

A Journey of Furan-Based Monomers in Polymerization Reactions

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Frontal ring-opening metathesis polymerization (FROMP) presents a rapid, scalable, and energy-efficient approach to produce high-performance polymers, leveraging the local heat generated from an exothermic polymerization to propagate an advancing reaction front directly converting monomer into polymer material. Typically, norbornene derivatives from Diels-Alder reactions were utilized in the FROMP reactions. Our study broadens the monomer repertoire for FROMP, incorporating the cycloaddition product of biosourced furan compounds and benzyne, namely oxa-benzonorbornadienes (OBNBD). The versatility of OBNBD-based materials was demonstrated through direct ink writing (DIW) to rapidly produce 3D structures without the need for printed supports.

Aside from the ROMP reaction catalyzed by Grubbs catalysts, we also found that the acid could effectively catalyze the isomerization of OBNBDs to generate the naphthols that cannot be incorporated into the polymer chains. When a thermally stable photoacid generator (PAG) was applied, we were able to achieve the orthogonal control of the isomerization and polymerization reaction of OBNBDs, which provided efficient tools for photo-controlled manufacturing of structures with spatially varying material properties, such as fluorescence, glass transition temperatures, and crosslinking density.

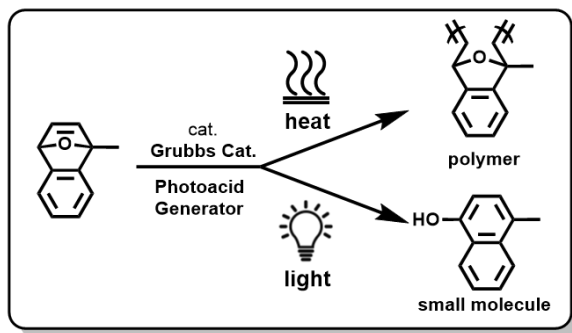


Figure 1. Orthogonal control of the isomerization and polymerization reaction of OBNBDs