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# Programmed Photodegradation of Polymeric/Oligomeric Materials Derived from Renewable Bioresources**

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**Abstract:** *Renewable polymeric materials derived from biomass with built-in phototriggers were synthesized and evaluated for degradation under irradiation of UV light. Complete decomposition of the polymeric materials was observed with recovery of the monomer that was used to resynthesize the polymers.*

In the past two decades considerable efforts have been made to convert biomass especially carbohydrates into value-added chemicals and as suitable alternates for constantly depleting fossil fuels. Biomass is inexpensive, abundant, and more importantly renewable.[1] There are a plethora of reports on conversion of carbohydrates, glucose or fructose into a number of industrially important intermediates[2] such as dimethyl furan,[2c,i] γ-valerolactone, ethyl levulinate, caprolactam, caprolactone, 1,6-hexanediol, adipic acid, 2,5-bishydroxymethyl furan, and 2,5-furandicarboxylic acid (FDCA). The common key chemical for accessing the chemicals mentioned above is 5-hydroxymethylfurfural (HMF).[1–3] FDCA an oxidation product of HMF was identified as an important building block for polymer synthesis.[4] Due to their industrial importance, both HMF and FDCA are listed among the top 14 bio-based chemicals by the U.S. Department of Energy.[1a] FDCA could possibly replace terephthalic acid in polyethylene terephthalate (PET), a polyester prepared in tons every year and the FDCA-glycol polymer has properties similar to PET.[4a] Though synthetic polymers play vital roles in daily life, their non/poor-degradability increases concerns regarding their impact on the environment (as they are mostly disposed in landfills). In addition, building blocks for polymers are mainly derived from fossil fuels.[1f] Great demand with diminishing fossil fuels necessitates finding alternate sustainable sources for building polymeric materials.[2a] To address the above issues of degradability and sustainability, we have invested our efforts toward polymer building blocks from renewable resources with built-in photocleavable unit(s) to obtain photodegradable polymers that can be pre-programed for degradation with light. To showcase our strategy, we have employed an FDCA-derived polymer that features a nitrobenzyl chromophore to trigger photo-degradation upon shining light (Figure 1). Our proof of principle strategy has shown that one can successfully append triggering units to monomers derived from biomass and recover them after degradation so that the monomers can be reused to minimize impact on the environment making the process both green and sustainable.

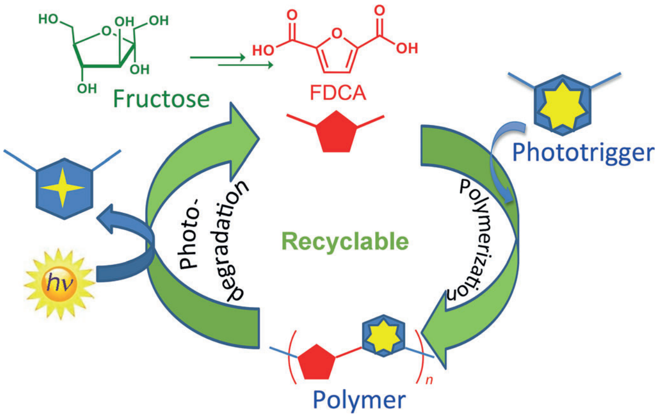

*Figure 1.* Concept of programmed photodegradation of bio-based oligomers/polymers derived from FDCA.

To evaluate the feasibility of our strategy, we first employed model compounds to establish the reaction conditions and to investigate degradation efficiency and recoverability (Scheme 1). We started with established literature procedures[3g] to convert fructose **1** to furan-based derivatives that is HMF **2** and FDCA **3** as they are synthetically accessible (Scheme 1).[3g] These bio-based furan derivatives were employed both as building blocks for model compounds and as monomers and were functionalized with 2-nitro-1,3-benzenedimethanol **6**, which served as a phototrigger. We chose to employ the 2-nitrobenzyl group to establish the proof of principle for our investigation as it has been widely used as a phototrigger[5] to evaluate photoresponsive micelles,[6] hydrogels,[7] and copolymers.[8] In addition, the photo-trigger-

