

PRF# 57806-DNI7
Synthesis of Advanced Functional Self-Immolative Polymers

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1. Progress of the research

1.1. Overview. We developed new methods for the synthesis of “self-immolative” polymers that undergo triggered depolymerization in response to externally applied chemical stimuli, as an avenue to advanced functional materials derived from petrochemical feedstocks. Furthermore, these unique materials can be functionalized with a diverse array of moieties post-polymerization, processed into thin film coatings, and cross-linked using photo-initiated thiol-ene click chemistry. These self-immolative thin films and bulk organogels disassemble into soluble component parts upon introduction of the chemical stimulus for end-to-end depolymerization.

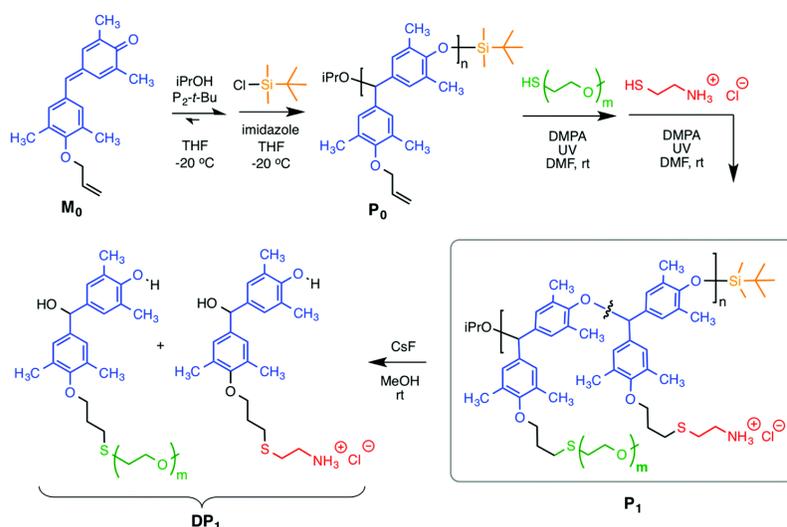


Figure 1. Synthesis of self-immolative poly(benzyl ether)s with functional side chains

1.2. Graft Copolymer Synthesis. Synthesis of the quinone methide monomer requires nucleophilic substitution of a bisphenol compound with one equivalent of allyl bromide, followed by an oxidation step, and purification by recrystallization from cyclohexane. Then, the monomer is subjected to anionic polymerization at low temperatures (typically $-20\text{ }^\circ\text{C}$, which is well below the ceiling temperature of this monomer, $T_c \sim 0\text{ }^\circ\text{C}$) in the presence of alcohol initiator and a phosphazine base, at a monomer concentration of 1M in THF. Following 4 hours of polymerization, the metastable chains are end-capped at low temperature to prevent premature chain unzipping. The end-capping agent can be any reagent that accepts the phenoxide ion as a nucleophile. For example, dimethyltertbutylsilyl chloride reacts with the active chain end to yield a fluoride labile TBDMS-capped polymer. Alternatively, NVOC chloride can be introduced to yield a polymer that unzips in response to UV light irradiation. Post-polymerization, these capped polymers bearing allyl side chains are subjected to photoinitiated thiol-ene radical addition to impart additional chemical functionality or to cross-link the polymer chains. In this example, we attached cationic amine groups and/or poly(ethylene glycol) side chains. The PEGylated graft copolymers are fully soluble in most nonpolar and polar organic solvents and even are water-soluble. In contrast, the cationic polyelectrolytes with no PEG grafts are soluble in polar organic solvents, but not water. Thus, it is found that the PEGylation route effectively masked the intense hydrophobic nature of the polymer backbone more effectively than amino groups. These copolymers can be triggered to unzip into small molecules upon introduction of a trigger (in this case, fluoride ions). The depolymerization proceeds smoothly and rapidly in polar aprotic solvents (DMF, DMSO) but slowly in protic solvents (MeOH, water). We found that the depolymerization in aqueous media can be greatly accelerated by elevating the pH of the system, which favors deprotonating of the phenoxy end group.

1.3. Self-Immolative Cross-linked Gel Networks. If the side chain functionalization is carried out only partially, then the self-immolative poly(benzyl ether)s contain some remaining unreacted allyl groups in the side chains. Using these partially substituted polycations, we have prepared cross-linked polymer networks composed of these self-immolative poly(benzyl ether)s in combination with 4-arm star polymers with thiol terminal groups. These cross-linked thermoset networks are robust under normal operating conditions but spontaneously erode into soluble molecules upon introduction of a chemical stimulus. Depending on the crosslink density and MW of 4-arm star PEG used to form these gels, one may access a broad range of materials with different mechanical properties, ranging from hard/glassy thermosets to sticky, elastomeric gels. These could be used in technical applications such as “smart” or “triggered release” surface coatings that delaminate from the substrate on demand.

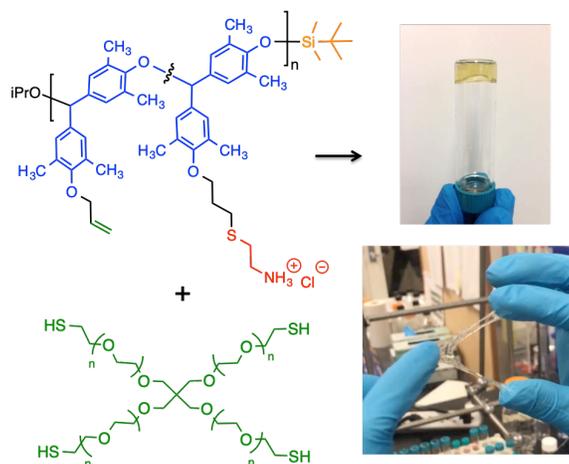


Figure 2. Fabrication of Self-immolative PBE/PEG Gels.

2. Impact of the research

The project was started by a graduate student who graduated with a PhD in Materials Science & Engineering in May 2019. The student is now embarking on her own career as a Process Engineer at Intel. She conducted many of the experiments related to these materials in our group, presented research results at three national conferences organized by the ACS, and has co-authored a total of four peer-reviewed journal articles on her thesis topic, which is related in part to self-immolative polymers. One postdoctoral researcher is currently supported by the PRF grant. He has acquired the necessary skills and knowledge related to polymers synthesis, characterization, processing, and thin film fabrication techniques. The postdoc also interacts with graduate students and undergraduates in the lab, often mentoring them on their projects. These positive interactions help foster a collaborative learning environment and rich interdisciplinary studies. The postdoc joined the group in February 2017 and will be supported by the PRF for two years, including a no-cost extension. This individual will design and execute experiments, present research at conferences, and publish results in peer-reviewed journal articles. His goal is to obtain employment in the chemical industry.

The PI's career has been positively impacted by the support provided by this ACS PRF grant. Results from this research have formed the basis for preliminary data that can be used to apply for external funding from federal agencies, including the ARO and NSF. Since starting his independent career at RPI in 2014, the PI has delivered more than 20 invited lectures at national and local conferences as well as at individual Universities, has published 16 papers in peer-reviewed journals, and received awards and honors including the NSF CAREER Award and the ACS PMSE Young Investigator award. All of these successes were fueled in part by early support from the PRF.