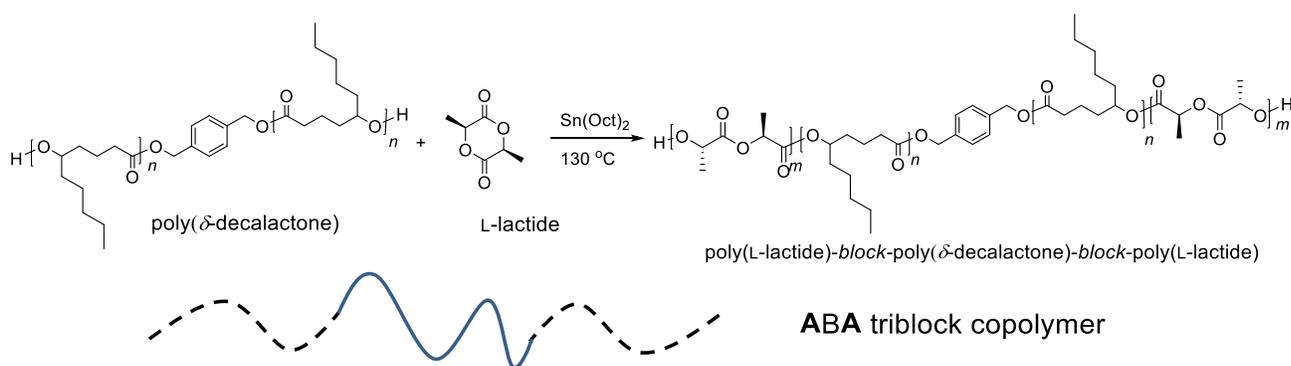


Since the resulting homopolymer is a viscous liquid, a strategy to convert it to a solid thermoplastic type material which can be molded involves addition of a second polymer chain or “block” to add hardening characteristics. An example of a commercial block copolymer comprised of polystyrene and polybutadiene blocks is called Kraton[®], which is used in shoe soles and adhesives. The unique elastomeric properties of many block copolymers such as Kraton[®] is a result of the different contributions of each homopolymer unit to the overall block copolymer structure. In this experiment poly(lactide), PLA, was chosen to add to the terminal alcohol groups of the poly(δ -decalactone) to create a triblock copolymer as illustrated in **Scheme 2**. PLA is derived from plants such as corn and sugarcane and the most prevalent eco-friendly biopolymer on the market today. Poly(L-lactide) has hard, brittle properties and when added to a flexible, soft polymer produces new materials described as thermoplastic elastomers (see **Table 1** for a description of terms). This triblock copolymer, represented by the ABA depiction below, will be isolated and processed by heating (annealed). Its ¹H NMR spectrum will be studied in order to estimate its size and composition and compared to its observable physical and mechanical properties such as opacity, flexibility, tackiness, brittleness, and more.

Scheme 2. Addition of L-lactide to poly(δ -decalactone) end groups



Hazards: Ethyl acetate, methanol, and toluene are flammable. L-Lactide, δ -decalactone, δ -dodecalactone, 1,4-benzenedimethanol, and tin(II) 2-ethylhexanoate are potential irritants. Chloroform-*d* is an inhalation hazard and suspected carcinogen. δ -Decalactone is reported to have an odor threshold detection limit in water of 100 parts per billion and has a persistent aroma. Therefore, it should be handled in a hood with gloves at all times. The product should be handled with gloves in the event that residual δ -decalactone monomer remains. Diphenyl phosphoric acid has no known hazards.

Procedure:

Day 1. Synthesis of δ -decalactone

Place a glass vial with a micro-stirbar in a beaker on a balance. Close all of the doors and tare the balance to zero. Open the door and add precisely 14 ± 1 mg of benzene dimethanol. Close the door to check the mass and record. Clamp the vial in the hood on a stirrer hotplate with cap nearby. Carefully, without spilling, add 1.76 mL of δ -decalactone and cap quickly. When ready to add the catalyst, remove the cap and add 0.058 g of diphenylphosphoric acid (also called diphenyl phosphate). Cap the vial tightly and stir for 30 minutes.

Wrap parafilm around the cap and place the vial in a beaker in your drawer for 7 days. Remember to record all observations before and after the polymerization. Calculate the theoretical molecular weight of the polymer based on quantities of the initiator and monomer used.

Day 2. Addition of L-Lactide end blocks

Record the appearance of the polymer prepared on Day 1.

Prepare a sandbath in a 50 mL heating mantle and place it on a stirrer hotplate resting on a ringstand (note, the hotplate will be used only for stirring, NOT heating). Attach a thermometer to the ringstand and place it in the sandbath. Plug the heating mantle into a variac (be sure not to plug it into a regular outlet) and set the variac to ca. 30-40 to begin heating. When the temperature reaches approximately 92-94 °C (the melting point of L-lactide), dig a well in the sandbath using a metal scoopula large enough for the vial and submerge the vial so that the level of the contents is below the level of the sand. Add 1.7 g of L-lactide through a glass funnel and stir with a metal spatula to mix. An opaque, white gel should form in 1-2 minutes as the L-lactide melts. Immediately add 0.75 ml 0.4 M tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) in toluene and stir. Continue to heat the sand bath until it reaches 130 °C and begin timing the reaction. Monitor the temperature throughout the experiment so the sand does not become too hot (above 140 °C). Either use mechanical stirring or the metal spatula to be sure mixing continues and two layers do not form. Lightly place the cap on the vial and heat at 130-140 °C for 50 minutes. As the new copolymer is formed, the solution may thicken.

