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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
**Abstract:** Photodegradable, recyclable, and renewable, crosslinked polymers from bionoressources show promise towards developing a sustainabile 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 ≈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.[6,7] 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

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**Figure 1.** Upcycling biomass-derived polymers with light.
Chemistry perspective is that the nitrobenzyl chromophore is derived from biomass 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 $\sim$300 nm (abscend 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. Pioneering work by Givens and co-workers showcased their versatility as a photo-releasing group for various functionalities. Mechanically, phenacyl based systems 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. 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 with vanillin 1 and the vanillin chromophore $2^\text{\textsuperscript{16–19}}$ we envisioned that bis ketone 7 leading to diacrylate 11a/b. To

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\text{Scheme 1. Photoreaction of phenacyl chromophores and developing a model system.}
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Programmed degradation of biomass-derived crosslinked polymers 12a, b.
achieve this, we brominated bis-ketone 7 using CuBr₂ leading to dibromo derivative 9 followed by nucleophilic substitution with acrylic or methacrylic acid 10a/b leading to the corresponding bis-functionalized acrylates 11a/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 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 C=O at 1732 cm⁻¹ along with C=C at 1636 cm⁻¹.[23] Disappearance of acrylate C=C and slight shift of acrylate C=O can be observed in the corresponding crosslinked acrylate polymer 12a. Similarly, the methacrylate monomer 11b featured an acrylate C=O and aromatic C=O stretching vibrations at 1714 cm⁻¹ and 1682 cm⁻¹ respectively and acrylate C=C at 1631 cm⁻¹. The corresponding crosslinked methacrylate polymer 12b shows acrylate C=O stretching vibrations at 1734 cm⁻¹ and aromatic C=O at 1669 cm⁻¹. The disappearance of acrylate C=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 (Tᵣ) around ≈96°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/photophysical 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 ≈64 kcalmol⁻¹ in ethanol glass at 77 K.

### 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                 | AIBN (1 mol %), synthesized from 7 isolated after photodegradation | 69         |                                  |
| 3     | 12b                 | AIBN (1 mol %), 1,4-dioxane, 70 °C, 8 h | 77         | 62                               |
| 4     | 12b                 | AIBN (1 mol %), 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.
Based on the photophysical data, we investigated the photodegradability of the insoluble crosslinked polymers 12a,b. For example, irradiation of 12b at $\lambda \approx 300$ 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 $^1$H 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). Comparison 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).\[20\] The thermal and PXRD

**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.

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