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Developing Depolymerizable Polymer Materials to Mitigate Plastic Pollution

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Synthetic polymers have approached a production level of more than 367 million tons worldwide as of 2020. While the application of polymer materials has significantly improved the quality of our life, disposal options of polymer materials at the end of their useful life are rather limited to landfilling and incineration. Because of their high stability, waste materials based on synthetic polymers have accumulated in the ocean and have led to serious concerns for marine ecosystems. To address the challenging pollution issue, we aim to develop a new class of polymer materials that are depolymerizable and have the potential to replace the current commercial polymers.

We started our SURF journey by designing and synthesizing two different small-molecule monomers (**Figure 1**). In a typical monomer synthesis, exo-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride was mixed with anhydrous methanol, triethylamine, and 2-aminoethanol to yield the first monomer (**M1**). The monomer was further purified by recrystallization in cold hexane. In addition, **M2** was generated in a similar approach (**Figure 1**). The yield for M1 and M2 were calculated to be 64%, and 15% respectively.

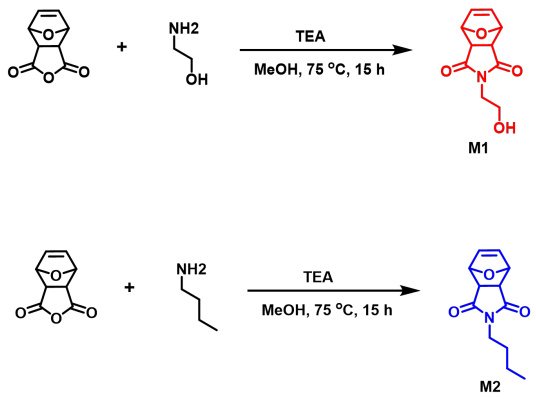

Figure 1. Design and synthetic strategies to M1 and M2.

After the successful synthesis of monomers, we harnessed ring-opening metathesis polymerization (ROMP) approach to turn those monomers into large polymers by using 3rd generation Grubbs catalyst (**Figure 2**). For the polymerization, anhydrous THF was added to the monomers, followed by the addition of 3rd generation Grubbs catalyst. The reaction was further left to stir for 2 hours at room temperature before ethyl vinyl ether was added to terminate the reaction. The polymer products were recovered by concentrating the solutions and precipitation into cold hexane for the first polymer (**P1**), and cold methanol for the second polymer (**P2**). Both P1 and P2 were further dried under vacuum before the next step.

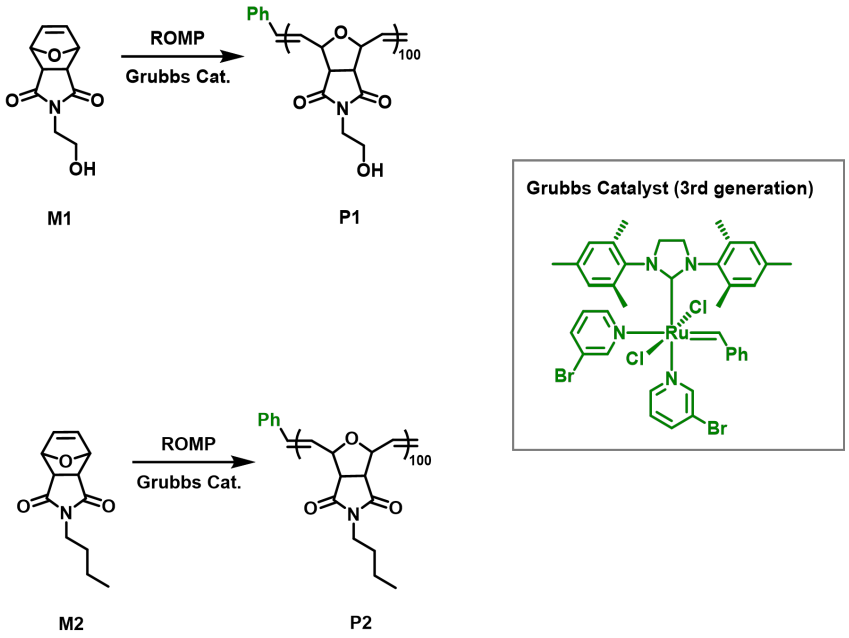

Figure 2. Synthetic approaches to P1 and P2 via polymerization of M1 and M2, respectfully.

Nuclear magnetic resonance (NMR) spectroscopy was used to confirm the structures of as-synthesized monomers and polymers. NMR spectra for M1 and M2 were in good agreement with the literature, indicating that the monomer synthesis was successful. NMR spectra for both P1 and P2 demonstrate that the original monomer signals disappeared upon the polymerization. This result unequivocally confirmed the successful polymerization of M1 and M2. More importantly, gel permeation chromatography, also known as GPC, was used to evaluate the molecular weights of P2 (**Figure 3**). According to GPC data, the molecular weights of polymers are tunable and controllable by adjusting the feeding ratio of monomers to Grubbs' catalyst. This would facilitate us to further control the polymer properties which is related to the molecular weights.

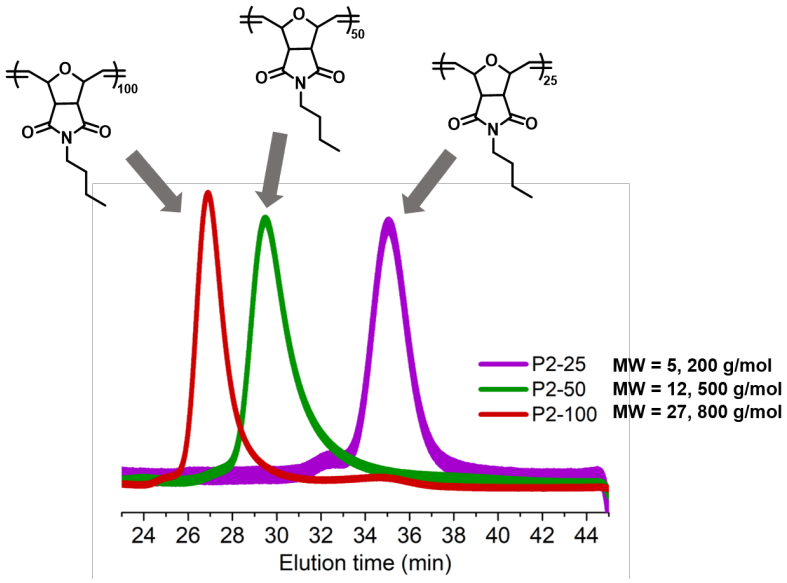

Figure 3. Gel permeation chromatography of new polymers synthesized in this project.

We are currently working on the modification our polymer materials (P1 and P2). Our near future goal is to transform P1 and P2 into depolymerizable polymers through ring-opening reactions of backbone cyclic ether. We envision the modified polymer can be depolymerize via ring-closing metathesis reactions.

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