

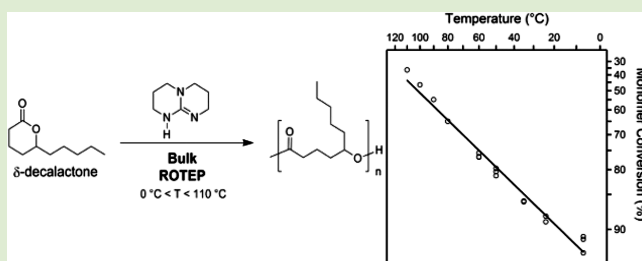
# Bulk Ring-Opening Transesterification Polymerization of the Renewable $\delta$ -Decalactone Using an Organocatalyst

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## Supporting Information

**ABSTRACT:** The bulk ring-opening polymerization of renewable  $\delta$ -decalactone using 1,5,7-triazabicyclo[4.4.0]dec-5-ene was carried out at temperatures between 7 and 110 °C. The equilibrium monomer concentration for reactions within this temperature range was used to determine the polymerization thermodynamic parameters ( $\Delta H_p = -17.1 \pm 0.6$  kJ mol<sup>-1</sup>,  $\Delta S_p = -54 \pm 2$  J mol<sup>-1</sup> K<sup>-1</sup>) for  $\delta$ -decalactone. The polymerization kinetics were established and high molar mass poly( $\delta$ -decalactone) was prepared with a glass transition temperature of -51 °C. Poly( $\delta$ -decalactone) samples with controlled molar mass and narrow molar mass distributions were realized by controlling the monomer conversion and initiator concentration. A high molar mass poly(lactide)-poly( $\delta$ -decalactone)-poly(lactide) triblock copolymer with a low polydispersity index was prepared by simple sequential addition of monomers. The product triblock exhibited two distinct glass transitions temperatures consistent with microphase segregation.



Polymerization of renewably derived monomers with moderate energy input, solvent-free conditions, innocuous reagents, and high molar mass in a controlled fashion is an important research endeavor given the global emphasis on sustainable materials development. The bulk, atom-economic, ring-opening transesterification polymerization (ROTEP) of cyclic esters using metal-free organocatalysts to give hydrolytically degradable polyesters fits nicely into this paradigm with many examples evident.<sup>1</sup> The importance of developing controlled polymerization strategies is realized in the preparation of block polymers, hybrid materials that combine disparate properties of two polymers into one macromolecule.<sup>2</sup> A recent example we reported was the preparation and evaluation of poly(lactide)-poly(menthane)-poly(lactide) triblock copolymers as thermoplastic elastomers and pressure-sensitive adhesives;<sup>3</sup> many other examples can be found in the literature.<sup>4</sup>

A key consideration in ring-opening polymerization is the ring-strain in monomer candidates. While six-membered rings are typically quite stable toward ring-opening, the simple  $\delta$ -valerolactone has appreciable ring-strain due in part to the presence of an  $sp^2$  hybridized carbon atom in the ring structure.<sup>5</sup> Because polymerizations are typically exothermic, the temperature dependence of this equilibrium leads to a preference for polymer formation at low temperatures.<sup>6</sup> While lower temperatures favor the polymer, polymerization rates are slower and thus highly active catalysts are required to achieve high conversions in practical reaction times. Finally, the equilibrium monomer concentration is a constant for a given temperature, so starting with as high a concentration of monomer as possible (i.e., neat monomer) is desirable for

