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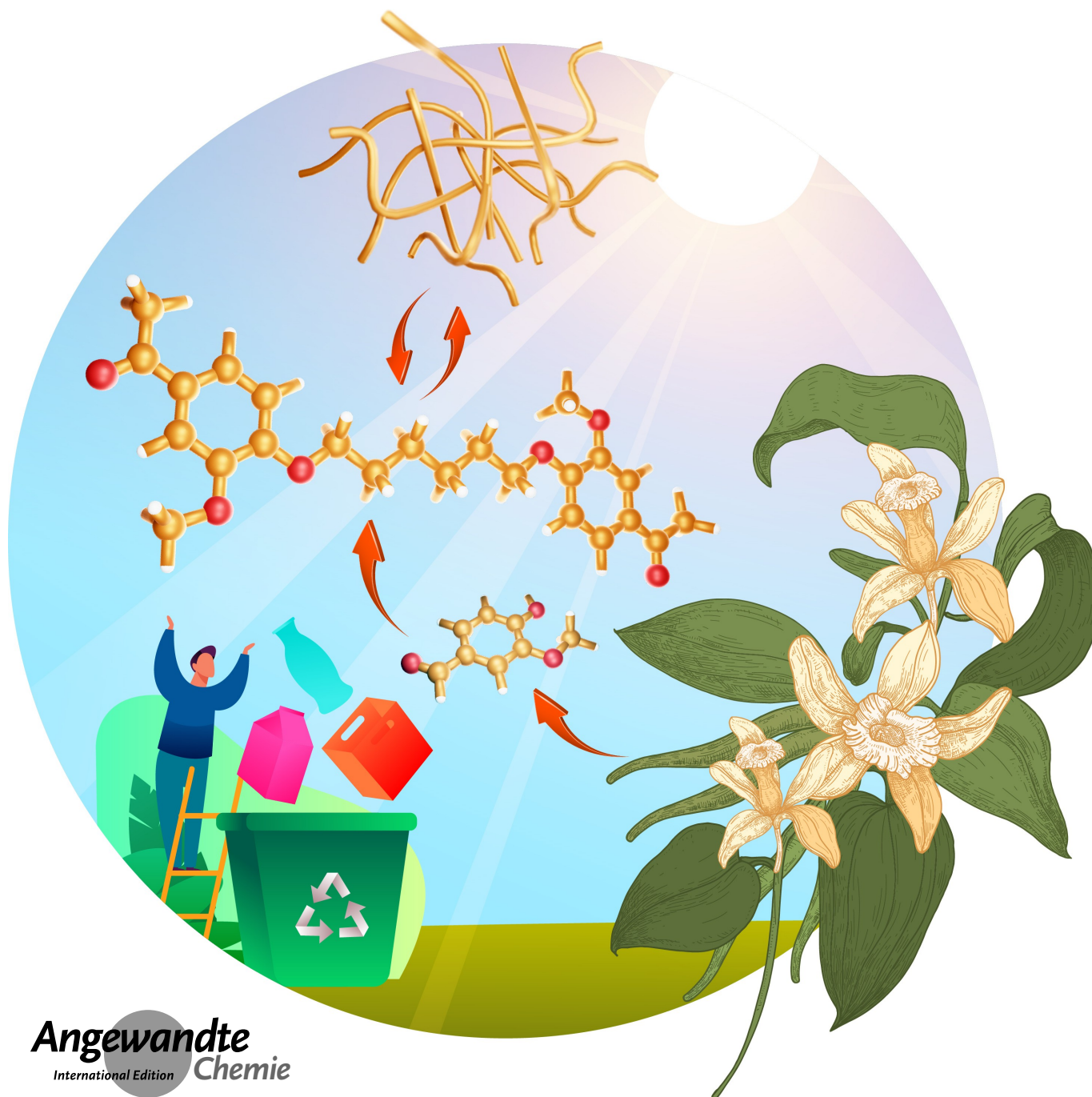
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Towards Upcycling Biomass-Derived Crosslinked Polymers with Light

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Dedicated to Professor Richard Givens on the occasion of his 82nd birthday

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Abstract: Photodegradable, recyclable, and renewable, crosslinked polymers from bioresources show promise towards developing a sustainable strategy to address the issue of plastics degradability and recyclability. Photo processes are not widely exploited for upcycling polymers in spite of the potential to have spatial and temporal control of the degradation in addition to being a green process. In this report we highlight a methodology in which biomass-derived crosslinked polymers can be programmed to degrade at ≈ 300 nm with $\approx 60\%$ recovery of the monomer. The recovered monomer was recycled back to the crosslinked polymer.

