

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.

1.2. Polymer Synthesis. The synthetic scheme (Figure 1) first involves preparation of a quinone methide monomer by means of nucleophilic substitution of a bisphenol compound with one equivalent of allyl bromide, followed by an oxidation step. The final product is purified by recrystallization from cyclohexane. Then, the quinone methide 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, 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.

1.3. Depolymerization. The depolymerization of the allyl-functional polymer, capped with TBDMS, was studied in THF, using tetrabutyl ammonium fluoride (TBAF) as the triggering agent. We followed the chain unzipping process by NMR as well as GPC. It is clear in the GPC chromatograms that the polymers chain revert to small molecules, mainly monomer with some dimeric and trimeric oligomers observed, within 1 hr of exposure to TBAF in THF at room temperature (well above the $T_c \sim 0\text{ }^{\circ}\text{C}$). Conversely, when the polymer is instead end-capped with methyl iodide to yield the inert methyl-capped product, as a negative control experiment, the exposure to TBAF has no discernable effect on the GPC chromatogram. The NMR experiments showed good agreement with the results of GPC. Specifically, we observed a continuous decline in the broad aromatic signals in the spectra around 7 ppm, combined with a continuous increase in the intensity of sharp peaks corresponding to monomer, as a function of time of exposure to TBAF in solution. Also, the inert methyl-capped control polymer showed no change in the

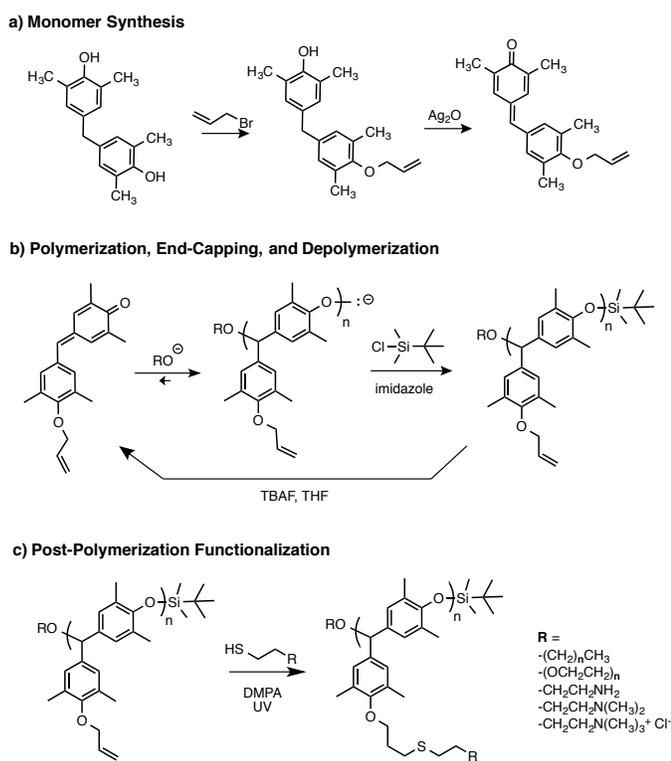


Figure 1. Synthesis of self-immolative poly(benzyl ether)s, triggered depolymerization into small molecules, and post-polymerization side chain functionalization by photoinitiated thiol-ene radical addition.

NMR spectra upon mixing with TBAF. Combined, these observations confirm that the system is self-immolative because the unzipping reaction is sensitive and specific to the designed stimulus (in this case, the F⁻ ion).

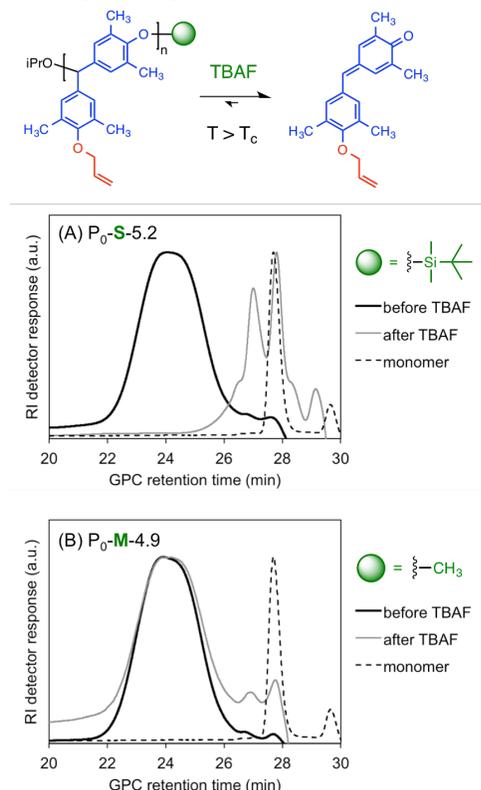


Figure 2. Sensitive and specific depolymerization induced by fluoride ion for polymers with silyl ether end caps, but not for those with methyl ether end caps, demonstrated by GPC data.

chemical stimulus. These could be used in technical applications such as “smart / triggered release” surface coatings that delaminate from the substrate on demand.

2. Impact of the research

The project has been performed primarily by a graduate student who joined RPI’s MSE department in 2014 and is near to graduating this year. She has conducted all 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. She is currently preparing her thesis defense and is on the job market for an industry position related to polymer materials and/or fine chemicals. One postdoctoral researcher is 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 was further assisted by one graduate student and one undergraduate. These positive interactions help foster a collaborative learning environment and rich interdisciplinary studies. The postdoc joined the group in 2017 and will be supported by the PRF for two years. 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 DoD and NSF. Since starting his independent career at RPI in 2014, the PI has delivered more than 10 invited lectures at national and local conferences as well as at individual Universities, has published 9 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.

1.4. Post-Polymerization Functionalization. These self-immolative poly(benzyl ether)s contain pendant allyl groups in the side chains. Whereas allyl groups are often employed as protecting groups for alcohols, we also found that they are competent substrates for thiol-ene click chemistry, which opens the door to functionalize the polymers with a diverse array of petrochemical substituents by employing the grafting-to type approach. Specifically, we selected the photoinitiator DMPA, which produces free radicals in solution upon illumination with a UV lamp. Thiols abstract the free radical and undergo a step-growth radical-addition to the allyl groups in the polymer side chains. NMR confirmed the quantitative conversion of the side chains via disappearance of the allyl signal and replacement with signals corresponding to the expected thiol-ether bond formation. This procedure is done with a diverse array of thiol-containing molecules, such as linear alkyl thiols, poly(ethylene glycol) thiol monomethyl ethers (PEG) of varying chain length, and even cysteamine hydrochloride and N,N-dimethyl cysteamine hydrochloride. The physical consistency and the solubility characteristics of the obtained grafted polymers are substantially altered by the side chain conversion. For example, the polymer with PEG side chains is soluble in all solvents we tested, having a broad range of dielectric constants, including chloroform, THF, toluene, DMF, DMSO and water, whereas the allyl pre-polymer only dissolved in the most non-polar solvents. Furthermore, 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