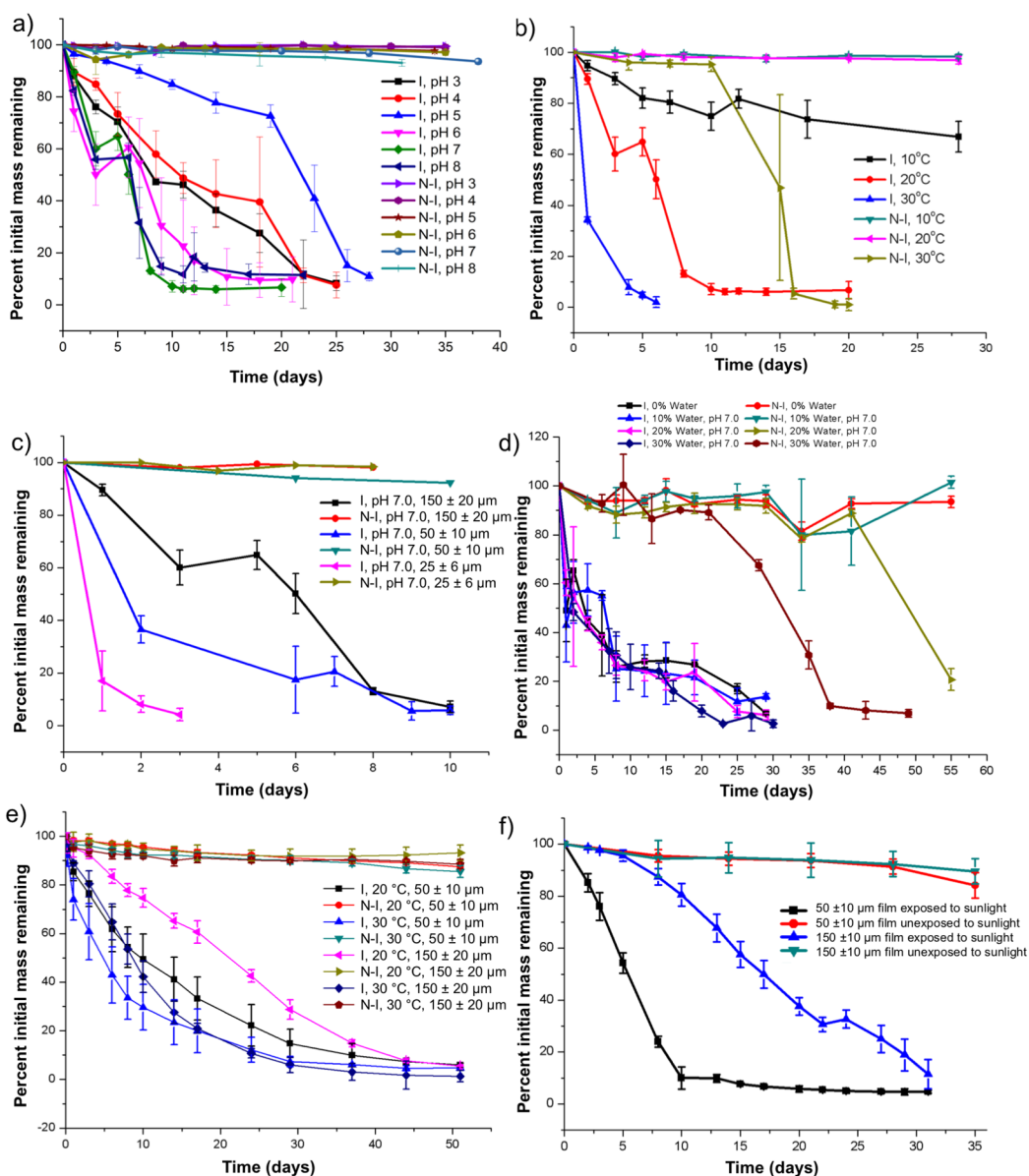


Figure 1. Mass loss profiles for UV light irradiated (I) and non-irradiated (N-I) PEtG-NVOC coatings under different conditions: (a) 150 μm thickness immersed at 20 $^{\circ}\text{C}$ in buffers of pH 3 – 8; (b) 150 μm thickness immersed at varying temperatures in pH 7.0 buffer; (c) Varying film thicknesses from 25 – 150 μm immersed in pH 7.0 buffer at 20 $^{\circ}\text{C}$; (d) 150 μm thickness immersed in soil with either 10, 20 or 30 mass % of pH 7.0 buffer at 20 $^{\circ}\text{C}$; (e) Film thicknesses of 50 or 150 μm in air (no aqueous immersion) at either 20 or 30 $^{\circ}\text{C}$; (f) Film thicknesses of 50 or 150 μm in air either exposed or not exposed to sunlight in a greenhouse. In each experiment, the error bars represent the standard deviation of the measurements for three samples.

The effect of temperature on the depolymerization rate was also explored by incubating irradiated and non-irradiated coatings in pH 7 buffer at temperatures of 10, 20, or 30 $^{\circ}\text{C}$. As expected on the basis of kinetics as well as entropic contributions to ΔG , temperature had a significant effect on the rate of coating erosion, with the irradiated coating at 30 $^{\circ}\text{C}$ requiring less than 1 day for 50% mass loss while more than 28 days was required at 10 $^{\circ}\text{C}$ (Figure 1b). The non-irradiated coatings were stable at 10 $^{\circ}\text{C}$ and 20 $^{\circ}\text{C}$ while at 30 $^{\circ}\text{C}$ degradation began at \sim 12 days. At this temperature the rate of backbone cleavage reactions in the presence of water becomes sufficient to cleave chains and initiate depolymerization.

A notable and unusual feature of the mass loss profiles in Figure 1a-b was a distinct plateau or even increase at \sim 40 % mass loss. We hypothesized that this was related to the surface accessibility of the polymers and resulting depolymerization products. It was proposed that the apparent mass increase might have arisen from the production and temporary trapping of EtGH as depolymerization occurred and water slowly penetrated into the coating, subsequently reacting to form this hydrate within the coating. Indeed ^1H NMR spectra of the residual coating material