With constant depletion of fossil fuels, worldwide efforts have been devoted towards converting biomass, especially carbohydrates, into fuels and chemicals.^[1–4] Biomass not only gives a greener perspective but also is generally inexpensive, abundant in nature, and most importantly it is renewable.^[5] This has placed an emphasis on deriving value added chemicals from biomass that can be utilized to build high performance materials.^[4,6] One of the fundamental issues that still need to be addressed is the degradability and recyclability of such materials, and this aspect is especially challenging for thermosets.^[7]

In this regard, employing light for upcycling polymers offers spatial and temporal control of the degradation process. In addition, the process of employing light to degrade and recycle polymers is not only novel but also is a

green methodology (Figure 1). To address this, we previously reported the controlled photodegradation of a polymer derived from renewable resources that featured a nitrobenzyl phototrigger in the polymer backbone.^[8] We had successfully demonstrated that the monomer can be recovered at $\approx 40\%$ and reused, thus making the process sustainable (Figure 1).^[8] Our proof-of-principle study utilized *ortho*-nitrobenzyl functionality as the phototrigger as it has a well-established mechanistic pathway for photodegradation.^[9,10] Recognizing the novelty of the strategy, the Department of Energy highlighted this in their recent report on polymer upcycling.^[11] While the above mentioned 1st generation strategy (Figure 1) was successful, there are several limitations associated with the *ortho*-nitrobenzyl trigger. These include i) the wavelength used for photodegradation (≈ 350 nm), ii) the time taken to release the leaving group, iii) formation of the *ortho*-nitroso derivative as by product during the cleavage process, iv) competitive light absorption of the formed photoproduct, and v) reactivity of the photoproduct that lowers the recovery of the monomer^[12–14] vi) the nitrobenzyl trigger unit was derived from fossil fuels, while the furan dicarboxylic acid (FDCA) backbone was derived from biomass. The ≈ 350 nm used for photodegradation of the polymer posed a serious limitation as it rendered the polymer with minimal application for daily use. This wavelength is abundantly present in the solar radiation reaching the earth's surface and hence limits its usage in the design of novel functional materials. In addition, the *ortho*-nitroso byproduct(s) absorbs strongly in the visible region and possess higher optical density than the parent *ortho*-nitrobenzyl phototrigger. This

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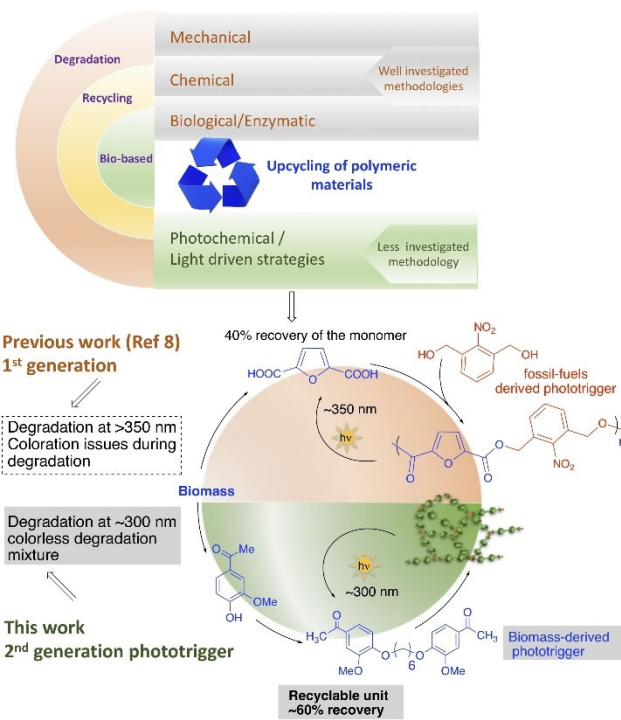
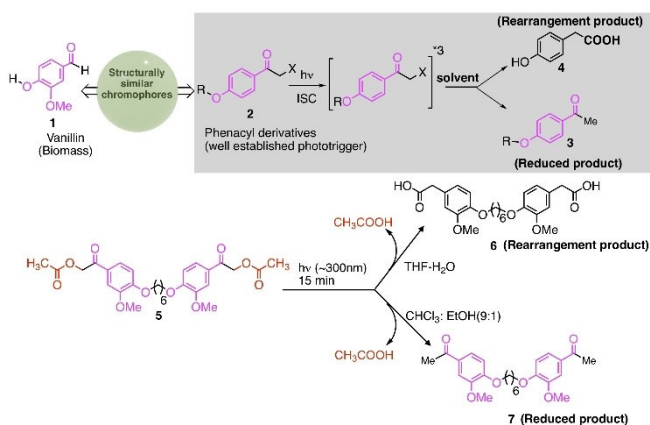


