

1. PRF Grant Number: 58911-DNI7
2. Project Title: Metathesis Polymerizations of Cumulated Bonds
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Narrative Progress Report

Summary of Results: The overarching goal of this project is to establish new protocols for installing cumulated bonds into polymer architectures. Cumulenes (or, more commonly, allenes) exhibit broad chemical reactivity, and they could represent valuable new handles for enabling post-synthetic modifications of polymer architectures. Our initial efforts focused on ring-opening metathesis polymerization (ROMP) of cyclic cumulenes (Figure 1). We selected 1,2-cyclononadiene as our model substrate, given that i) cyclononadiene is easily synthesized and can be stored/isolated at ambient temperature, and ii) the modest ring strain was expected to be sufficient to drive metathesis. The putative monomer was synthesized using the classic two-step Skattebøl pathway in excellent yield (80% overall). With cyclononadiene in hand, we proceeded to investigate ring-opening metathesis polymerizations using a variety of Ru and Mo catalysts (Figure 1). To our surprise, however, we did not observe any polymer product under a variety of reaction temperatures (ambient \rightarrow 70 °C) and times (14 \rightarrow 42 h). We performed a ^1H NMR spectroscopic experiment wherein we added a stoichiometric amount of 1,2-cyclononadiene to Grubbs' 3rd generation catalyst (C6; Figure 1), and we did observe the formation of a new resonance that we believe can be attributed to the formation of a Ru vinylidene. Addition of this new species to cyclononadiene, however, did not result in any polymerization. These data suggest that, although metathesis catalysts can insert into the cumulene, the resultant vinylidene complex is not sufficiently active to promote subsequent insertions.

In order to address this problem, we initially turned our attention to the preparation of a more strained cumulene (Figure 2). Although significantly more reactive than 1,2-cyclononadiene, 1,2-cyclooctadiene does exhibit persistence at cryogenic temperatures (< -35 °C) in the absence of light. We surmised that we could potentially trap the transient allene *in-situ* using ROMP; thus, 1,2-cyclononadiene was synthesized using the two-step Skattebøl route.

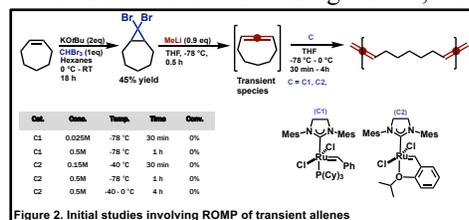


Figure 2. Initial studies involving ROMP of transient allenes

Immediately following the Skattebøl rearrangement, metathesis catalysts were added to the crude reaction mixture at -78 °C or -40 °C (Figure 2). Unfortunately, we did not observe any polymeric product; thus, we modified our procedure by allowing the polymerization reaction to warm from -40 °C \rightarrow 0 °C (which should help with the kinetics of initiation). Unfortunately, we were only able to isolate putative dimers from [2+2] reactions of the 1,2-cyclooctadiene. We are currently exploring other routes that would use ROMP as the key polymerization strategy (e.g. ROMP of a cyclic monomer that contains a strained olefin and an allene).

Given the fidelity with which allenes can be installed into molecular architectures through the Skattebøl pathway, we decided to change our focus and explore post-synthetic incorporation of an allene into a polymer backbone. We selected polynorbornene as our model substrate, given that it is relatively easy to polymerize via ROMP and the cyclopentane core was expected to improve solubility of the final allene-containing material. We initially prepared polynorbornene using Hoveyda-Grubbs catalyst (C2), which afforded polymers with 60% *cis*-olefin incorporation (as determined by ^1H NMR spectroscopy). Subsequent cyclopropanation with dibromocarbene afforded the *gem*-dibromocyclopropane precursor to the final allene in good conversion and yield (up to 96% and 80%, respectively). While subsequent treatment with MeLi promoted the desired Skattebøl rearrangement, we noted that a significant mass of insoluble material formed. Upon closer inspection of the *gem*-dibromocyclopropane precursor, we noted that significant isomerization of the *trans*-cyclopropane products to the vinyl-, allyl-dibromide had occurred (which is a known side reaction). We hypothesized that network formation during the Skattebøl rearrangement could occur with this motif (i.e. through interchain $\text{S}_{\text{N}}2$ attack). To explore this possibility, we prepared a mostly *trans*-polynorbornene and subjected it to cyclopropanation with a dihalocarbene. As expect, we observed significant isomerization to the vinyl-, allyl-dihalide; subsequent ^1H NMR studies revealed that titration with alkyl lithium

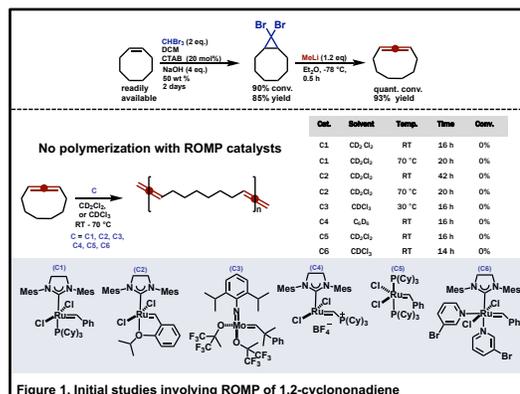


Figure 1. Initial studies involving ROMP of 1,2-cyclononadiene

consumed the vinyl-, allyl-dibromide moiety without forming allene. Instead, the alkyl region became complex, and significant precipitation of polymer material was observed.

