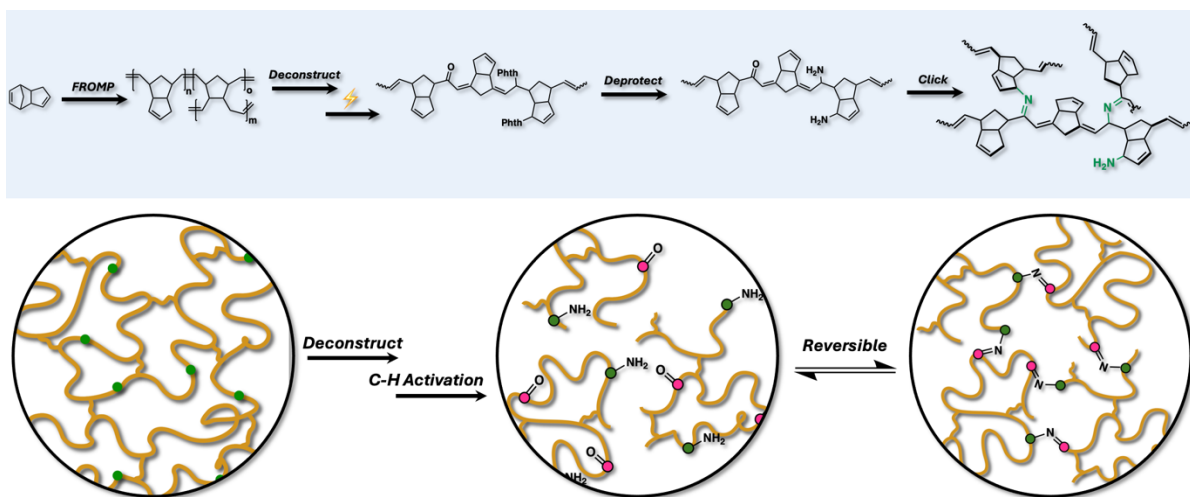


Regeneration of Thermoset Network via Electro-catalyzed C-H Bond Modification

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Abstract. The highly entangled and crosslinked polymeric backbone of polydicyclopentadiene (pDCPD) provides excellent mechanical properties, making it vital for many applications. However, this unique microstructure poses a significant challenge in recycling, as the covalently crosslinked backbone makes reprocessing difficult and prevents degradation over time. Recent advancements demonstrated that incorporating cleavable comonomers during frontal polymerization of DCPD produces a polymer with identical properties to pure DCPD, while enabling degradation under mild conditions into soluble, recyclable oligomers.¹⁻³ However, achieving true recycling or upcycling of post-consumer thermosets requires more than just breaking them down into soluble fragments. The key lies in regenerating the crosslinked network of these materials to transition from a linear life cycle to a genuinely circular thermoset economy.

Considering the complex nature of recycled pDCPD oligomer backbones and the relatively low cost of several redox mediators, we report the first electrocatalyzed dual functionalization of pDCPD polymer. This process simultaneously incorporates both C=O and C-N bonds along the backbone of recycled thermoset polymers, driven by an applied external electric potential. This approach not only allows for direct modification of the polymer backbone post-polymerization but also preserves the general structural framework of the recycled pDCPD oligomers. Simultaneously, the newly introduced combination of amine and ketone functional groups enables the conversion of recycled pDCPD fragments into a covalent adaptable network containing reversible dynamic bonds.



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