at 3 day and 6 days (pH 7, 20 °C) contained peaks assignable to EtGH (Figures S8-S9). To further evaluate this phenomenon, coatings of different thicknesses were prepared and studied. As shown in Figure 1c, the plateau for a ~50 μm thick coating was at ~80% mass loss while no plateau was observed for an even thinner film of ~25 μm . This confirms that accessibility of depolymerizing polymers to the coating surface is indeed important for coating erosion. This can likely be attributed to the fact that released EtG can potentially re-add to the polymer terminus if it is not rapidly released from the coating or trapped by water to form the hydrate. This presents an opportunity to tune the coating erosion time by simply changing the coating thickness for various applications. It should be noted however that upon increasing the coating thickness to 300 μm , the mass loss did not proceed beyond ~60% (Figure S12). This presumably results from incomplete end-cap cleavage due to the inability of sufficient UV light to penetrate these thicker coatings using our experimental set-up. ^1H NMR spectra of the 150 μm -thick coatings did not show any end-cap, confirming complete cleavage (Figures S8-S9), whereas intact end-cap could be clearly observed for non-irradiated coatings (Figure S10-S11).

Conditions of pH 7.0 and 20 °C and a coating thickness of 150 μm were selected to further probe the erosion mechanism. Water-insoluble degradable polymers can undergo surface erosion or bulk erosion. Which process dominates for a given polymer is generally dependent on the relative rates of bond cleavage, diffusion of water into the polymer and the dimensions of a given polymer specimen.⁴² As shown in Figure 1a-c, the degradation profiles for the irradiated polymers suggest a surface erosion process, as mass loss began immediately. This was supported by minimal changes in the molar mass characteristics of the bulk polymer as determined by size exclusion chromatography (Figure 2a). The initial small drop in M_n can likely be attributed to

some depolymerization that occurred in the THF SEC solvent after sample dissolution of each of the irradiated samples as depolymerization can occur slowly in THF.