Having established the need to limit *trans*-cyclopropanes in our material, we prepared a polynorbornene containing predominantly *cis*-olefins (Figure 3). Subsequent cyclopropanation proceeded smoothly without significant isomerization, and treatment alkyl lithium afforded the desired allene-containing polymer in excellent yield. ¹H and ¹³C NMR spectroscopic characterization was consistent with the desired material, as was IR spectroscopic analysis (Figure 3). To our surprise, we also observed strong fluorescence from the final polymer (even in the solid state). This unexpected phenomenon was attributed to aggregation induced emission, and, indeed, the final polymers were reticent to undergo solvation. In order to ascertain the minimal amount of allene incorporation required to access this unusual photophysical property (but still exhibit solution processability), we prepared materials that had varying degrees of cyclopropanation (16%, 34%, 66%, and 100%). Skatteböl rearrangement of each material afforded the corresponding allene-containing polymer, and we found that each sample retained fluorescence. As the materials became highly insoluble above 34% allene incorporation, we selected this material for further studies. We found that allene incorporation made the materials significantly less brittle (as evidenced by a reduction in Young's modulus and a doubling in the strain at break; Figure 3). We also found that we could photochemically or thermally cross-link the allenes (presumably through [2+2] cycloadditions), which could find applications in self-healing materials. We are currently wrapping up our investigation of the thermomechanical and chemical properties of these materials.

Finally, we have also started investigating other unique materials that can be accessed using allenes (data not shown for space considerations). For example, we are exploring the vinyl-addition polymerization of cyclic allenes. Cyclic olefins are extremely reticent to undergo vinyl-addition polymerization, with norbornene being the predominant monomer in this field. We have found, however, that cyclic allenes polymerize extremely readily under vinyl-addition conditions to produce an array of materials that contain cyclic side chains. As these could have unique tribological and mechanical properties, we expect that these polymers will be of general interest to the community.

Impact: The positive impact this award has had on my student's trajectory (as well as my own) cannot be overstated. The ACS PRF award is a highly prestigious honor that has increased my laboratory's visibility within the broader community. Moreover, the data we have collected during the course of this investigation has led to multiple new research thrusts. We are currently writing three manuscripts detailing work that was supported (either partially or fully) by the donors of the ACS PRF, and we have several new ideas for future directions that build upon our discoveries. The impact on my student who was funded by this award has also been immeasurable. Nick's work during this project has led to several new discoveries that we are currently detailing in scientific monographs that will be submitted for publication in peer-reviewed journals. Having the resources to acquire data early on his scientific career (Nick has just finished his second year of graduate school) has given Nick a distinct advantage in the laboratory, and his early successes will set him apart from his peers when he ultimately pursues the next stage of his career in science. Nick's visibility within the community (which will also help his career prospects) has been impacted by this award in other ways as well. Nick presented his work at the Polymers Gordon Research Conference this summer. Multiple colleagues were impressed by the aplomb with which Nick discussed his research (and the quality of his work). As such, my laboratory would not be on the path to success were it not for this generous award.

There are relatively few examples of synthesizing soft materials that contain cumulated bonds; thus, a broad swath of chemical space has been largely untapped by the polymer science community. The allene motif has emerged as a key linchpin in numerous chemical transformations (e.g. electrophilic additions, oxidative cyclizations, electrocyclizations, etc.). The ability to harness this beautiful chemistry in the context of polymers could unlock new opportunities for creating modifiable polymers that can be synthetically elaborated with exquisite complexity. As the physical properties of materials are inextricably linked to their structures, installing new motifs that can be tailored creates the opportunity to precisely tune polymer function and properties. Our own work is a testament to this possibility; for example, we have shown that installing cumulenes within polynorbornene creates highly fluorescent materials (a phenomenon not observed for the olefin-containing precursor). We are currently investigating the application of these fluorescent materials as chemosensors for a variety of pollutants. We have also shown that installing cumulenes (even at <50% incorporation) dramatically alters the mechanical properties of the bulk material. Thus, we believe that our work will inspire future efforts into the syntheses of novel polymers, and serve as a foundation for designing next-generation, functional materials.

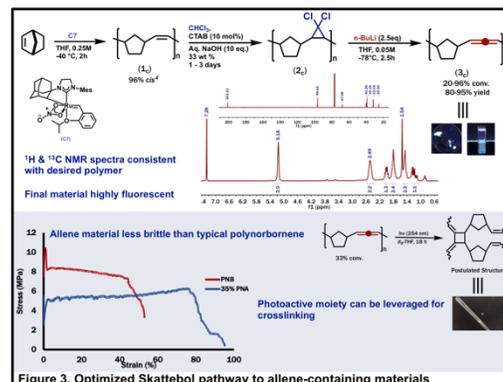


Figure 3. Optimized Skatteböl pathway to allene-containing materials