Figure 1. Upcycling biomass-derived polymers with light.

competitive absorption of the product interferes with the release of the leaving group decreasing the efficiency of degradation. The high absorptivity and reactivity of *ortho*-nitroso compound impacted the recovery yield of the monomer (after polymer degradation) leading to sub-par recyclability.^[8] An important shortcoming from a green chemistry perspective is that the nitrobenzyl chromophore is derived from fossil fuels while the furan monomer is derived from biomass. To alleviate the above challenges and to make the system more practical, we embarked on developing alternative phototriggers derived from biomass that could be employed for programmed degradation of polymers. In this work, we present our evaluation of phototriggers derived from vanillin **1** that form the polymer backbone with programmable degradability at ≈ 300 nm (absent from solar radiation on the earth surface) with $\approx 60\%$ recovery of the monomer (Figure 1) leading to recyclability and sustainability.

Phototriggers based on *p*-hydroxy phenacyl chromophores were initially reported by Anderson and Rees in 1962.^[15] Pioneering work by Givens and co-workers showcased their versatility as a photo-releasing group for various functionalities.^[16–19] Mechanistically, phenacyl based systems **2** react from the triplet excited state and undergo Favorskii rearrangement upon photo-irradiation to give the corresponding phenyl acetic acid **4** (Scheme 1) with minor amounts of the reduced ketone product **3**.^[16–19] However, to address recyclability, we were interested in identifying systems which would not undergo the Favorskii rearrangement but will lead to the reduction product **3** after photodegradation. Due to the similarity of phenacyl chromophores **2** and the vanillin chromophore **1** (Figure 1), we envisioned phototriggers based on a vanillin backbone to open up opportunities in developing photo-degradable and recyclable biomass-derived polymers that can be tailored to undergo photochemical reactivity towards the reduction product.^[20,21]

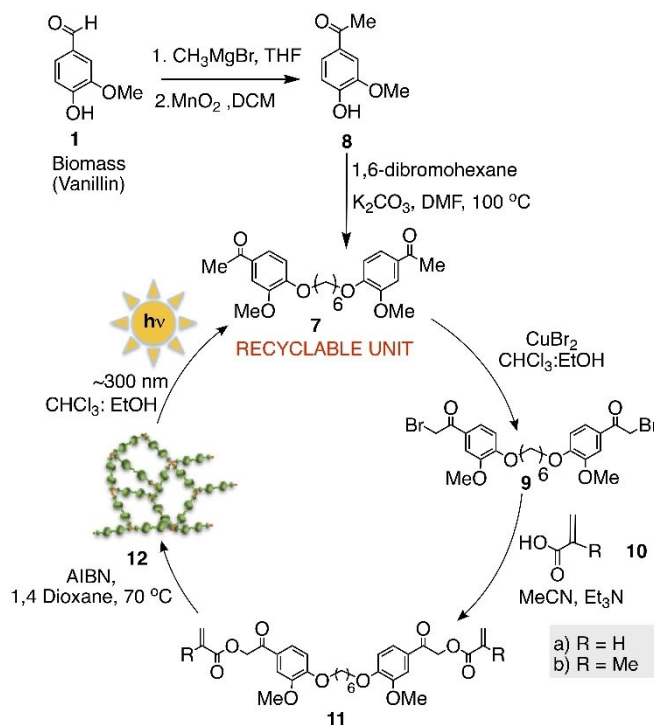
One of the main issues that had to be addressed was the programmed regeneration of either the monomer or its precursor upon photodegradation of the polymer. Based on



