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Degradable antioxidant polymers from petroleum-derived monomers

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Research progress

The goal of this project is to synthesize a novel class of degradable antioxidant polymers produced from petroleum-derived methacrylate monomers. Our plan is to synthesize "smart" polymers that can provide protection from oxidizing conditions and then fragment into smaller units once the redox activity of the polymer has been depleted. This project includes synthesis of novel difunctional initiators that degrade upon oxidation, synthesis of monomers with pendent reducing agent moieties, and synthesis of several polymer compositions. This research is intended to demonstrate that the proposed initiators and polymers lead to a new type of system with materials that have rationally tunable lifetimes and degradation profiles under oxidizing conditions. The proposed materials could find use as antioxidant additives in drilling muds, lubricants, drag-reducing agents, anti-corrosion coatings, degradable packaging, and biomedical applications.

During the first year of funding period, we prepared a novel difunctional initiator for atom transfer radical polymerization (ATRP) with an aryl boronic ester core that is susceptible to oxidation. Aryl boronic esters act as protected phenols that undergo a quinone methide rearrangement in the presence of H_2O_2 (Figure 1).

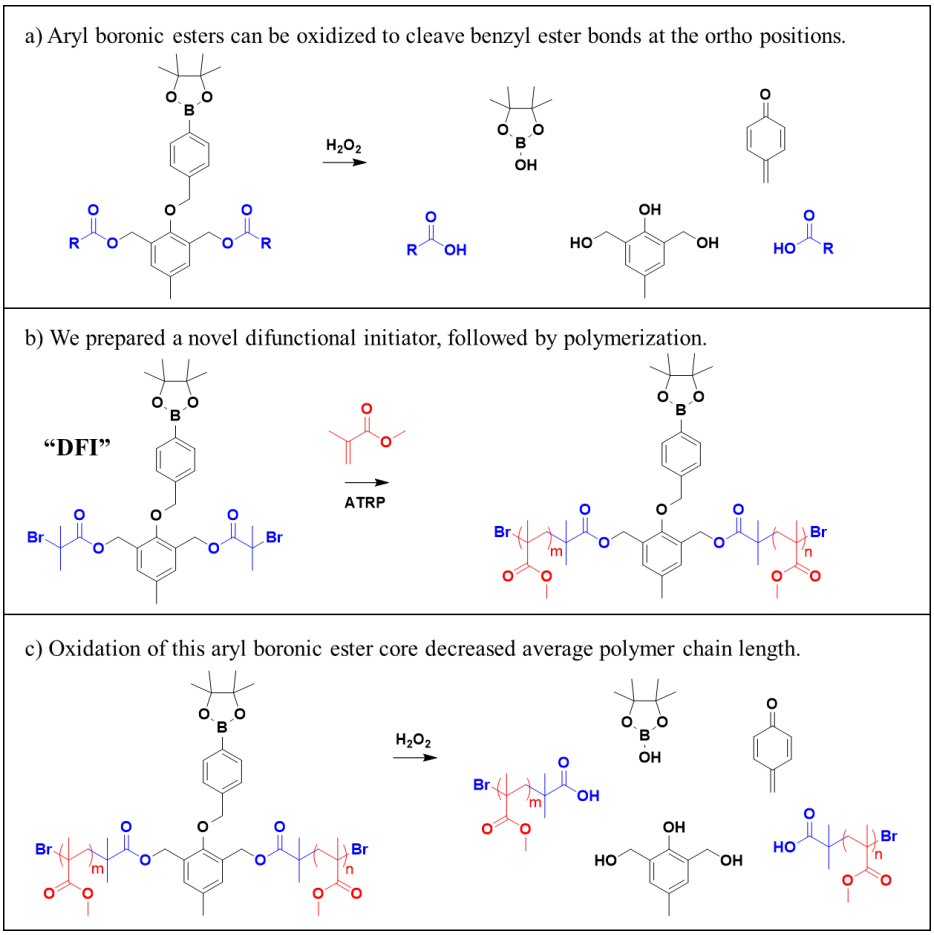

Figure 1. a) Scheme showing degradation of aryl boronic esters in the presence of peroxide. b) Scheme showing structure of a difunctional ATRP initiator with aryl boronic ester core (DFI), and polymerization of methyl methacrylate. c) Scheme showing degradation of pMMA with degradable boronic ester core in the presence of peroxide