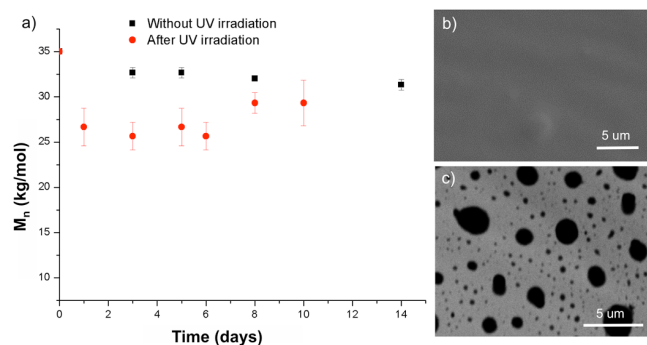


Figure 2. (a) Number average molar mass (M_n) of polymer remaining on the coating during the mass loss study, as measured by SEC.; (b,c) SEM images of the polymer coating after 5 days of immersion in 0.1 M, pH 7.0 phosphate buffer at 20 °C (b) control without UV irradiation and (c) with UV irradiation.

The surfaces were also imaged by SEM. The non-irradiated coating retained a smooth and intact surface (Figure 2b) while the irradiated coating developed holes (Figure 2c). The smooth appearance of these surfaces can be attributed to the amorphous nature and low T_g (-9 °C) of PEtG.²³ The surface erosion mechanism can be explained by the rapid decomposition of hemiacetals, combined with the importance of surface accessibility for diffusion of the depolymerization products out of the coating. In contrast, the delayed mass loss of the non-irradiated coating is more characteristic of a bulk degradation mechanism, where water diffuses through the polymer, resulting in slow bond cleavage.⁴² In this case bond cleavage would involve slow, non-specific hydrolysis of the polymer backbone. However, unlike polyesters such as poly(lactic acid) that commonly undergo bulk erosion,⁴³ non-irradiated PEtG does not undergo

changes in molar mass prior to the onset of mass loss (Figure 2a). Polyesters can undergo multiple bond cleavages in the polymer backbone throughout the bulk polymer matrix prior to the loss of mass, as shorter polymer chains remain insoluble. In contrast, even a non-irradiated PEtG undergoes complete backbone depolymerization to water-soluble small molecules following a single backbone scission event. This highlights another key difference between the end-to-end depolymerization mechanism of PEtG and the random backbone hydrolysis that occurs in conventional degradable polymers.

It was also of interest to investigate the erosion of PEtG in the natural environment, so mass loss was investigated in soil-like conditions with varying water content (Figure 1d). A significant dependence on the water content was observed for the non-irradiated coatings. This can be attributed to the requirement for water to participate in any cleavage reaction of the end-capped polymer, including ester, acetal, or carbonate hydrolysis. On the other hand, the erosion rate of irradiated coatings exhibited no significant dependence on water, suggesting that water was not required for end-to-end depolymerization. This led to the discovery that irradiated PEtG coatings readily depolymerized under ambient conditions with the depolymerization time dependent on temperature and coating thickness (Figure 1e). In the absence of water, the polymer matrix is presumed to serve as a proton transfer agent and EtG is the final degradation product (Scheme S4). Having a boiling point of 110 °C, similar to toluene, it readily evaporates from the surface. No plateau in the mass loss was observed in these studies, consistent with the above explanation relating to the trapping of EtGH in coatings that were immersed in aqueous conditions. It was also found that sunlight could trigger depolymerization under ambient conditions resulting in a coating erosion time that was dependent on its thickness (Figure 1f). This thickness dependence can arise from the decreased penetration of the light through the thicker coating and also from

the inherent dependence of the coating depolymerization time on thickness that was observed in Figure 1c and e. Combined, these data demonstrate that solid-state PEtG-NVOC has the ability to degrade in an essentially traceless manner under ambient conditions in response to a specific external stimulus and that the coating depolymerization time can be tuned by adjusting parameters such as coating thickness.

