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# Sustainable Polymers in the Organic Chemistry Laboratory: Synthesis and Characterization of a Renewable Polymer from $\delta$ -Decalactone and L-Lactide

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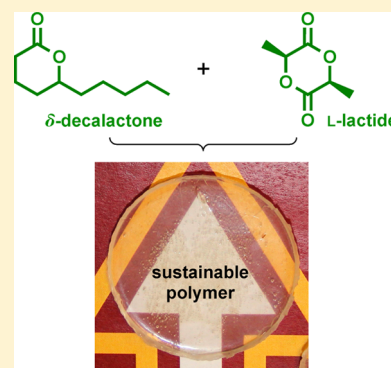
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## S Supporting Information

**ABSTRACT:** The importance of green syntheses and sustainable polymers is highlighted in a new experiment developed for incorporation into the introductory organic chemistry laboratory curriculum.  $\delta$ -Decalactone, a naturally occurring cyclic ester used by the food and flavor industry for its coconut fragrance and taste, is polymerized under acidic conditions with a diol initiator. The solvent-free, room-temperature reaction conditions result in a viscous homopolymer from which the catalyst is easily removed. Subsequent chain extension of this homopolymer with the renewable monomer L-lactide, followed by purification, isolation, and annealing in an aluminum pan, affords a block copolymer product as a transparent, flexible film. Well-resolved resonances in the <sup>1</sup>H NMR spectrum of the individual polymer repeat units facilitate quantitative analysis of polymer composition and molecular weight determination. This experiment introduces students to structures and fundamental concepts of polymer chemistry and exemplifies modern advances in sustainable materials.

**KEYWORDS:** Second-Year Undergraduate, Organic Chemistry, Laboratory Instruction, Polymer Chemistry, Catalysis, Esters, Green Chemistry, Polymerization, NMR Spectroscopy, Material Science



Although plastics are ubiquitous in our daily lives, most students leave college with a limited understanding of what defines a polymer and how the structures of these macromolecules are related to their remarkable physical properties. Polymer chemistry has historically been relegated to the last chapter of introductory organic chemistry textbooks, and polymer experiments are generally not well represented in the curricula of introductory undergraduate chemistry laboratory courses. Barriers to using polymer experiments include the fact that established approaches to syntheses often require stringent reaction conditions and that products are difficult to characterize with standard teaching laboratory instrumentation. Additionally, many of the traditional polymerization experiments, though procedurally simple, require the use of toxic or hazardous reagents and solvents. Classic examples are the nylon rope demonstration<sup>1,2</sup> and synthesis of polystyrene.<sup>3,4</sup>

Efforts to address the lack of polymer experiments for teaching laboratories are demonstrated by the recent increase in appearance of publications on the subject in this *Journal*. These experiments cover a broad range of topics related to polymer science, including the chemical recycling of polymer products,<sup>5,6</sup> the synthesis of conducting polymers,<sup>7,8</sup> self-healing materials,<sup>9</sup> polyurethane foams,<sup>10</sup> biopolymer films,<sup>11</sup> and renewable and degradable polymers.<sup>12–14</sup>

A new polymer experiment was sought for use in a second-year undergraduate organic chemistry laboratory course to complement its current emphasis on green chemistry principles<sup>15</sup> and techniques. Goals were to introduce students to fundamental terms and structure representations of polymers through the synthesis of an environmentally friendly copolymer derived solely from renewable monomers. The targeted polymer material would have properties that students could process, manipulate, or test, and the experiment would incorporate techniques and instrumentation already familiar to students in an introductory organic chemistry laboratory. The latter would help bridge their understanding of small organic molecules with polymer chemistry.

## ■ BACKGROUND

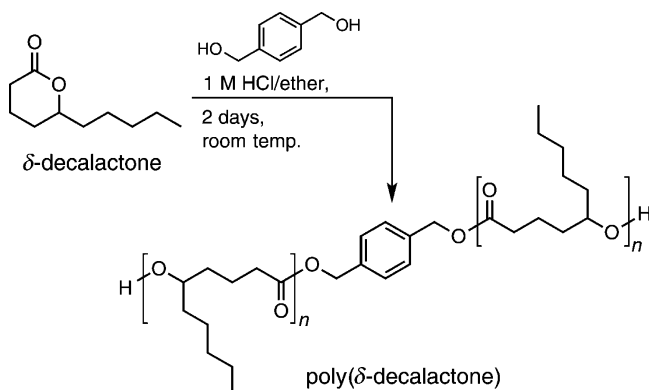
Recently, the ring-opening polymerization of  $\delta$ -decalactone was reported.<sup>16</sup> This cyclic ester is a natural product that can be isolated from the bark of the *Cryptocarya massoia* (Lauraceae) tree.<sup>17</sup> It is used by the food and flavor industry for its creamy coconut peach aroma<sup>18</sup> and is commercially available in racemic form.<sup>19</sup> The controlled ring-opening polymerization of  $\delta$ -decalactone (a renewable monomer) was reported to proceed catalytically at room temperature in the absence of solvent. This