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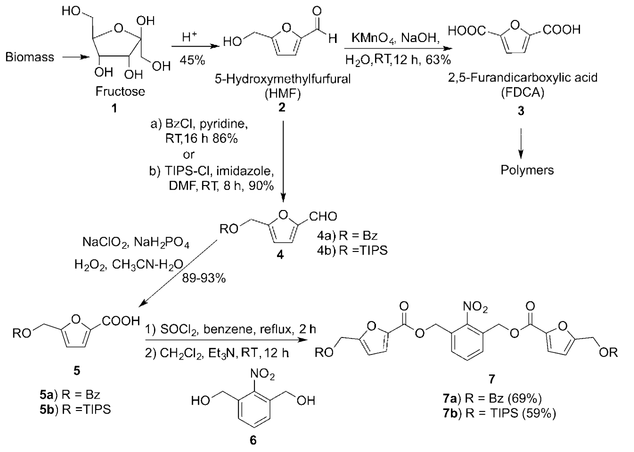
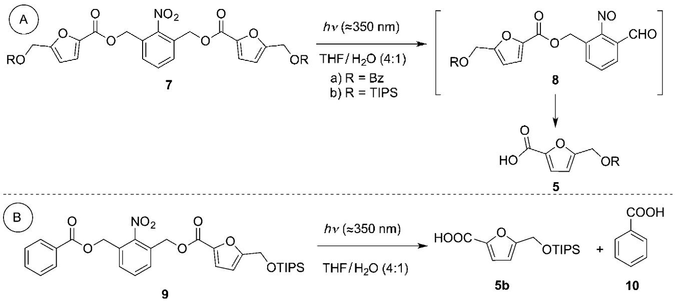
Supporting information for this article including syntheses and characterization of monomers derived from biomass, model compounds, oligomers/copolymers, irradiation conditions for photodegradation, and analysis of the photoproducts is available on the WWW under http://dx.doi.org/10.1002/anie.201408492.



***Scheme 1.*** Synthesis of model compounds from renewable materials for programmed degradation. Bz = benzyl, TIPS = triisopropylsilyl, and DMF = *N*,*N*-dimethylformamide.

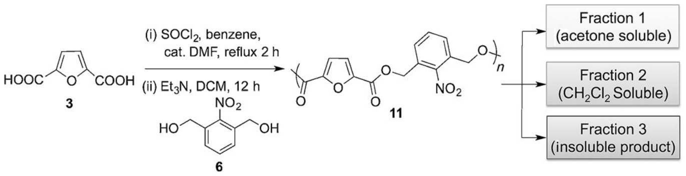
ing mechanism of 2-nitrobenzyl functionality is well established in the literature.[9]

Irradiation of model compounds was carried out in a Rayonet reactor equipped with sixteen 14-Watt lamps (ca. 350 nm). A known concentration of symmetrically substituted esters **7a** or **7b** in a THF/$H_2O$ mixture (**7a**: 1 mM or 0.1 mM and **7b** = 1 mM or 0.1 mM; THF = tetrahydrofurane) was irradiated at approximately 350 nm (Scheme 2). Progress of the reaction was monitored every 30 minutes by both UV/Vis and $^1$H NMR spectroscopy. Analysis of $^1$H NMR spectra[10] revealed that the photocleavage of **7a** and **7b** was very efficient with excellent mass balance of 89 and 80, respectively. The *ortho*-nitrobenzyl proton resonance at 5.45 ppm was used as an NMR handle to monitor the reaction progress. As expected, we observed the formation of the nitrosoaldehyde **8** that was substantiated by the appearance of the aldehyde proton resonance at 9.17 ppm. The nitrosoaldehyde **8** underwent further decomposition to give furan carboxylic acid **5** (based on the methylene proton resonance at ca. 4.82 ppm). As the model compound **7** was a symmetrically substituted substrate, we also evaluated the unsymmetrically substituted ester **9** and found that it underwent decomposition with equal effectiveness. This proof of study with the model compounds clearly substantiated that the strategy of employing a nitrobenzyl trigger for the programmed degradation of oligomers/polymers derived from **5** (Scheme 1) was indeed viable as we could not only use monomers derived from biomass but also recover them with high fidelity.