The depolymerization of polymers back to volatile monomers under ambient conditions is very rare. “Traceless” depolymerization has been reported using poly(vinyl sulfone)s (PVS) and it has been shown that these polymers undergo depolymerization in the presence of ionizing radiation, UV light, heat, or mechanical force.⁴⁴⁻⁴⁸ However, a key limitation is that the overall stability of PVS is directly correlated with their susceptibility to undergo depolymerization as it is backbone cleavage itself that triggers depolymerization. Consequently, their inherent instability may limit their application. In contrast, end-to-end depolymerization of PEtG is initiated by end-cap cleavage and this is triggered by different stimuli and conditions than backbone cleavage, as demonstrated above. Effectively, the end-cap affords a removable barrier to the otherwise thermodynamically favorable depolymerization process, allowing the polymer to be utilized above its inherent ceiling temperature. Among the other backbones that undergo end-to-end depolymerization, polyphthalaldehyde has also been demonstrated to depolymerize in the solid state.^{21,22} However, the *o*-phthalaldehyde depolymerization product is a solid at room temperature with a melting point of 55 – 58 °C and a boiling point of 266 °C. High vacuum is required to volatilize it, making the recollection of monomer difficult, and it tends to sublime rather than distill.

To demonstrate the proof-of-concept for a potential application of the unusual behavior of PEtG-NVOC, a full cycle of material degradation and regeneration at the molecular level was

performed. PEtG-NVOC was irradiated with UV light, and then moderate heating (50 °C) and modest vacuum (240 mTorr) were used to accelerate the depolymerization and transfer of EtG monomer to a second flask (Figure 3). More than 85% of the material could be collected over less than 10 h and the identity of the product was confirmed to be ethyl glyoxylate by ^1H NMR spectroscopy (Figure S14). Without further processing, this monomer could be repolymerized and end-capped to afford again PEtG-NVOC (Figure S15-S16). In contrast, applying the same conditions without UV irradiation did not result in any conversion of the polymer to liquid monomer and no monomer was transferred to the collection flask, confirming the end-capped polymer's stability under the experimental conditions.

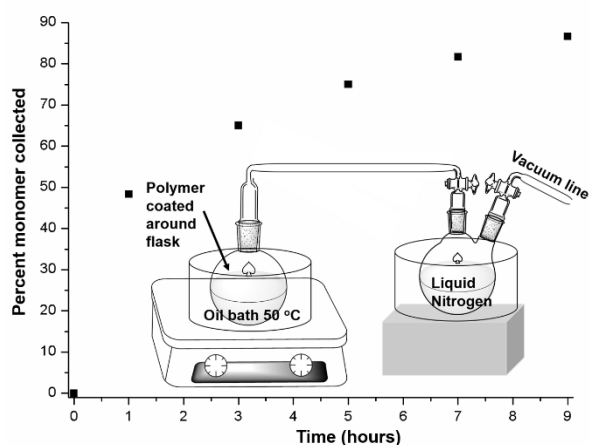


Figure 3. Collection of depolymerized ethyl glyoxylate monomer over time after irradiation of PEtG-NVOC and the corresponding experimental set-up.

Recently, depolymerization as a means of potentially recycling polymers has been a topic of increasing interest. For example, it was shown that polycarbonates that were prepared from epoxides and CO_2 could be depolymerized in solution to either their monomers or cyclic carbonates depending on the particular polymer backbone and the depolymerization conditions.⁴⁹⁻⁵¹ It was also recently demonstrated that poly(γ -butyrolactone) could be

depolymerized to monomers due to the thermodynamically favorable generation of the 5-membered lactone ring.⁵² However, high temperatures of 220 °C and 300 °C were required to achieve depolymerization for the linear and cyclic forms of the polymer respectively. Poly(aromatic ester)s derived from benzodioxepinones were also found to undergo reversible polymerization and depolymerization using Al catalysts in solution depending on the temperature and concentration of the material.⁵³ Furthermore, poly(benzyl ether)s could be selectively depolymerized in the presence of polystyrene or polypropylene and then the monomers could be selectively dissolved, purified by extraction, and then repolymerized.⁵⁴ To the best of our knowledge, in comparison with PEtG, there is no other polymer that has been depolymerized and repolymerized through such a simple process under mild conditions.