higher monomer conversions in addition to other practical concerns.<sup>7</sup>

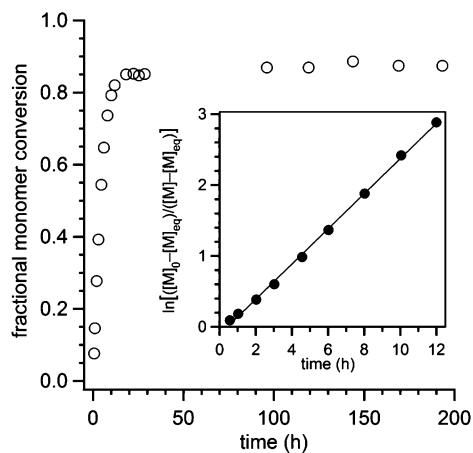
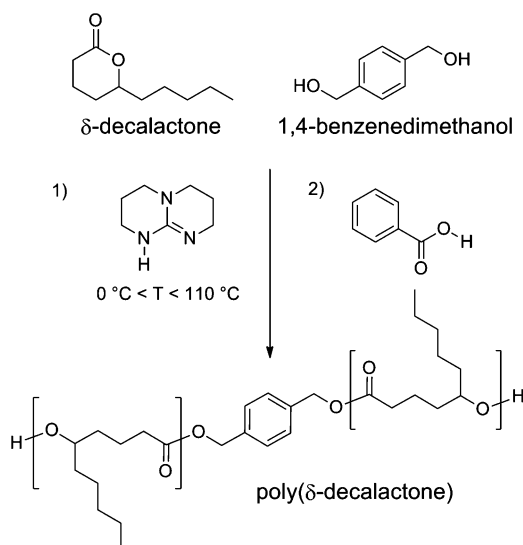
With the above considerations in mind and motivated by expanding the pallet of renewable monomers, we explored the organocatalytic ROTEP of  $\delta$ -decalactone, a racemic alkyl substituted valerolactone, at low temperature in the bulk.  $\delta$ -Decalactone, among various C8–C12 natural aliphatic  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -lactones, is used in the flavor and fragrance industry and is available on a large scale.<sup>8</sup>  $\delta$ -Decalactone is a natural product of *Cryptocarya massoy* (the flowering plant *Lauraceae*).<sup>9</sup> However, large quantities are produced by enzymatic hydroxylation, lactonization, and hydrogenation of fatty acids and essential oils.<sup>10</sup> Based on previous experience and reports, we expected the resultant aliphatic polyester to be noncrystalline material with a low-glass transition temperature and thus desirable as a midblock in technologically relevant polyester triblock copolymers.<sup>3,11,12</sup> Targeting high rates at low temperature, we chose to explore one of the most active organocatalysts developed to date, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).<sup>13,14</sup> The overall reaction, including the difunctional initiator 1,4-benzenedimethanol (BDM) and the catalyst quencher benzoic acid, is depicted in Scheme 1.

The addition of TBD to neat  $\delta$ -decalactone in the presence of 1,4-benzenedimethanol at room temperature leads to rapid conversion to the corresponding polymer, as shown in Figure 1 (see Supporting Information for all experimental details). The

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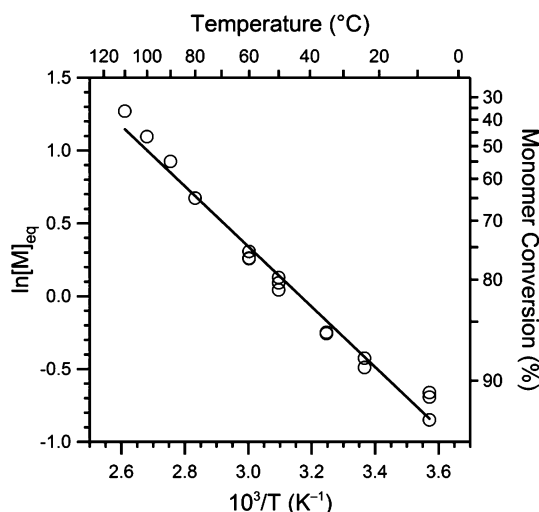
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**Scheme 1. Ring-Opening Polymerization of  $\delta$ -Decalactone with TBD Followed by Benzoic Acid Quench**


**Figure 1.** Fractional  $\delta$ -decalactone conversion as a function of time at room temperature. As shown in the inset, using an equilibrium monomer concentration  $[M]_{\text{eq}} = 0.74$  M, the apparent first order rate constant  $k_{\text{app}} = 0.249 \pm 0.003$  h $^{-1}$ . In this particular example,  $[\delta\text{-decalactone}]_0 = 5.60$  M,  $[\text{TBD}]_0 = 29$  mM, and  $[\text{1,4-benzenedimethanol}]_0 = 95$  mM.