Scheme 1. Photoreaction of phenacyl chromophores and developing a model system.

the photochemistry of the phenacyl phototrigger (Scheme 1 top),^[15–18] we envisioned that ketone **7** will be ideal for making recyclable polymers that can be programmed to degrade at a specified wavelength. To test this hypothesis, we designed a model system **5** (Scheme 1-bottom) derived from vanillin and evaluated its photochemistry at ≈ 300 nm in a Rayonet reactor (16 lamps X 14 watts each).^[22] By utilizing 9:1 CHCl_3 :EtOH as the solvent, we were able to exclusively get the reduced product **7** in good isolated yields (the desired product for developing the upcycling protocol). The quantum yield of reaction of **5** leading to **7** was found to be 0.45% at 310 nm (using valerophenone as the standard).^[22] On the other hand, in $\text{THF-H}_2\text{O}$, the phenyl acetic acid product **6** was observed. Having ascertained the conditions to access the reduced ketone product which is the key for developing an upcycling protocol to recycle the degraded polymeric materials, we developed a strategy to build biomass-derived polymers that can be programmed to degrade at ≈ 300 nm with recovery of monomers leading to recyclability and sustainability. To achieve this we started from vanillin **1** and converted the aldehyde functionality to a methyl ketone by simple Grignard reaction followed by MnO_2 oxidation (Scheme 2).^[22]

By utilizing the reactivity of the phenolic hydroxyl group, we converted ketone **8** to bis ketone **7**. A six-carbon spacer was utilized to improve solubility in organic solvents. Closer examination of Schemes 1 and 2 reveal that bis-ketone **7** is the main photoproduct observed upon irradiation of **5** at ≈ 300 nm. Keeping this in mind, we judiciously functionalized bis-ketone **7** leading to diacrylate **11 a/b**. To



Scheme 2. Programmed degradation of biomass-derived crosslinked polymers **12 a, b**.

achieve this, we brominated bis-ketone **7** using CuBr_2 leading to dibromo derivative **9** followed by nucleophilic substitution with acrylic or methacrylic acid **10 a/b** leading to the corresponding bis-functionalized acrylates **11 a/b**. Radical polymerization of the monomer was carried out in the presence of 1-mol % AIBN for 8 hours in 1,4-dioxane at 70°C (Table 1). The reaction was quenched by exposing the reaction mixture to ambient condition and cooling followed by the addition of cold methanol to precipitate the polymer and the polymer was separated from the reaction mixture by filtration. The yield of the insoluble crosslinked polymer

Table 1: Synthesis and programmed degradation of vanillin-based crosslinked polymers.

Entry	Crosslinked polymer	Synthesized conditions	Yield [%] ^[a]	% Recovery of 7 after degradation
1	12a	AIBN (1 mol %), 1,4-dioxane, 70°C , 8 h	82	65
2	12a	synthesized from 7 isolated after photo-degradation	69	
3	12b	AIBN (1 mol %), 1,4-dioxane, 70°C , 8 h	77	62
4	12b	synthesized from 7 isolated after photodegradation	56	

[a] By gravimetric analysis. Photodegradation performed at ≈ 300 nm in a Rayonet reactor (Reference [22]). The reported values carry an error of 8%.

