# Characterizing Mesophases in Biodegradable Polymers

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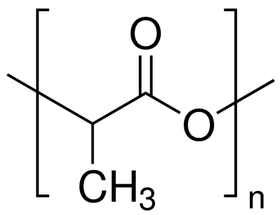
## Background

When designing a polymer-based drug delivery system, it is essential that the correct amount of medication is being released to the body's tissues. This is controlled by the polymer's morphology, where an ordered, crystalline structure would restrict delivery whilst a disordered, amorphous structure would promote it. The mesophase is an intermediate of both structures and has been a point of interest when researching polymer drug delivery systems. The goal of this research is to characterize mesophases as a foundation for future study relating to delivery systems.




**Molecular Formula**
**$(C_3H_4O_2)_n$**
**Glass Transition ≈ 60°C**
**Melting Point ≈ 160°C**

**Figure 1:** Structure and thermal properties of Poly-l-lactic Acid (PLA)

## Materials and Methods

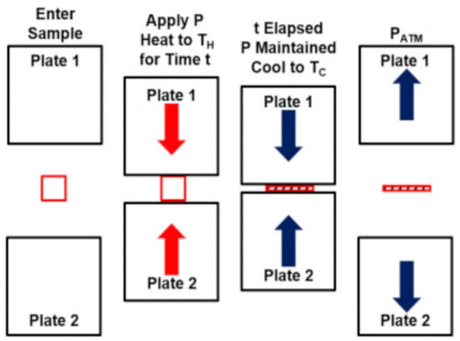



**Figure 2:** Graphical representation of the processing procedure. Samples were placed into press and exposed to pressures (P) ranging from 2,000 to 20,000 lbs. at temperatures (TH) ranging from 52 to 120°C for 5-15 min (t). Once the time has elapsed, samples were cooled to the temperature (TC) and released from the press.

**Polarized Light Microscopy (PLM):** Small pieces cut from samples were placed on an optically transparent quartz dish and heated at a rate of 10°C/min from room temperature until full melt for birefringence optical analysis.

**X-Ray Diffraction (XRD):** To analyze structural evolution during the melt, processed PLA samples were heated to various temperatures ranging from 25°C to 200°C using a modular temperature stage. Samples were maintained at each temperature for 5 minutes.

**Modulated Temperature Differential Scanning Calorimetry (MTDSC):** A step-wise temperature profile was applied in which the temperature was raised 2°C at a rate of 10°C/min, held constant, cooled, and then reheated in a cyclic manner. The heat flow response from this temperature profile was then be split into the corresponding reversing and non-reversing curves.