conversion of  $\delta$ -decalactone is approximately 80% in about 10 h and then reaches a plateau at 88%, consistent with this being the equilibrium value at room temperature. Addition of more monomer to a room temperature polymerization after 18 days leads to further reaction and reestablishment of the same limiting conversion demonstrating that the catalyst is still active and that the maximum conversion is dictated by polymerization thermodynamics and not catalyst deactivation.<sup>15</sup> After quenching with benzoic acid and precipitation, the products of similar reactions are polymeric by size-exclusion chromatography and give  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra that are consistent with poly( $\delta$ -decalactone) containing secondary alcohol end groups as in Scheme 1.

We carried out similar polymerization reactions at temperatures ranging from 7–110  $^{\circ}\text{C}$  at fixed TBD and BDM concentrations. All of the polymerizations reached equilibrium conversions and the equilibrium monomer concentrations are plotted as a function of inverse absolute temperature in Figure



**Figure 2.** Polymerization thermodynamics for  $\delta$ -decalactone. All of the reactions were carried out with the following conditions  $[\delta\text{-decalactone}]_0 = 5.60$  M,  $[\text{TBD}]_0 = 30 \pm 3$  mM, and  $[\text{1,4-benzenedimethanol}]_0 = 56 \pm 3$  mM. The  $[M]_{\text{eq}}$  was calculated based monomer conversion, determined by  $^1\text{H}$  NMR spectroscopy, and the room temperature monomer and polymer densities of 0.95 and 0.97 g cm $^{-3}$ , respectively.

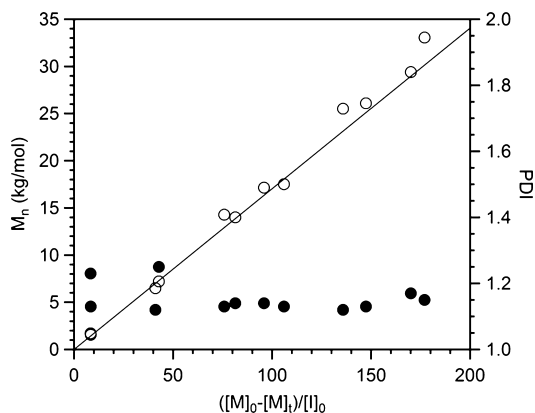
2. As a check of catalyst stability at high temperature, we added more monomer to a reaction that had been carried out at 100  $^{\circ}\text{C}$  for 3 h and again achieved further conversion of monomer to the equilibrium value with an expected rate considering the lower concentration of TBD in the diluted reaction. Thus, we have established that TBD is an effective catalyst for the bulk polymerization of  $\delta$ -decalactone at 100  $^{\circ}\text{C}$  and does not suffer from significant deactivation under these conditions.<sup>16,17</sup>

From the data in Figure 2, we determined  $\Delta H_p = -17.1 \pm 0.6$  kJ mol $^{-1}$  and  $\Delta S_p = -54 \pm 2$  J mol $^{-1}$  K $^{-1}$ . Interestingly, the exothermicity for the bulk polymerization of  $\delta$ -decalactone is 2-fold greater than  $\delta$ -valerolactone<sup>18</sup> and 25% larger than both  $\delta$ -caprolactone<sup>18</sup> (methyl-substituted valerolactone) and 1,4-dioxan-2-one.<sup>19</sup> The entropy of polymerization for  $\delta$ -decalactone is unfavorable, as expected, and follows the trend for the valerolactones reported by Save et al.:  $\Delta S_p = -15$  J mol $^{-1}$  K $^{-1}$  for  $\delta$ -valerolactone and  $\Delta S_p = -41$  J mol $^{-1}$  K $^{-1}$  for  $\delta$ -caprolactone.<sup>18</sup> The difference in  $\Delta S_p$  between  $\delta$ -caprolactone and  $\delta$ -decalactone (13 J mol $^{-1}$  K $^{-1}$ ) is smaller than that between  $\delta$ -valerolactone and  $\delta$ -caprolactone (26 J mol $^{-1}$  K $^{-1}$ ). We have observed this same trend in polymerization entropies previously with a doubly substituted seven-membered-ring lactone (i.e., menthide) compared to  $\epsilon$ -caprolactone.<sup>20</sup> Practically, at 110  $^{\circ}\text{C}$  the limiting conversion for the bulk polymerization of  $\delta$ -decalactone is about 35%, and at 7  $^{\circ}\text{C}$  over 90% conversion can be achieved.