***Scheme 2.*** Photodegradation of model compounds derived from biomass. A) symmetrical ester **7**. B) unsymmetrically ester **9**.

With the knowledge gained through the photocleavage of model compounds, we proceeded to synthesize polymer/oligomers from FDCA **3** that featured the nitrobenzyl functionality to evaluate the efficiency of photocleavage as well as the recovery of monomer **3**. In a one-pot reaction, **3** was converted to the corresponding acid chloride with thionyl chloride and reacted with nitrobenzyl phototrigger **6** to obtain a pale brown solid (Scheme 3). The insoluble product was washed with methanol to remove any unreacted monomer. The product was then triturated followed by the addition of acetone and $CH_2Cl_2$ to remove low-molecular-weight oligomers. The leftover insoluble solid was then washed with methanol and dried under reduced pressure and was characterized by FTIR spectroscopy, GPC, powder X-ray diffraction (PXRD), NMR spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).[10] As the residue was partially soluble in THF at room temperature, the material was suspended in THF and sonicated for 5 h. The solution was filtered and the supernatant was analyzed by GPC (Figure 2B). Inspection of Figure 2B shows that the material is a mixture of polymer ($M_w$ = 81000; $M_n$ = 54000 and PDI = 1.5) and oligomer ($M_w$ = 450; $M_n$ = 340 and PDI = 1.3). The synthetic procedure for accessing the polymer/oligomer **11** was repeated for reproducibility and characterized by PXRD. Inspection of the FTIR spectrum of the pale brown solid (Figure 2A) revealed a strong vibration band at 1739 cm$^{-1}$ indicating an ester functionality. In addition, the presence of the nitro group was unequivocally established by its characteristic asymmetric and symmetric stretching at 1529 and 1367 cm$^{-1}$, respectively. All these clearly pointed out that the insoluble solid material **11** was a polymer/oligomer between **3** and **6**.



***Scheme 3.*** Synthesis of polymer/oligomer **11** derived from biomass.

To further characterize the material obtained from the condensation of **3** and **6**, we made a completely soluble solution of **11** by heating a suspension in [D$_6$]DMSO at 60–80 °C as it was insoluble in common organic solvents ($CHCl_3$, EtOAc, MeOH) at room temperature. The solution was analyzed by $^1$H NMR spectroscopy[10] that showed aromatic resonances corresponding to the furan and phenyl functionalities.[10] In addition, two singlet resonances at 5.48 ppm and 5.29 ppm indicated two distinct benzylic functionalities with

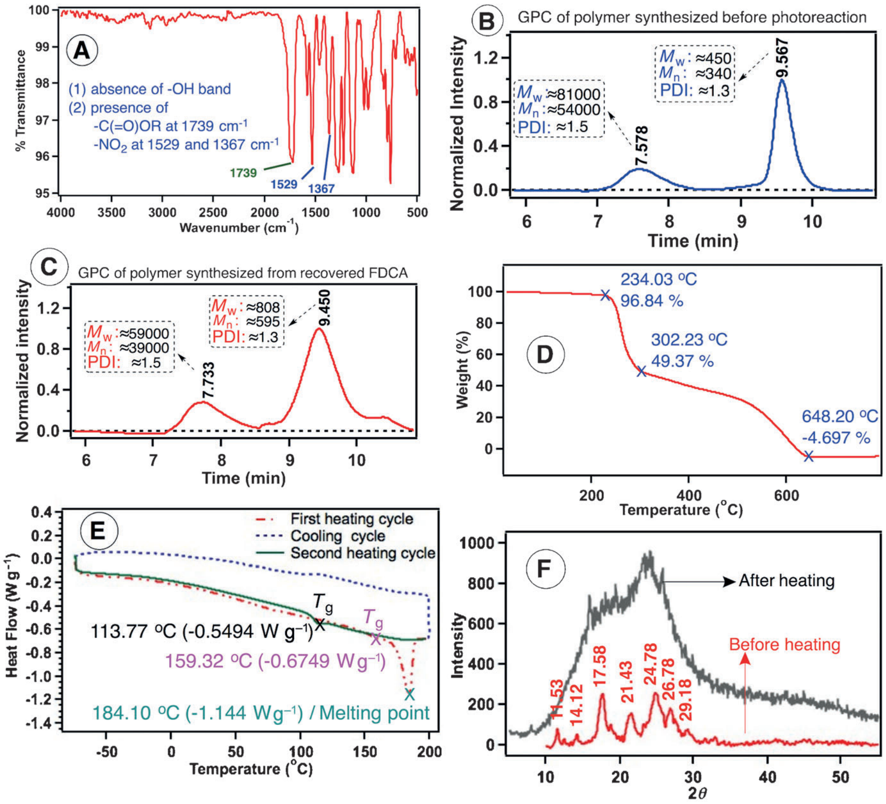
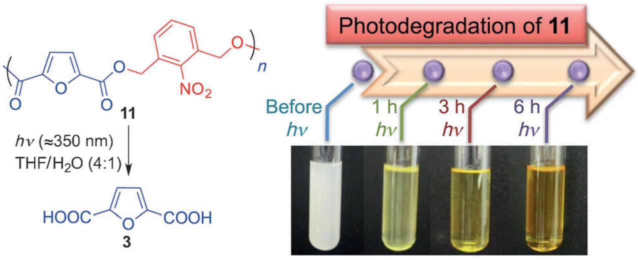