To further demonstrate the utility of the ambient depolymerization, PEtG-NVOC was investigated as a material for traceless one-step patterning. Metal masks with 500 µm or 20 µm holes were placed over PEtG-NVOC films and they were then irradiated with UV light. Over a period of 6 days, the corresponding features appeared in the polymer films without any further intervention or treatment under ambient conditions. Shown in Figure 4 are the masks and the optical images of the resulting microscale features. The irradiated areas show holes while the integrity of the surrounding thin film is preserved. These results highlight the possibility of using such an approach for micro or nanofabrication processes. All photopolymers used for standardized micro- (UV lithography) and nano-scale (electron beam lithography) production require a wet chemical processing step for both the developing and lift off steps. With our approach we envision the possibility of reducing the use of developing chemicals for lithography processes. Nevertheless, further work will be needed to investigate and optimize the aspect ratio of the obtained structures and their compatibility with other microfabrication steps. In addition, it

would be ideal to increase the rate of pattern formation. This might be achieved by increasing the temperature or using a more volatile glyoxylate such as methyl glyoxylate.

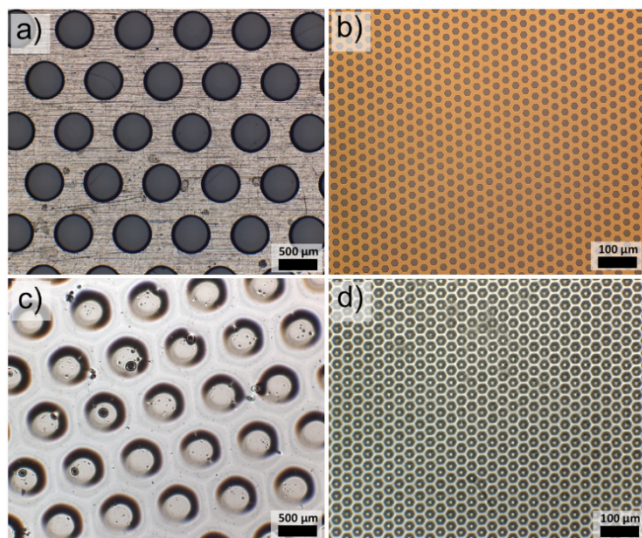


Figure 4. Digital optical microscopy of ambient self-developed patterns: The metal masks are shown in (a) and (b) while the corresponding 500 μm and 20 μm reservoirs fabricated from these masks are shown in (c) and (d) respectively.

Conclusions

In conclusion, this study of PEtG depolymerization in the solid state has demonstrated several unique features of PEtG depolymerization that clearly differentiate it from conventional polymer degradation processes. Through studies of the pH dependence, it was shown that the mildly acidic conditions that accelerate backbone cleavage of conventional polyacetals actually slow the depolymerization process as the hemiacetals cleave more readily under neutral conditions. It was also shown that the rapid end-to-end depolymerization combined with the surface erosion mechanism results in an unusual plateau in the mass loss, while the transfer of degradation products out of the film catch up with depolymerization. In addition, while the time required for depolymerization depended in a predictable way on temperature and coating thickness, it was not

dependent on water, leading to the discovery that after end-cap cleavage, PEtG exhibits a rare ability to undergo depolymerization to volatile products under ambient temperature and pressure. This was demonstrated to offer unique capabilities for the direct reprogramming or recycling of polymers under mild conditions as well as for the preparation of self-developing patternable coatings.

Supporting information

¹H and ¹³C NMR spectra of polymers, SEC data, proposed depolymerization mechanisms, additional degradation data, monomer collection and repolymerization set-up. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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