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polymerization already conforms to many green chemistry principles, making it an attractive starting point for a new laboratory experiment. Additionally, the authors demonstrated that the polymerization of  $\delta$ -decalactone was living by chain extension of the homopolymer with D,L-lactide to produce a triblock copolymer. These results suggested potential versatility of this chemistry and the opportunity to illustrate the synthesis and tunable properties of block copolymers. That is, the  $\delta$ -decalactone homopolymer is a viscous liquid, whereas strategic addition of a second polymer block that would add rigidity and produce a solid material would be of greater interest to students.

As described in the Supporting Information, modification of the literature procedure was required to adapt the synthesis to the less stringent environment of the teaching laboratory for a two-day experiment (Schemes 1 and 2). A broad range of

**Scheme 1. Ring-Opening Transesterification Polymerization of  $\delta$ -Decalactone (Day 1)**



catalysts was explored; however, no single catalyst effectively polymerized both reactions. Though tin(II) 2-ethylhexanoate ( $\text{Sn}(\text{Oct})_2$ ), commonly used for the polymerization of lactide, was capable of catalyzing the polymerization of  $\delta$ -decalactone, poor conversion was observed because of poly( $\delta$ -decalactone)'s low ceiling temperature.<sup>20</sup> Ultimately, a two-catalyst sequence was developed that used catalytic hydrochloric acid in diethyl ether for bulk polymerization of  $\delta$ -decalactone, followed by removal of this volatile catalyst, and then bulk chain extension

of the poly( $\delta$ -decalactone) with L-lactide using  $\text{Sn}(\text{Oct})_2$ . In the first step, students are introduced to the concept of an initiator (1,4-benzenedimethanol) and are asked to calculate the expected number-average molecular weight ( $M_n$ )<sup>20</sup> for the poly( $\delta$ -decalactone) as well as the approximate number of repeating units,  $n$ . The diol initiator also provides a handle for students to write the acid-catalyzed transesterification mechanism for the reaction, a reaction previously studied in the organic lecture. During the first day, the polymerization of  $\delta$ -decalactone using an initiator is carried out. During the second day, the triblock copolymer is synthesized and isolated by precipitation and filtration as a white, waxy-looking solid. Upon heating, students observe the process of annealing and the transformation of their product into a clear, thin, flexible film. Analysis of the  $^1\text{H}$  NMR spectrum of the copolymer challenges students to apply their NMR skills to a new type of problem wherein the composition and the overall molecular weight ( $M_n$ ) of the polymer is determined.

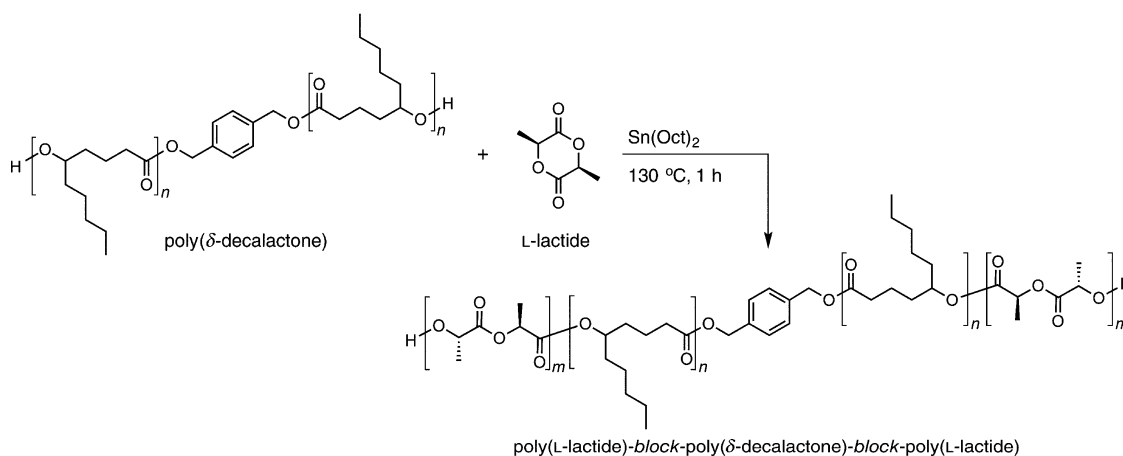
## ■ EXPERIMENTAL SECTION

Two three- or four-hour laboratory periods are required, one for each step, with a minimum of 40 h between the two laboratory sessions. The first laboratory period involves the homopolymerization of  $\delta$ -decalactone (Scheme 1) using a monomer:catalyst:initiator mole ratio of 120:2:1. The reagents are combined in a vial, stirred at room temperature for 30 min, and then sealed and stored in a desk drawer until the next laboratory period. After two days, polymerization is evident by a thick, clear, viscous oil produced.