Polymethyl methacrylate (pMMA) was synthesized by ATRP from the difunctional initiator (DFI) shown in Figure 1c., and this polymer was exposed to H_2O_2 in DMF/water. Size exclusion chromatography before and after degradation experiments (Figure 2a) show a significant decrease in molecular weight after exposing the pMMA with the degradable linkage to peroxide for 96 hours. However, a much smaller decrease in molecular weight was observed under the same conditions for pMMA synthesized without a degradable linkage (Figure 2b). These experiments showed that the DFI can be used to synthesize polymers that degrade under oxidizing conditions.

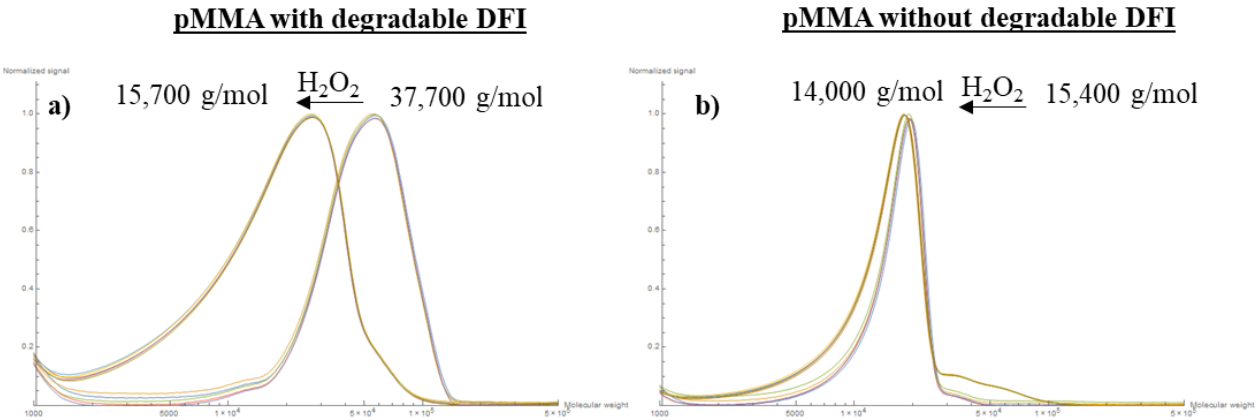

Figure 2. SEC traces for polymers after treating with peroxide in DMF/water for 96 hours. a) pMMA synthesized using DFI to include a degradable linkage. b) pMMA synthesized using the monofunctional initiator ethyl α-bromoisobutyrate (EBiB).

Our next goal is to synthesize a polymer with pendent ascorbic acid functionalities. This goal requires synthesizing a monomer with protected ascorbic acid pendent groups, polymerization of this monomer, and removing the protecting groups. We have synthesized a methacrylate monomer with TBS-protected ascorbic acid moieties in small quantities, and we are currently working to scale up this synthesis to enable polymerization experiments. Finally, we will synthesize polymers with varying feed ratios of ascorbic acid-containing monomer to determine if these functionalities can delay degradation of the boronic ester core.

Impact on students and the PI

ACS-PRF funding enabled me to pursue a new area of research on degradable polymers. One additional master's student was recruited to work on this project this year and he will receive a full year of funding. Four undergraduate students participated in this research during the first year of the funding period. One of these students is a dual-enrolled high school / undergraduate student who will continue to work on this project in the coming academic year. This student received summer support through her on-campus high school (Gatton Academy of Mathematics and Science) and she was awarded a grant from the university to present her research at the upcoming spring 2020 ACS meeting. The other three undergraduate students graduated in spring 2019. One of these students completed an undergraduate honors thesis based on this research, and he plans to apply to chemistry PhD programs this year. The remaining two students are currently enrolled in professional schools; one student went to a pharmacy doctorate program (University of Kentucky) and the other student went to veterinarian school (Auburn). All students participating in this research presented their work at a local conference in spring 2019. Research resulting from this funding has had a significant impact on the career trajectories and quality of life for the above students.