NSF Engineering Research Center for Biorenewable Chemicals

Bio-derived block copolymers: synthesis and characterization

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INTRODUCTION AND MOTIVATION

As a result of the accelerating depletion of our planet's fossil resources, the increasing emission of greenhouse gases and toxic wastes, and the unsustainable utilization of our nonrenewable resources, it is essential for science and industry to seek to implement the principles of green chemistry whenever possible.

Plant oils are already a very important renewable resource for the chemical industry. Due to their inherent double bond functionality, they offer the possibility of being transformed via several catalytic processes. Specifically, new developments in olefin metathesis allow chemists to chemically introduce a variety of functional groups to these renewable resources in a very efficient and environmentally sustainable manner.(1)

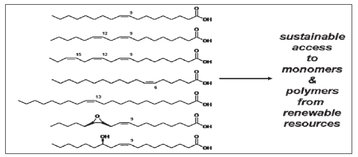

Figure 1: Examples of renewable plant-oil derived chemicals that can be used in polymer chemistry.(1)

Polymers can be divided into two main types: soft and hard. Soft polymers have the advantage of increased flexibility and ability to absorb mechanical stress, but are structurally weaker and thus, not ideal for building materials. Hard polymers are rigid and able to maintain a fixed shape under mechanical stress, but they also have minimal flexibility, limiting their applications.

Therefore, it is often desirable to chemically engineer hybrid block polymers which demonstrate improved flexibility, ductility, and high-impact resistant properties, while also maintaining high mechanical strength and durability.

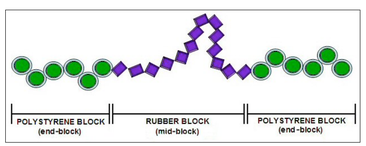

Figure 2: A visual representation of a generic structure for a tri-block coplymer.(2)

As part of this engineering process, poly(lactic acid) (PLA) is an attractive candidate for replacing non-renrewable petrochemical polymers because it is biodegradable and can be produced from annually renewable resources.(3)

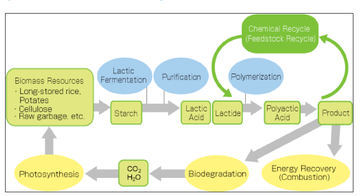

Figure 3: Flowchart depicting the chemical transformation of biomass into PLA polymer end-product.(4)

However, PLA-only polymers have an inherent brittleness and thermal instability that limits their commercial applications.(5) As a result, there is a currently great interest in formulating PLA-based triblock copolymers.

MATERIALS AND METHODS

1. In the current study, polylactide monomer was synthesized using Ring-Opening Polymerization (ROP). Figure 4 illustrates ROP the process.

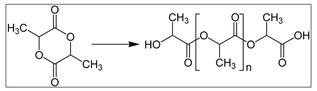

Figure 4: Catalytic and thermolytic ring-opening polymerization of lactide (left) to polylactide (right).(9)

2. Normal monomers with 0-4% end cappers were synthesized with Grubbs catalyst. Resulting end cap monomers contained end regions able to chemically attach and form triblock copolymers. Figure 5 illustrates this process.

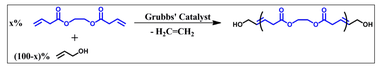

Figure 5: Synthesis of end-cap monomers using a 1st Generation, Grubbs catalyst ® (Molecular formula: $C_{43}H_{72}Cl_2P_2Ru$).

3. Lastly, A-B-A triblock PLA copolymers were synthesized using a tin catalyst (see Figure 6). These triblock copolymers demonstrate hybrid mechanical properties of 2 different monomers.

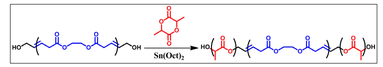

Figure 6: Synthesis of PLA-based triblock copolymers using Tin (II) 2-ethylhexanoate catalyst. (Molecular formula: $C_{16}H_{30}O_4Sn$).