During the second lab period, the synthesis is continued with formation of the block copolymer (Scheme 2). First, the HCl/ether catalyst is removed from the viscous poly( $\delta$ -decalactone) by blowing air over and around the polymer for approximately 15 min using a plastic syringe barrel. The escape of HCl is monitored periodically by holding a piece of pH paper over the reaction vessel while driving off the vapors. Removal of the acid is necessary to prevent destruction of  $\text{Sn}(\text{Oct})_2$  added in the next step.

L-Lactide and  $\text{Sn}(\text{Oct})_2$  are added (monomer:catalyst mole ratio of 155:1), and the reaction is submerged in a 130 °C oil bath. The viscosity of the polymerization initially decreases upon addition and melting of the L-lactide monomer but later increases as the poly(L-lactide) blocks grow. In many cases, the

**Scheme 2. Addition of L-Lactide End Block to Poly( $\delta$ -decalactone) (Day 2)**





**Figure 1.** (A) Crude block copolymer from filtration. (B) Annealing of the block copolymer on a hot plate. (C) Typical student poly( $\delta$ -decalactone-*L*-lactide) block copolymer (diameter = 4 cm, thickness = 3 mm). The University of Minnesota trademark is used with permission.

polymer solidifies as the reaction proceeds. After 60 min, the heat is removed, the reaction cooled for 5 min, and the polymer dissolved in warm ethyl acetate. The block copolymer is considerably more soluble in chloroform and dichloromethane than ethyl acetate; however, the latter more environmentally benign solvent was chosen to preserve the green integrity of the experiment. The cloudy ethyl acetate solution is slowly poured into a beaker containing methanol to remove unreacted *L*-lactide and  $\delta$ -decalactone monomers from the copolymer. The resulting suspension of a flocculent precipitate is gravity filtered and then dried further by vacuum filtration.

The collected white, wax-like poly(*L*-lactide)-*block*-poly( $\delta$ -decalactone)-*block*-poly(*L*-lactide) copolymer is transferred to a small round aluminum weigh boat (diameter 4 cm) and heated on a hot plate in a hood (Figures 1A and 1B). During the melting process, bubbling is observed as residual solvent is removed and the material spreads to form a film of uniform thickness (3 mm) and clear appearance. For copolymers with a weight percentage of *L*-lactide between 35–45%, 15 min of cooling results in a transparent polymer film that can be carefully peeled away from the aluminum tray (Figure 1C). These films retain a faint coconut odor and are flexible but easily torn, as is illustrated by the missing piece under Goldy Gopher's elbow that was removed for  $^1\text{H}$  NMR analysis. Polymers containing a lower percentage of *L*-lactide take longer to solidify or remain semisolids with sticky or rubbery characteristics. Student  $^1\text{H}$  NMR samples are prepared for analysis by dissolving 30–40 mg of the triblock polymer in  $\text{CDCl}_3$ .

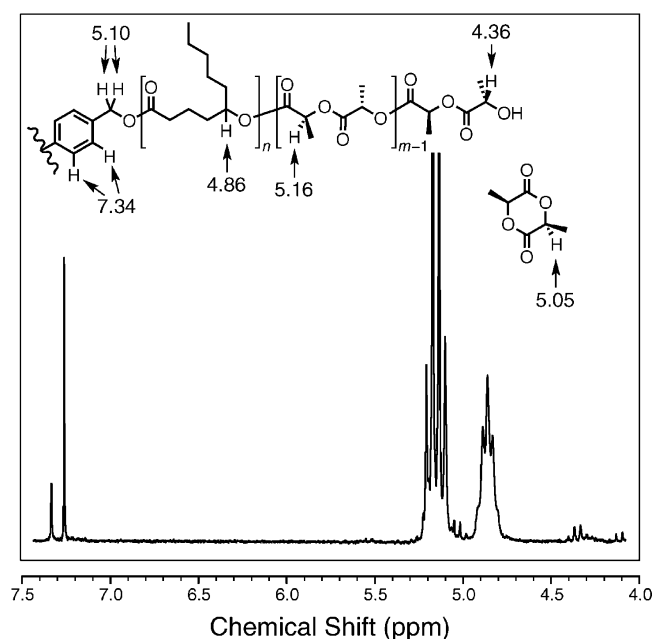
## HAZARDS

Ethyl acetate, methanol, diethyl ether, and toluene are flammable. The ether solution of hydrogen chloride is highly volatile, corrosive, and an irritant. *L*-Lactide,  $\delta$ -decalactone, 1,4-benzenedimethanol, and tin(II) 2-ethylhexanoate are potential irritants. Chloroform-*d* is an inhalation hazard and suspected carcinogen.  $\delta$ -Decalactone is reported to have an odor threshold detection limit in water of 100 parts per billion<sup>21</sup> and has a persistent aroma. Therefore, it should be handled in a hood with gloves at all times. The copolymer product should be handled with gloves in the event that residual  $\delta$ -decalactone monomer remains.

