Tunable, Recyclable, and Stimuli-Responsive Bio-Derived Polymers for Real-World Challenges

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In 2019, the world produced 353 million metric tons of plastic waste, with 73 million metric tons attributed from the United States alone. This rapid accumulation causes environmental issues where plastic waste harms wildlife and affects communities. To address these concerns, several alternatives to conventional, petroleum-based consumer plastics have emerged to enhance reusability and recyclability.

One method currently used to increase recyclability is through introduction of dynamic covalent bonds. Dynamic covalent chemistry allows for facile thermal reprocessing of polymer thermosets, a trait typically lacking in crosslinked materials. Several types of chemical bonds undergo dynamic exchange at elevated temperatures: imine, ester, amide, vinylogous urethane, disulfide, and diels-alder type bonds amongst others. However, dynamic covalent chemistry has not yet been widely deployed in plastic manufacturing. Much of the limited use can be attributed to difficulty in scaling the chemistry to existing manufacturing and recycling processes, but some hesitation is also due to unimpressive material properties. Two approaches are presented here to address these issues with a focus on sustainable synthesis.

Approach 1: Here, a completely bio-based, wavelength-tunable approach to developing photoresponsive vitrimers is proposed. Resveratrol, an antioxidant commonly found in grapes, is composed of two aromatic rings linked by a double bond which exists as either the cis- or trans-isomer. When irradiated with UV light, the internal double bond undergoes photoisomerization, converting from the trans- to cis- isomer. Functionalization of resveratrol with 4-methylchlorobenzaldehyde will yield tri-aldehyde crosslinkers with distinct photoresponsivity. Subsequent reaction of these crosslinkers with bio-based diamines (putrescine, cadaverine, or diaminooctane) or diols will generate strong, dynamically crosslinked networks. Incorporation of the resveratrol moiety should enable photo-melting effects, aiding material reprocessability by lowering the glass transition temperature (T_g) on demand.

Approach 2: Phase separation is a common issue in bio-derived polymers and plastics given the highly phenolic nature of lignin and lignin derivatives. Utilization of a lignin model compound, like tannic acid, could help identify how dynamic covalent chemistry can be utilized to trap polymer networks in metastable physical states where miscibility is increased. In highly phase-separated networks, heating above the dynamic bond activation energy will increase miscibility; rapid cooling will lock in a tougher state, while slow cooling will restore the original properties.