*Figure 2.* Characterization of **11** by A) FTIR spectroscopy. B) GPC of **11** synthesized from a monomer derived from biomass. C) GPC data from recycled monomer, D) TGA, E) DSC, and F) powder XRD. In the GPC data $M_w$ = Weight average molar mass, $M_n$ = number average molar mass, and PDI = polydispersity index.

a ratio of about 11:1.[10] The mixture of polymers/oligomers is consistent with the NMR studies that showed two singlet resonances for the benzylic protons once again reflecting the distinct oligomer/polymer compounds present in our system (consistent with GPC data). TGA analysis of polymer/oligomer **11** showed that it was thermally stable with no considerable weight loss up to 234 °C (Figure 2D). When the temperature was increased to 302 °C, a 50 % weight loss was observed which is likely because of decomposition of the polymer/oligomer. Decomposition of the remaining residue was complete at 648 °C. DSC analysis (Figure 2E) of polymer/oligomer **11** showed a glass-transition temperature ($T_g$) at 159 °C followed by melting at 184 °C during the first heating cycle suggesting that polymer/oligomeric **11** was a mixture of amorphous and crystalline states.[10] The cooling cycle showed a slight recrystallization but was not sharp as expected because of the lack of crystallinity in the oligomer. The second heating cycle showed a more discernible $T_g$ at 113 °C suggesting a mostly amorphous oligomer. To substantiate this observation we analyzed the synthesized oligomer/polymer **11** by powder XRD diffraction (PXRD). Closer inspection of the PXRD data (Figure 2F) indicated that **11** as synthesized had sharp peaks (2$\theta$ value) and the percentage crystallinity was estimated to be 24.34 % using cristobalite ($SiO_2$) as the reference standard. Upon heating the sample to 200 °C and cooling **11**, there was a complete loss of crystallinity with a broad peak in the PXRD indicating that the sample was likely amorphous (Figure 2F).

While **11** was not soluble in common organic solvents, we were interested in evaluating its photodegradability and in gauging the amount of the monomer that could be recovered for recycling. Photodegradation of **11** was evaluated as a suspension in a 4:1 THF/$H_2O$ mixture (Scheme 4). Irradiation of the slurry at about 350 nm resulted in a slightly turbid solution after 1 h and the solution became completely transparent after 3 h of light exposure. The irradiated samples were analyzed by NMR spectroscopy that showed complete decomposition of **11** to give the monomer, FDCA **3** (Scheme 4). The formation of the parent monomer was further confirmed by comparing the NMR spectra of the sample after irradiation with an authentic sample of **3** synthesized by an independent route (Figure 3). Irradiation of **11** was



*Scheme 4.* Programmed degradation of **11** as a suspension in a 4:1 THF/water mixture.