## LABORATORY IMPLEMENTATION

This experiment was successfully performed by over a thousand students working in pairs in a second-year undergraduate organic chemistry laboratory course over three semesters. The first day of the experiment was very short and allowed time for group discussion of polymer calculations and the mechanism. Typical yields of copolymer ranged between 60–80%. The products were analyzed by  $^1\text{H}$  NMR spectroscopy. Student

spectra were expanded from 3.5–7.5 ppm to exclude the large alkyl peaks upfield and amplify the pertinent protons needed for calculations. A typical student spectrum is shown in Figure 2



**Figure 2.** Sample student spectrum (200 MHz  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ) of poly( $\delta$ -decalactone-*L*-lactide) block copolymer showing key protons used for  $M_n$  calculation and % *L*-lactide incorporation.

with the poly( $\delta$ -decalactone) block identifiable by the methine signal at 4.86 ppm and poly(*L*-lactide) methine at 5.16 ppm. Though end groups (4.36 ppm for this sample) are generally used for molecular weight determination of polymers, the automated collection of student spectra introduced phasing and integration problems, and thus, the aromatic initiator peak at 7.34 ppm proved more reliable for calculations. Based on integration values, the calculated  $M_n$  for the sample shown in Figure 1C was 22 kg/mol, whereas the  $M_n$  for this same sample was determined to be 12.5 kg/mol by size exclusion chromatography (SEC) in the research laboratory.<sup>22</sup> Therefore, use of the initiator aromatic hydrogens tended to overestimate  $M_n$ . Nevertheless, the NMR analysis proved instructive and valuable for students in understanding the size and composition of the polymer they prepared, especially relating the calculated weight percent of *L*-lactide to the physical properties of their sample. The Supporting Information contains more details on this topic.



## ■ POSSIBLE VARIATIONS

This experiment has many potential variations. For example, the infrared spectra (IR) and  $^{13}\text{C}$  NMR spectra of the triblock copolymer also have separate and distinguishable peaks for each polymer unit and either tool could be used in place of the described  $^1\text{H}$  NMR analysis (see Supporting Information for more details). The experiment could be adapted for an advanced polymer laboratory class using size exclusion chromatography (SEC) or differential scanning calorimetry (DSC) for characterization of the homopolymers and block copolymer prepared. Because the stiffness and strength of the film depends on both molecular weight and composition of the polymer, the procedure has the potential to be adapted as an inquiry-based project.

Though degradation studies of this particular block copolymer have not yet been performed, a degradation study of similar lactide-based block copolymers<sup>23</sup> suggests that the product will be hydrolytically degradable. Discussion of modern compostable polymers, such as polylactide (PLA), is a natural extension of the experiment.

## ■ SUMMARY

A new experiment that introduced students to the structures and fundamental concepts of polymer chemistry through the synthesis of a representative sustainable polymer was developed. Two renewable resource monomers were used and the two-step reaction sequence exemplified green chemistry principles through solvent-free conditions, catalysis, and mild conditions. Unique to this experiment was the opportunity for students to observe how two polymers that alone vary greatly in physical properties—one a viscous liquid and the other a hard, brittle plastic—react to form a flexible and moldable block copolymer. Students responded favorably to learning about current sustainable polymer syntheses and many expressed enjoyment in isolating a high molecular weight rubbery material as a change from the usual small molecule organic liquids and solids found in the introductory organic laboratory.

Based on teaching assistant feedback and student performance on the polymer worksheet that accompanied the student handout, it was concluded that the second-year organic chemistry laboratory students successfully learned how to calculate the theoretical molecular weight of their polymer and relate these values to the synthesized polymer structure. Though a fifth of the students surveyed commented that the  $^1\text{H}$  NMR spectral interpretations were challenging, the majority expressed confidence in using integration values to estimate molecular weight and composition of their polymer. Overall, the experiment proved to be amenable to the introductory organic chemistry laboratory and successful in introducing polymers in an accessible and environmentally conscientious way.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental handout for students; student worksheet and grading key; instructor information including definitions of polymer terms;  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra; SEC and DSC data. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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