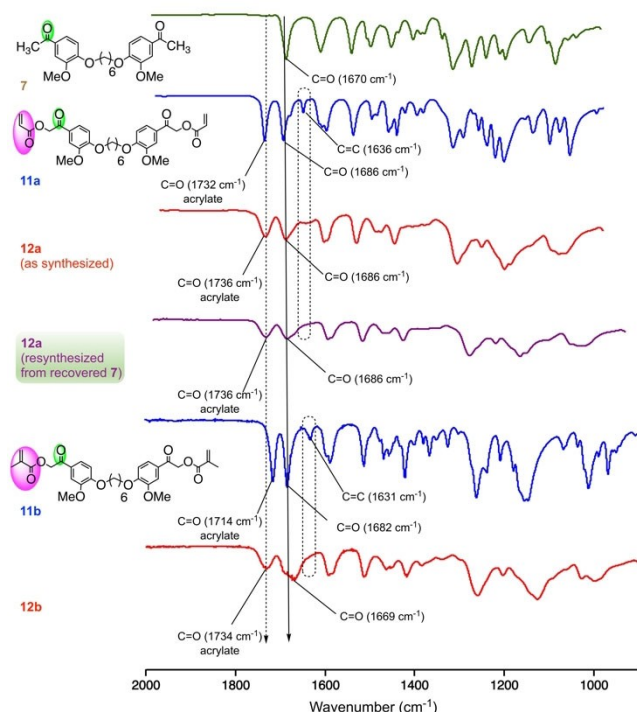


Figure 2. Attenuated total reflection Fourier transform infra-red (ATR-FTIR) spectroscopy of **7**, **11a**, **11b**, **12a**, **12a** (resynthesized) and **12b**.

12a/b (ascertained by gravimetric analysis) varied from 77–82 % (Table 1; entries 1 and 3). The yield did not change significantly for 8 h and 24 h reactions. The synthesized polymer was characterized by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and attenuated total reflection Fourier transform infra-red (ATR-FTIR) spectroscopy. Infrared spectroscopic analysis of the monomer **11**, polymer **12** and the recyclable unit **7** (as synthesized) are shown in Figure 2. In the case of the acrylate system (Figure 2), monomer **11a** featured aromatic carbonyl stretching vibrations at 1686 cm^{-1} and acrylate $\text{C}=\text{O}$ at 1732 cm^{-1} along with $\text{C}=\text{C}$ at 1636 cm^{-1} .^[23] Disappearance of acrylate $\text{C}=\text{C}$ and slight shift of acrylate $\text{C}=\text{O}$ can be observed in the corresponding crosslinked acrylate polymer **12a**. Similarly, the methacrylate monomer **11b** featured an acrylate $\text{C}=\text{O}$ and aromatic $\text{C}=\text{O}$ stretching vibrations at 1714 cm^{-1} and 1682 cm^{-1} respectively and acrylate $\text{C}=\text{C}$ at 1631 cm^{-1} . The corresponding crosslinked methacrylate polymer **12b** shows acrylate $\text{C}=\text{O}$ stretching vibrations at 1734 cm^{-1} and aromatic $\text{C}=\text{O}$ at 1669 cm^{-1} . The disappearance of acrylate $\text{C}=\text{C}$ in samples **12a** and **12b** likely points to the formation of crosslinked polymer **12a/b**. TGA of the polymeric samples showed good thermal stability (until 337°C for **12a**; Figure 3A). TGA analysis of the synthesized polymer **12a** showed that it is stable until 337.6°C with only 5 % decomposition and 50 % weight loss was observed when the temperature was increased to 450°C and complete decomposition occurred at 622°C (Figure 3A).^[22] As shown in Figure 3C, the polymer sample was amorphous as ascertained by PXRD. The synthesized polymer **12a** (blue Figure 3C) is amorphous. DSC of **12a** (Figure 3D) shows a glass-transition temperature (T_g) around $\approx 96^\circ\text{C}$. The cooling cycle and second heating cycle suggests that the acrylate polymer **12a** was mostly amorphous and can be correlated to the results of powder XRD analysis.