When 10 minutes remain, begin to warm 20 mL of ethyl acetate on a hot plate (setting 4). Record the reaction time and remove the vial from the heat. Allow to cool for NO MORE than 1-2 minutes since the polymer will begin to solidify to an opaque solid and will make the next step difficult. Slowly add the warmed ethyl acetate in small portions while stirring vigorously with a glass stir rod to dissolve the solid pieces of polymer. The solution will remain opaque during this process. Use the minimal amount of ethyl acetate necessary. Pipette the dissolved polymer, slowly with stirring, into 40 mL of methanol which has been cooled in an ice bath. The polymer should be a flocculent white powder material. If a solid forms, continue with workup A. If no precipitate forms, go to workup B.

Workup A for solids. Allow the polymer to settle. Setup a gravity filtration apparatus with a large piece of filter paper, a glass funnel, and 125 mL Erlenmeyer flask. Slowly pour the polymer through the filter paper to collect the solid. Note: vacuum filtration is not used at this stage to prevent introduction of any remaining monomer into the house vacuum line. Once the polymer material is collected, transfer carefully to a vacuum apparatus fitted with a Buchner funnel to dry. Break up any chunks with the thin metal spatula and dry for 10 minutes. Continue below.*

Workup B, if solids have not formed. If no precipitate formed, leave in an ice bath for 10 minutes undisturbed. Decant off the methanol and scrape the viscous polymer into the pre-weighed aluminum tin. Continue below.*

*Weigh a small aluminum weigh boat. Transfer the white polymer material to the aluminum boat on a hot plate and heat (setting of 3.5-4.0 and increase if necessary) to remove excess solvent, and melt. Use your wooden or metal test tube holder to handle the aluminum tin (not your fingers). Samples with a large amount of L-lactide incorporation and high yield may be slow to anneal. In these cases, place a second aluminum boat or aluminum foil tent over the top to heat more uniformly and decrease the annealing time required. Record any change in appearance of the polymer during this process. When it appears that all or most of the solvent bubbles have been removed and a uniform polymer is formed, remove from the hotplate and cool to room temperature. Prepare a ^1H NMR sample using 20 mg of sample in CDCl_3 . Place the annealed polymer in a beaker in your drawer for further curing. Determine the mass of the polymer isolated.

Characterization and Mechanical Properties

Remove the polymer from the tin by using a spatula to loosen the sides or by peeling away the aluminum boat. Fully describe the physical characteristics of the copolymer (e.g. odor, color, flexible, stiff, sticky, brittle, opaque, etc.) and/or test the flexibility of each sample by clamping it to a ring stand and using a

paper clip to hang a cork ring. Use a protractor to measure the degree of bending. Use the ^1H NMR spectrum of the product and the appropriate integration values given on the worksheet to determine the ratio of each monomer present and its approximate overall M_n . Each section will compare the % of L-lactide incorporation determined by NMR with the observed flexibility.

Waste Disposal

The polymer filtrate (containing mostly methanol and ethyl acetate) should be disposed of in the **ORGANIC SOLVENT HAZARDOUS WASTE**. The vial and all glassware that come in contact with the polymers should be rinsed immediately with acetone into the **ORGANIC SOLVENT HAZARDOUS WASTE**. The aluminum tins can be placed in the green trash cans.

Table 1: Common Terms Used to Describe Polymers and Copolymers

Symbol	Term	Definition
M_n	number average molar weight (mass)	The total molecular weight of all the chains in the polymer sample divided by the number of polymer chains in the sample
M_w (M_m is now recommended)	weight (mass) average molecular mass	A weighted average that takes into account the weight fraction of each chain. Since heavier chains are given more weight in averaging, $M_w > M_n$ unless the sample is made up of chains that are all exactly the same length
\bar{D} (PDI)	Dispersity (formerly polydispersity)	A measure of the distribution of polymer chains in a sample. $\bar{D} = M_w/M_n \geq 1$, The larger the dispersity the greater the variation in chain length. A uniform polymer has a dispersity close to 1.
T_m	melting temperature	Temperature, upon heating, where the crystalline domains of a semi-crystalline polymer transition from an ordered solid to an amorphous liquid. For a semi-crystalline polymer $T_m > T_g$
T_g	glass transition temperature	Temperature, upon heating, where the amorphous domains of a polymer transition from an amorphous solid to an amorphous liquid and softening is observed
T_c	ceiling temperature	The temperature at which a monomer at a specified concentration will not polymerize. That is the rates of depolymerization and polymerization are equal.
	chain-growth polymerization	A type of polymerization where monomers add to the propagating site of a growing polymer chain one at a time.
	living polymerization	A specific type of chain-growth polymerization in which a polymer chain grows without the ability to terminate. In addition the polymerization must also occur without chain transfer; that is, the propagating species remain on the polymer chain and does not get transferred to monomer or solvent.
	ring-opening polymerization	A specific form of chain growth polymerization where cyclic monomers are opened as they add to propagating polymer. The driving force for ROP is usually, but not always the release of monomer ring strain.
	amorphous regions of a polymer	Regions of a polymer where chains are randomly arranged in space and have weak intermolecular interactions
	crystalline regions of a polymer	Ordered regions of a polymer where strong intermolecular interactions exist (crystallites). Examples of interactions are van der Waals or hydrogen bonding.
	thermoplastic	A class of material that can become pliable or moldable above a specific temperature and returns to a solid upon cooling.
	elastomer	Polymeric material that can be deformed to large strains and recover from this strain (a rubbery material that is stretchy).
TPE	thermoplastic elastomer	Mixture of polymers (copolymer) with both thermoplastic and elastomer properties (elastic materials that can be molded)