CONCLUSIONS

Evidence of successful conversion of center-block monomers into triblock copolymers was was confirmed by ^{1}H NMR data. DSC data suggests an increase in the glass transition temperature when PLA concentration is increased. This is consistent with literature, suggesting PLA may reinforce the molecular backbone structure of a triblock copolymer, giving it greater rigidity and mechanical strength.

Overall, results suggest that plant oils, such as PLA, may be a valuable renewable resource for the polymer industry and that olefin metathesis can be an ideal tool for environmentally-sustainable production of industrial and commercial polymers.

RESULTS AND CHARACTERIZATION

Differential Scanning Calorimetry (DSC):
Of particular interest in polymer chemistry is the glass transition temperature (T_g) of a material, the temperature at which a polymer transitions from a hard, glass-like state to a rubber-like state(6). Figure 7 graphically illustrates this principle. In the present experiment, T_g was determined using a differential scanning calorimeter (see Figure 8). This instrument is able to thermoanalytically measure the T_g of a polymer. Experimental results are displayed in Figures 9 and 10.

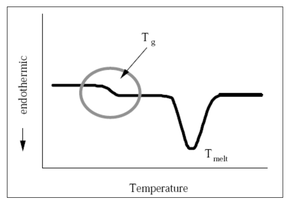

Figure 7: T_g is the exact midpoint of the sloped line highlighted above.

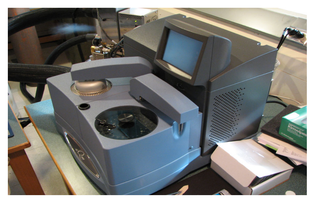

Figure 8: DSC Q2000 (TA Inst.) with modulated temperature control, autosampling robot, and LN2 cooling system.

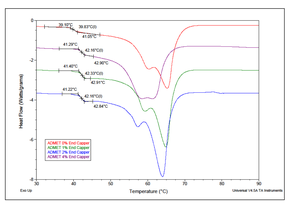

Figure 10: Sample DSC heat transition curve, illustrating approximate T_g values for end cappers.

		Approximate T_g (°C)
Center Block End-Cap Polymers	0% PLA	39.83 °C
	1% PLA	42.16 °C
	2% PLA	42.33 °C
	4% PLA	42.16 °C
Pure PLA Polymer	100% PLA	68.85 °C
Triblock Copolymers	1% PLA	48.90 °C
	2% PLA	49.40 °C

Figure 9: T_g values (°C) for end-cappers, pure PLA polymer, and triblock copolymers. Triblock T_g values suggest a possible increased T_g with increased PLA concentration.

Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR): is a powerful tool used in the determination of the molecular structure of unknown organic compounds. The ^{1}H NMR spectrum of a compound provides chemists with information concerning (1) the number of different types of hydrogens present in the molecule, (2) the relative numbers of the different types of hydrogens, (3) the electron environment of the different types of hydrogens, and (4) the number of hydrogen "neighbors" a hydrogen has.(7)

Figure 11: A 600 MHz NMR Machine located in Hach Hall at Iowa State University.(8)

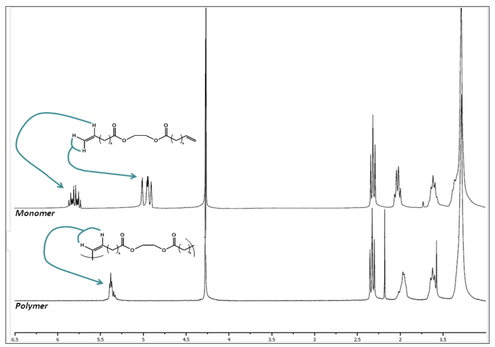

Figure 12: NMR for center block polymer. Of key significance is that none of the unique peaks for the monomer (at ~6.0 – 6.3 and 5.0 – 5.3) were present in the center block polymer, indicating successful synthesis of the center block polymer.

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FOR FURTHER INFORMATION

Please contact Dr. Michael Kessler (mkessler@iastate.edu) or Timothy Mauldin (mauldin@iastate.edu). More information on this and related projects can also be obtained at the Polymer Composites Research Group Website: *http://polycomp.mse.iastate.edu/*.