To understand the nature of the excited state in vanillin derived systems, we performed photophysical experiments on model compound **5** and compared its excited state characteristics with parent compound, vanillin **1** and bis-ketone **7** (Figure 4). Inspection of the absorbance of **1** and **5** (Figure 4A) at similar concentrations showed that the two vanillin chromophore units in the molecule behaved independently with minimal interaction of photochemical/photo-physical consequence. The bis-ketone **7** also had similar absorptivity indicating that the chromophore is not altered by functionalization. No fluorescence was observed for vanillin **1**, model system **5** and bis-ketone **7** in non-polar solvents and polar aprotic solvents. A weak fluorescence was observed for vanillin model system in polar protic solvents. Compounds **1**, **5** and **7** gave phosphorescence at 77 K in EtOH glass matrix. Based on the absorption and emission data of **1**, **5** and **7**, it was clear that there was no noticeable interaction between the two acetophenone chromophore in **5** separated by the alkyl linker. Based on the phosphorescence data, the triplet energy of the model system was estimated to be $\approx 64\text{ kcal mol}^{-1}$ in ethanol glass at 77 K.

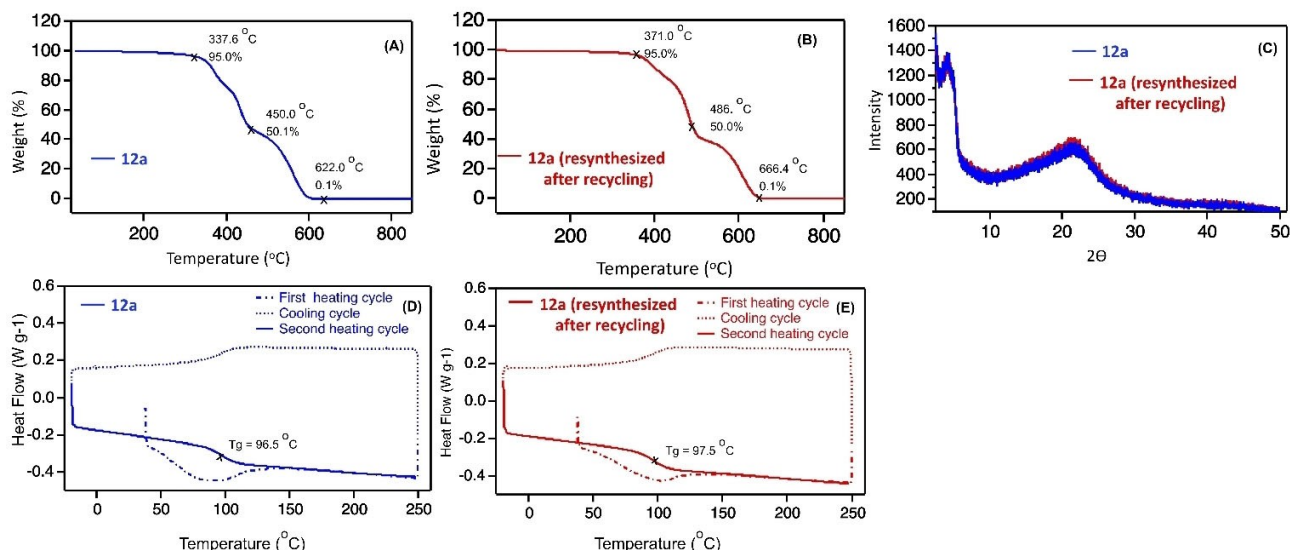


Figure 3. TGA of acrylate polymer **12a** as synthesized from biomass (A) and after photodegradation and resynthesis from recycled monomer (B). PXRD of acrylate polymer **12a** as synthesized (bottom; blue) from biomass and after re-synthesis (top; red) from recycled monomer (C). DSC analysis of **12a** as synthesized (D) and resynthesized from recycled monomer (E).

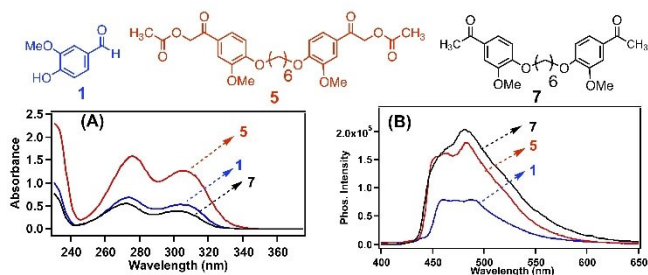


Figure 4. A) Absorbance spectra of vanillin **1** (blue), model compound **5** (red) and bis-ketone derivative **7** (black) at 0.08 mM in MeCN. B) Phosphorescence spectra of vanillin **1** (blue) model compound **5** (red) and bis-ketone derivative **7** (black) at 77 K in EtOH glass.

