

## Depolymerization of hydroxylated polymers via light-driven C-C bond cleavage

### Scientific Achievement

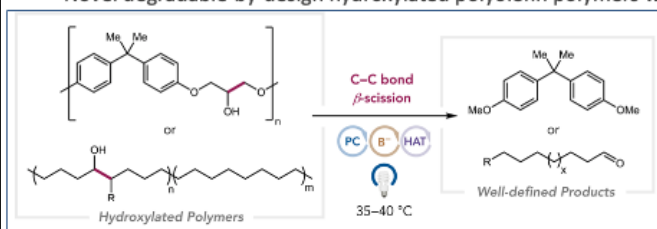
A new light-driven strategy for chemical recycling of hydroxylated polymers, including commercial phenoxy resins.

### Significance and Impact

Low-energy breakdown of waste polymers can make useful building blocks for new materials.

### Research Details

- The use of excited-state catalysts provides the driving force necessary to enable challenging C–C bond-breaking reactions using PCET-based bond cleavage.
- These materials can be depolymerized together in a single plastic waste stream and in the presence of other polymeric materials, and the process produces well-defined, isolable small-molecule products.
- Novel degradable-by-design hydroxylated polyolefin polymers with diverse yet tunable properties.



Depolymerization of hydroxylated polymers enabled by light-driven O-H proton-coupled electron transfer: Approach is compatible with insoluble polymers, and involves no stoichiometric reagents. In addition, new degradable-by-design polymers with tunable physical properties were produced.

S. T. Nguyen, E. A. McLoughlin, J. H. Cox, B. R. Fors, R. R. Knowles, *J. Am. Chem. Soc.* (2021), 143(31), 12268; DOI: 10.1021/jacs.1c05330.



The accumulation of persistent plastic waste in the environment is widely recognized as an ecological crisis. New chemical technologies are necessary both to recycle existing plastic waste streams into high-value chemical feedstocks and to develop next-generation materials that are degradable by design. Here, we report a catalytic methodology for the depolymerization of a commercial phenoxy resin and high molecular weight hydroxylated polyolefin derivatives upon visible light irradiation near ambient temperature. Proton-coupled electron transfer (PCET) activation of hydroxyl groups periodically spaced along the polymer backbone furnishes reactive alkoxy radicals that promote chain fragmentation through C–C bond  $\beta$ -scission. The depolymerization produces well-defined and isolable product mixtures that are readily diversified to polycondensation monomers. In addition to controlling depolymerization, the hydroxyl group modulates the thermomechanical properties of these polyolefin derivatives, yielding materials with diverse properties. These results demonstrate a new approach to polymer recycling based on light-driven C–C bond cleavage that has the potential to establish new links within a circular polymer economy and influence the development of new degradable-by-design polyolefin materials.