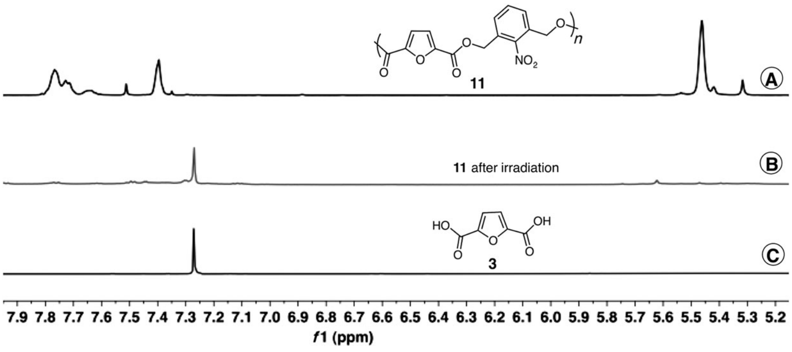


*Figure 3.* $^1H$ NMR spectra (500 MHz, [$D_6$]DMSO) of polymer **11** A) before irradiation and B) after irradiation. C) The authentic FDCA **3**.

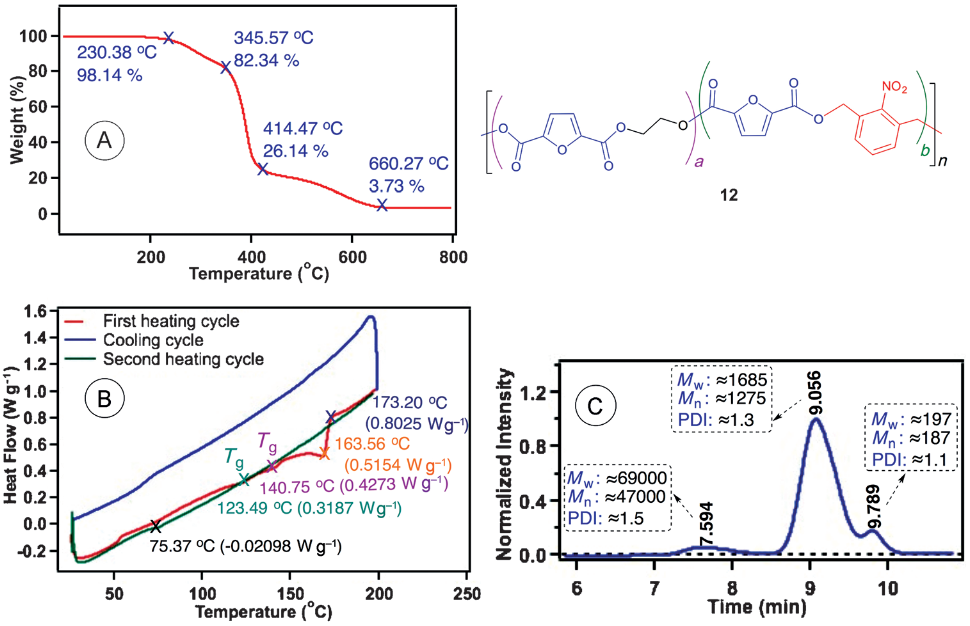
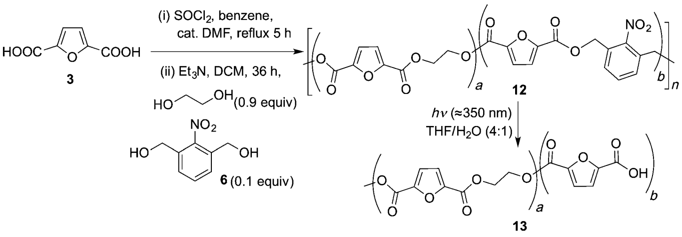


***Figure 4.*** Characterization of copolymer **12** by a) TGA, b) DSC, and c) GPC.

also evaluated in solid state under UV light irradiation that showed slow degradation, when compared to slurry irradiation where complete degradation was observed.[10] Based on recovery after irradiation as a slurry (THF/H$_2$O = 4:1), 40(±5)% of monomer **3** was isolated. We were also successful in recycling the recovered monomer **3** back to the polymer (Figure 2C) that highlighted the viability and practicality of our strategy.[10]