Based on the photophysical data, we investigated the photodegradability of the insoluble crosslinked polymers **12a,b**. For example, irradiation of **12b** at ≈ 300 nm in 9:1 v/v CHCl_3 -EtOH resulted in the degradation of the polymer leading to the formation of **7**. Of note, photodegradation of **12b** was complete in 30 minutes in spite of the polymer being insoluble in 9:1 v/v CHCl_3 -EtOH. The insoluble slurry of **12b** before irradiation became transparent clear solution with the formation of bis-ketone **7** (Figure 5) after irradiation. The formation of the bis-ketone **7** was confirmed by ^1H NMR analysis of crude reaction mixture and the isolated yields were found to be ≈ 62 – 65% (Table 1; entries 1 and 3). This recovery of the monomer is 20–30% higher than the first-generation system that showed 40% recovery of the monomer.^[8]

To showcase the recyclability of the system, the recovered bis-ketone **7** was converted back to the polymer **11a/b** (Scheme 2). The resynthesized polymer was characterized by PXRD, TGA, and DSC (Figure 3B, C and E). Compar-

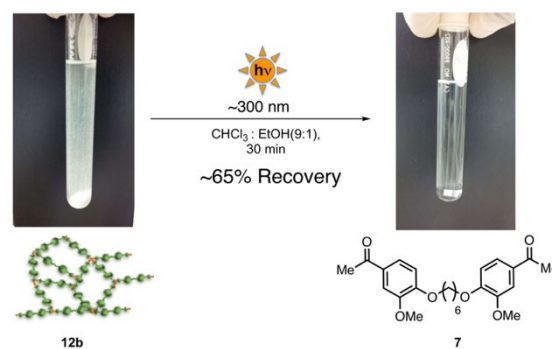


Figure 5. Programmed degradation of biomass-derived insoluble cross-linked polymer **12b**.

ison of the characteristics (Figure 2) of the polymer synthesized from biomass (1st cycle) and the resynthesized polymer after degradation (2nd-cycle) shows that they have similar characteristics (compare Figures 3A, B for TGA, Figure 3C-blue and red traces for PXD and 3D, 3E for DSC analysis). The degradation and recyclability of the system can also be conveniently followed by ATR-FTIR spectroscopy. Degradation of the polymer furnished the recyclable diketone **7** (Figure 5) that featured C=O vibration at 1670 cm^{-1} (Figure 2). As shown in Figure 3, both the recycled polymer **12a** and the original polymer as synthesized from biomass were both amorphous in nature. The amorphous nature of the crosslinked polymer is consistent with crosslinked acrylates and methacrylates.^[24] TGA analysis of the recycled polymer **12a** showed that it is stable until 371°C with only 5% decomposition and 50% weight loss observed when temperature was increased to 486°C and complete decomposition occurred at 664°C (Figure 3B).^[22] The thermal and PXRD

characteristics of the native and recycled crosslinked materials showcase that our methodology of degradation and recyclability generates similar polymeric scaffolds making the process eco-friendly and sustainable. Of note, this programmed photodegradation was demonstrated at a wavelength (300 nm) that is outside the earth's solar spectrum range. This ensures there is no degradation of material at ambient conditions and hence provides a margin of safety. At the same time the proposed methodology enables programmed photodegradation and recyclability of the monomer.

Our study has clearly demonstrated that one can develop photoactive triggers from biomass that can be utilized as a handle for programmed degradation of polymers. In the present study, we have showcased the use of vanillin-based triggers can be degraded with good efficiency around ≈ 300 nm. Efforts are underway to understand the utility of the triggers in novel functional materials.^[25]

Supporting Information: Experimental procedure, characterization data, photophysical studies.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Biomass · Photodegradation · Phototriggered Materials · Polymer Degradation · Upcycling

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