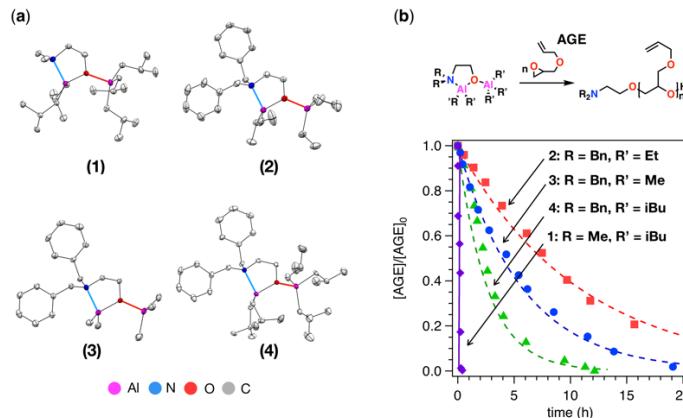


## Research Progress

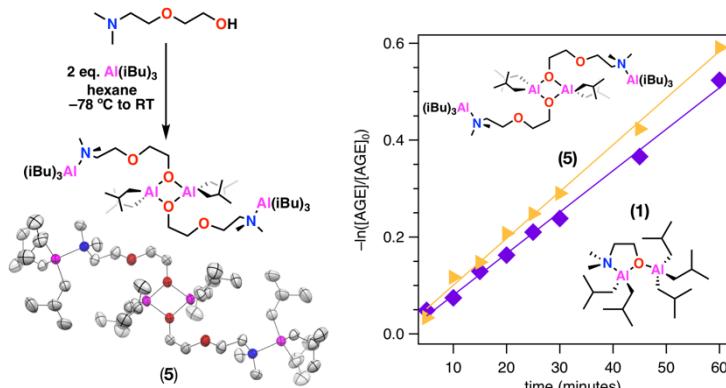
Polyethers represent a promising class of macromolecular materials with applications in elastomers,[1] biomedical materials,[2] solid-state energy storage,[3] and recently electrically conductive amorphous polymers.[4] Among the synthetic methods that are currently available for research and production of polyether materials, catalytic methods currently generate high molecular weight, and isotactic or isotactically-enriched materials, and are limited in terms of substrate scope. Traditional anionic ring-opening polymerization (AROP) offers greater functional group and monomer structure tolerance, but chain-transfer-to-monomer in substituted epoxides limits molecular weight.[5] Typically, molecular weights of less than 10,000 g/mol are reported for functional polyethers derived from substituted epoxides.[4, 6, 7] To connect the desire for new materials development with the array of synthetic tools available, our research effort has focused on creating new concepts in polyether synthesis that improves the functional group tolerance and molecular weight control of AROP using new organoaluminum catalysts and initiators.

In the first year of our Petroleum Research Fund Doctoral New Investigator grant, we studied the mechanism of the Vandenberg catalyzed polymerization of epoxides in order to gain useful insights into organoaluminum catalyzed epoxide polymerization.[8] In doing so, we discovered a new polymerization platform based on mono( $\mu$ -alkoxo)bis(alkylaluminum) species that were both initiator and catalyst in a single unified molecular species. [9, 10] In the final year of support, we reported a new mono( $\mu$ -alkoxo)bis(alkylaluminum) initiator that is shown in comparison with three previously published in **Figure 1**. The structures obtained by X-ray crystallography are shown in Figure 1a, and the consumption of allyl glycidyl ether (AGE) for a targeted 10 kg/mol is compared using compounds **1–4** as initiators in Figure 1b. Significantly, the rate of polymerization of AGE increased by a factor of nearly 400-fold using the new compound **1**. This remarkable enhancement in polymerization rate was obtained by changing the alkyl substitution on the nitrogen atom from dibenzyl to dimethyl. This surprising result suggested that the dialkylamine was present at the site of monomer enchainment at every addition. We attempted to observe the polymerization intermediate in order to gain mechanistic insight to explain the increase in polymerization rate. As shown in **Figure 2**, we isolated a bis( $\mu$ -alkoxo-alkylaluminum) (BOD), and through kinetic comparison with **1**, and spectroscopic observation of the dimerization of **1** in polar solvent (THF) characterized the actual polymerization intermediate as a BOD formed from dimerization of pre-catalyst **1**. Significantly, we proposed that the emergent nitrogen-aluminum adduct was functioning as catalyst, while the aluminum alkoxide acted as the site of



**Figure 1.** We discovered four mono( $\mu$ -alkoxo)bis(alkylaluminum) species (a) and compared their rates of polymerization based on a targeted 10 kg/mol allyl glycidyl ether (AGE) (b). Species **1** produced a 400-fold increase in polymerization rate over 2.

2 eq.  $\text{Al}(i\text{Bu})_3$   
hexane  
–78 °C to RT



**Figure 2.** A bis( $\mu$ -alkoxo-alkylaluminum) (BOD) complex was proposed to be the active polymerization intermediate based on X-ray, kinetic, and spectroscopic evidence supporting the dimerization of **1** into a BOD during the early stages of polymerization. Kinetic comparison between **1** and **5** are shown.

monomer enchainment. As a synthetic tool, the final BOD structure exhibits a rapid rate of polymerization, control of end-group structure, molecular weight, and is tolerant of a broad range of monomer functionality.

### **Impact of Research on my Career**

The PRF DNI support has been instrumental to kick-starting my independent academic career. This was the first grant that was given to my laboratory to pursue new concepts in the polymer chemistry of polyethers. This support led to the discovery of new concepts in polymerization catalysis as originally proposed, and unanticipated discoveries made later have led to promising new directions. Currently, my laboratory has two students who dedicate their thesis research toward furthering the concepts proposed in the original proposal. The rest of my laboratory uses these synthetic concepts to create materials for research. With student expertise in catalysis having been established over the past two years of support, a follow-up effort has identified a new class of catalysts with improved stability. Additionally, I was awarded the 2018 Arthur K. Doolittle Award offered through the PMSE division of the American Chemical Society for a research presentation given on this PRF-funded research.

### **Impact of Research on the Students' Careers**

Both Małgorzata Chwatko and Jennifer Imbrogno worked on this PRF-funded research effort. Both students gained expertise in polymerization catalysis and each was able to present their research at a national ACS meeting both because of the productive science done in the course of the funded research, and also using the travel funds that were supplied as a part of the budget. The students received feedback and encouragement from other workers in the field, and were also introduced to the polymer chemistry community. Both Ms. Chwatko and Imbrogno have passed their qualifying exams, and are progressing toward completion of their Ph.D. in chemical engineering. Ms. Chwatko will graduate in mid-2019, and Ms. Imbrogno will defend her thesis in early 2020.

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