To evaluate if our strategy can be extended to copolymers incorporating glycols other than the phototrigger **6**, we synthesized copolymer **12**. In a single-pot reaction (Scheme 5), FDCA **3** was converted to the corresponding acid chloride with thionyl chloride and subsequently reacted with a mixture of ethylene glycol (0.9 equiv) and **6** (0.1 equiv). After the reaction was complete, methanol was added to the reaction that resulted in the copolymer **12**, which was characterized as before.[10]



***Scheme 5.*** Synthesis and photocleavage of copolymer **12**.

Due to the presence of the ethylene glycol unit, copolymer **12** showed a higher solubility than **11** and was partially soluble in common organic solvents (acetone, CHCl$_3$, DMSO) at room temperature but was completely soluble in DMSO at 75 °C. $^1$H NMR spectroscopic analysis[10] of copolymer **12** in [D$_6$]DMSO showed proton resonances for the furan functionality around 7.39 ppm and the resonances of the nitrophenyl unit appeared around 7.76 and 5.45 ppm.[10] The proton resonances of the ethylene glycol units appeared at 4.91, 4.59, 4.28 and 3.65 ppm.[10] FTIR spectra of **12** showed the ester carbonyl vibration at 1739 cm$^{-1}$ as well as the characteristic asymmetric and symmetric stretching vibrations of the nitro group at 1581 and 1308 cm$^{-1}$, respectively.[10] The copolymer **12** (Scheme 5) was sonicated in THF and the residue was filtered followed by GPC analysis of the supernatant. Inspection of Figure 4 shows that the residue is a mixture of polymer ($M_w$: 69000; $M_n$: 47000 and PDI: 1.5), oligomer ($M_w$: 1685; $M_n$: 1275 and PDI: 1.3) and unreacted **6** (retention time 9.789 minutes). TGA analysis of the copolymer **12** showed that it was thermally stable up to 230 °C. A weight loss of 13% was observed in the temperature range of 230–345 °C, and a 56% weight loss was observed in the temperature range of 345–414 °C that likely indicated a decomposition of the co-oligomer/polymer. The decomposition was complete at 660 °C.[10] The DSC thermogram of **12** showed two glass-transition temperatures at 123 and 140 °C during the first heating cycle that were likely due to the mixture of copolymers present in the material that is a FDCA-glycol-nitrobenzyl copolymer and a FDCA-glycol polymer. There was an endotherm at 168 °C that did not correspond to a melting point as no visible crystallization exotherm was observed during the cooling cycle. During the second heating cycle, a shift in the glass-transition temperature (75 °C) was observed that indicated an amorphous material. The DSC data for **12** was strikingly similar to the one observed for **11** (Figure 2E). Having characterized the copolymer **12**, we proceeded to evaluate its photodegradability. A suspension of the copolymer mixture in 4:1 THF/H$_2$O was irradiated at about 350 nm. The turbid solution turned transparent after irradiation and the solution was concentrated under reduced pressure. Analysis of the residue by $^1$H NMR spectroscopy[10] indicated that the copolymer **12** with the nitrobenzyl unit photodegraded efficiently. Thus our strategy of employing phototriggers to degrade oligomers/polymers derived from biomass was successful with good recoverability of the monomer.

Our efforts towards addressing degradability of oligomers/polymers derived from biomass-based monomers have the potential to foster development to address the need to use renewable resources to build materials that are environmentally benign.[11] While our initial study detailed in this report is only on model systems, the test of our hypothesis demonstrated that programmed degradation of oligomers/polymers derived from biomass is indeed feasible. In addition, our strategy allowed for recovery of the monomer(s) derived from biomass and reuse them to build polymers/oligomers. Our strategy has the potential to build novel materials from biomass that are degradable with light after usage mitigating the stress of unwanted chemicals in our environment. Studies to address these aspects are currently underway in our laboratories.

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**Keywords:** bio-renewable materials · green chemistry · photodegradation · phototriggers · sustainable materials

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