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# Bridging the Molecular/Material Divide: An Investigation into the Properties of Polyesters

Terra Marie M. Jouaneh
*University of Rhode Island*, terrajouaneh@gmail.com

While most don't realize it, many of the objects encountered on a daily basis consist of polymers. These polymers may be synthetic, like the plastic in disposable bags and water bottles, or natural, like the starch in cereals or glycogen in the liver. Polymers by definition consist of large molecules composed of small, repeating units called monomers. These monomers give characteristic features to polymers, whether they be the melting points, the folding character, or the inherent stability. It is easy to think that the properties of a single monomer can deduce the properties of a polymer, composed of dozens, if not hundreds or thousands, of monomers. However, it's not that simple. At what length, or degree of polymerization (DP), do polymers start to exhibit material properties rather than molecular properties? Can the initiators used during polymerization affect these material properties? If so, when do the differences in the initiator effects become negligible?

Polymers can be synthesized in a number of ways. In the Kiesewetter Lab, polymers are synthesized through ring-opening polymerizations (ROP) using urea/thiourea and base co-catalyst systems. This method allows for precise control of the polymerization to yield polymers with minimal transesterification and accurate DP. Lactone and lactide polymers are commonly worked with in the lab. These polymers have numerous applications in the medical industry as components of drug delivery agents and in medical devices. Polymers can be characterized through nuclear magnetic resonance (NMR) to determine DP, gel permeation chromatography (GPC) to determine molecular weight, and differential scanning calorimetry (DSC) to determine melting point and stability.

In order to answer the questions posed earlier, I conducted numerous polymerizations of lactones and lactides (L-Lactide, δ-Valerolactone, and ε-Caprolactone) at varying DPs (2, 5, 10, 25, 50, 75, and 100) with two initiators (benzyl alcohol & 1-pyrenebutanol), and subjected the polyesters to three characterization methods: NMR, GPC, and DSC. By comparing the monomer and polymer melting points found in academic literature to the results obtained in this project, I was able to pinpoint the DP where the polymers start to seemingly change their characteristic properties from molecular to material. The data also yielded results about the initiator effects on the melting points of the polyesters.

Throughout the course of my undergraduate education, I have taken a number of courses in chemistry. The BSPS program and the premedical requirements entail chemistry as a core competency of the curriculum. By chance, I also happened to really enjoy taking those courses, whether they be general, organic, biological, or medicinal chemistry. In May 2017, I began working in Dr. Matthew Kiesewetter's lab. Under the guidance of one of the graduate students, Nayanthara Dharmaratne, I learned the basic techniques in ring-opening polymerization of lactones and lactides, as well as the appropriate characterization methods. I used these skills I obtained, as well as a thorough literature review, the helpful graduate students in the lab, Dr. Kiesewetter's guidance, and the URI Chemistry Department facilities to conduct the research required for this two semester project.

Over the course of this project I hoped to achieve three goals. The first of which was to gain a better understanding in applying the scientific method and executing it from start to finish. The requirements of the honors project itself helped me to do so as the process began with posing a question and hypothesis, and concluded in a presentation of the research findings. My second goal was to gain independence and confidence in my research abilities. The previous projects I worked on were in collaboration and under the guide of other graduate students. This was the first project where I took the reigns. My final goal was quite simple: to further my knowledge in organic chemistry. The past two years in the Kiesewetter Lab has been the ultimate learning experience, applying all the material I learned in the classroom to hands-on chemical reactions. Over the course of this past year, I was able to get down to the nitty gritty aspects of polymerization mechanisms, to go back to the basics of organic chemistry that snagged my interest initially nearly four years ago.