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## Rate Acceleration of Organocatalytic Ring-Opening Polymerization rough the Application of Bis- and Tris- ( io)Urea H- Bond Donors

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As can be seen in the accompanying poster, my honors project involved the rate acceleration of organocatalytic ring-opening polymerization (ROP) through the application of bis- and tris- (thio)urea H-bond donors. My development of these bis- and tris- cocatalysts has given rise to reactions rates up to 100 times greater than those of the catalytic systems involving the monomeric analogue. While a significant result on its own, this increased activity is far more meaningful if the high selectivity associated with H-bond mediated catalysis is retained. My findings indicate that polymerizations involving these new bis- and tris- (thio)urea cocatalysts do in fact retain a high level of selectivity and the characteristics of a 'living' polymerization: low polydispersity, predictable molecular weight, and linear evolution of molecular weight with conversion.

The highlights of this study can be found in be Table 1 and Figure 1 in the poster. Table 1 displays various reaction conditions for the ROP of the cyclic monomers valerolactone and caprolactone, the associated reaction times, and the molecular weights and polydispersity indices (PDI) of the polymer products. Almost all PDIs are <1.1, and the molecular weights are fairly consistent – two results that demonstrate high selectivity. The most telling result from this table can be found by observing the reactions whose reaction times are bolded; the mono-thiourea (labeled 1-S in the poster) cocatalyzed ROP of caprolactone went to almost full conversion in 45 hours, while the bithiourea (2-S) cocatalyzed ROP took only 10 hours, and the trisurea (3-O) only 26 minutes. The first order kinetics plot (Figure 1) depicts this result graphically, with the slope of each line being equal to the reaction rate for those reaction conditions.

As mentioned previously, these polymerizations retain the characteristics of a 'living' polymerization, which is demonstrated in part by Figures 2 and 3. Figure 2 shows the GPC traces of a polymer resulting from the trisurea cocatalyzed ROP of caprolactone, before and after an addition of more monomer. The movement of the GPC trace to the left following the addition of monomer indicates that the polymer chain ends are not terminated, and that even after monomer has been used up, further polymerization is still possible. Thus, the system is 'alive.' Figure 3 simply depicts the linear relationship between conversion and molecular weight of the polymer, another characteristic associated with 'living' polymerizations.

Although these results are significant, it is desirable to understand the mechanism behind this rate enhancement so that further developments can be made to these systems. The proposed mechanisms for both bis- and tris- (thio)urea cocatalyzed ROPs involve the self-activated of the

cocatalysts. In other words, it is believed that one moiety of (thio)urea activates another moiety of (thio)urea, which in turn makes the activated (thio)urea moiety more able to polarize an incoming monomer for ring-opening polymerization. Also seen in the proposed mechanism for just the bithiourea is the possibility that both thiourea moieties are activating the monomer simultaneously.

While the previously disclosed results and explanations comprise the significant technical findings of this study, what is perhaps most important is my personal growth throughout this project. I have become far more confident in my abilities in a lab environment, whether I am performing an experiment, analyzing the results, or especially deciding what to do next. I emphasize the latter since this is often the largest hurdle for young scientists. While I cannot say that I am confident in every situation presented to me, I am far more comfortable making decisions on a regular basis than I was at the start of this project, and that maturation is something I will take with me to graduate school and continue to develop.