## Results

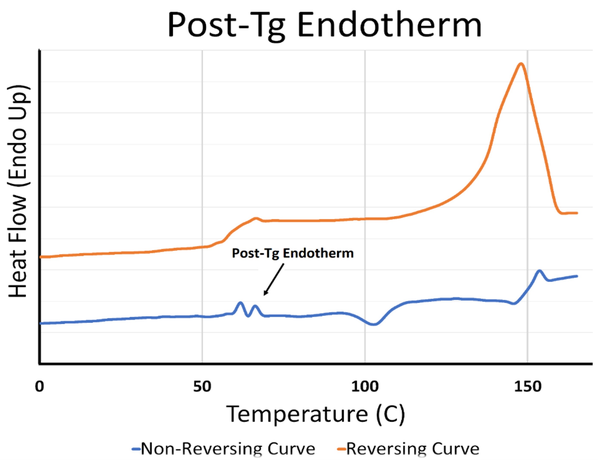



**Figure 3:** MTDSC scan of PLA processed at 63 °C showing a post-TG endotherm during scan.

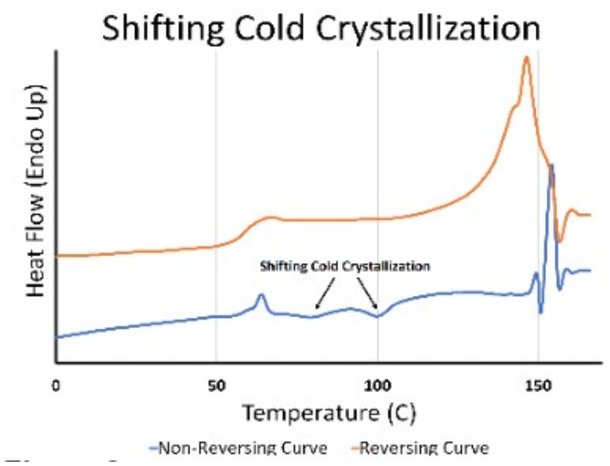



**Figure 4:** MTDSC scan of PLA showing a cold crystallization phase during scan.

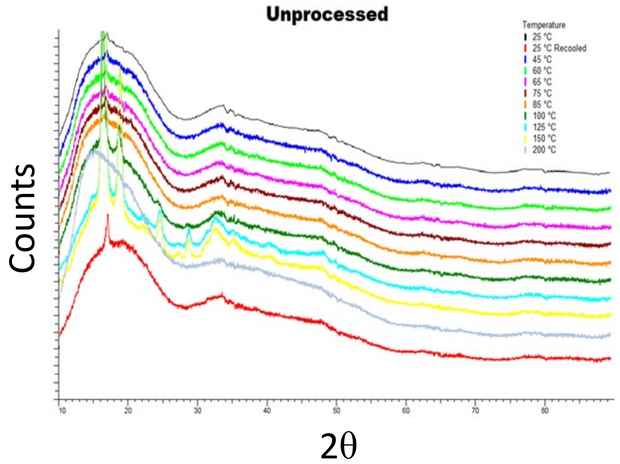



**Figure 5:** Graph of XRD profiling of unprocessed PLA.

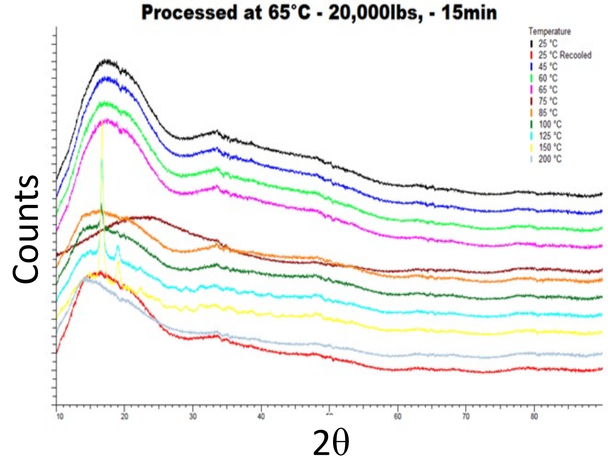



**Figure 6:** Graph of XRD profiling of PLA processed at 65 °C and 20,000 lbs for 15 min.

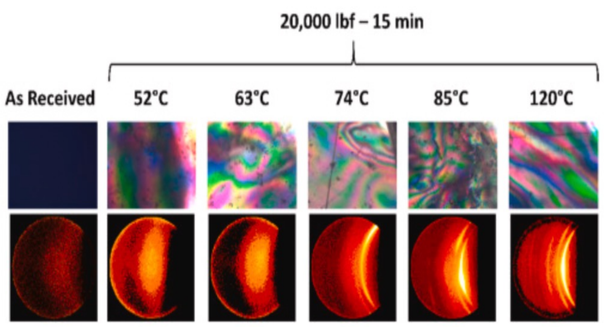



**Figure 7:** Comparison of PLM and XRD images of processed PLA samples

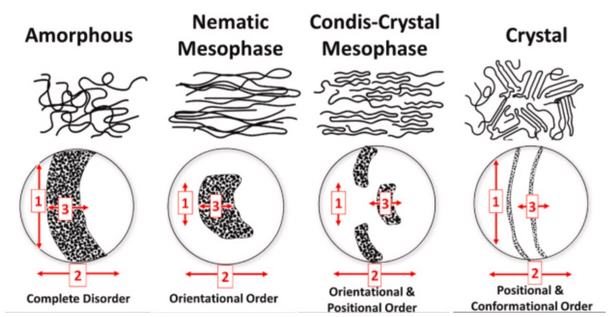



**Figure 8:** Summary of XRD scattering images as they relate to polymer morphology. Provided by Cameron Baptista from the Mathiowitz Lab

## Discussion

Figure 3 shows a post-Tg endotherm in the non-reversing curve of the MTDSC scan that resulted from the processing of PLA at 63 °C. This is caused by an enthalpy loss due to the polymer relaxing as it transitions from glassy to rubbery state, requiring more heat flow.

Figure 4 shows a broad cold crystallization exotherm shifting to lower temperatures in the non-reversing curve of the MTDSC scan. The original crystals within the samples serve as a starting point that can cause crystal growth at lower temperatures.

Figures 5 and 6 show the XRD profiles of unprocessed and processed PLA at increasing temperatures. The unprocessed samples show lots of broadened peaks with several samples having sharper peaks. These broadened peaks show more amorphous morphology, whereas the sharp peaks are crystalline. In the PLA samples processed at 65 °C and 20,000 lbs. for 20 min are shown to have more samples that have broad peaks, with only three samples having sharp peaks. The processed sample heated to 25 °C shows broadened peaks, which is a sign of mesophase formation. The broadening peaks at higher temperatures (above Tg) shows signs of mesophase disappearance.

Figure 7 shows PLM and 2D XRD scattering images of PLA at increasing temperatures. The unprocessed PLA does not show birefringence its in PLM image, while the scattering is broad and a bit faint, showing unprocessed polymer in its amorphous state. All images of processed PLA show birefringence, showing signs of mesophase formation. XRD images at lower temperatures show orientation within the amorphous region, which is a sign of a nematic mesophase. Samples processed at higher temperatures show sharp, staggered rings within the amorphous regions of the image. This shows a morphology more aligned with the condis-crystal mesophase.

## Conclusion

This research uses various analysis techniques to show the characteristics of induced mesophases on Poly-L-Lactic Acid. We were able to gain thermal and structural information about PLA processed under different conditions. We can use this research to determine whether other polymers, like Polyethylene Oxide, are able to have mesophases induced into their morphology, allowing for more potential polymer vehicles to be used for drug delivery purposes.

## References

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