The linear plot in the inset of Figure 1 is consistent with pseudo-first-order kinetics for reversible ROTEP of  $\delta$ -decalactone.<sup>21</sup> An apparent room temperature first-order rate constant  $k_{\text{app}} = 0.249 \pm 0.003$  h $^{-1}$  was determined using 0.42 wt % TBD. Thus, under these conditions, the time to reach 97% of the equilibrium conversion (i.e.,  $\sim 5$  half-lives or  $5 \times t_{1/2} = 5 \times \ln 2/k_{\text{app}} = 5 \times 2.8$  h) is approximately 14 h. We also analyzed the polymerization kinetics at 60  $^{\circ}\text{C}$  under identical conditions and determined  $k_{\text{app}} = 0.496 \pm 0.006$  h $^{-1}$  and, thus,  $t_{1/2} = 1.4$  h. These two pieces of data give an apparent activation energy for  $k_{\text{app}}$  of 17.3 kJ mol $^{-1}$ . In addition to heating the reaction, our

preliminary work suggests that the rate of the reaction can also be increased by increasing the catalyst loading.

With the polymerization thermodynamics and kinetics established, we turned our attention to control of molar mass and evaluation of the polydispersity indices for the product poly( $\delta$ -decalactone). In Figure 3, the  $M_n$  values for poly( $\delta$ -



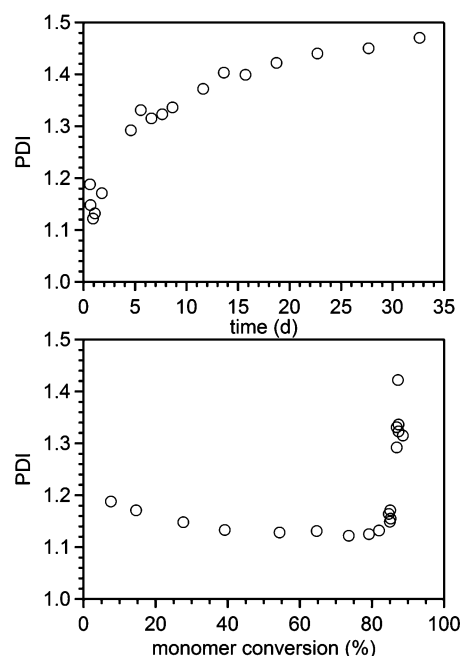
**Figure 3.** Molar mass control of poly( $\delta$ -decalactone). The reactions were carried out at room temperature with  $[\delta\text{-decalactone}]_0 = 5.60$  M and  $[\text{TBD}]_0 = 16 \pm 2$  mM. The molar mass ( $\circ$ ) and PDI ( $\bullet$ ) were determined by  $^1\text{H}$  NMR spectroscopy and SEC, respectively.

decalactone), as determined by  $^1\text{H}$  NMR spectroscopy (assuming exactly two end groups per chain), are plotted as a function of the ratio of converted monomer ( $[M]_0 - [M]_t$ ) to initial concentration of the initiating species BDM ( $[I]_0$ ) from polymerizations performed at room temperature. The  $M_n$  was calculated based on the methylene protons from the initiator, assuming both alcohol groups initiated polymerization; the integration ratio of the methine protons at the hydroxyl termini to the initiator protons was approximately 2:1 and, thus, consistent with this assumption. The  $M_n$  determined by  $^1\text{H}$  NMR spectroscopy correlated well with the  $M_n$  values determined by SEC based on polystyrene standards (see Table S1). Polymerizations were quenched prior to reaching equilibrium (70–80% monomer conversion) in an effort to achieve narrow molecular weight distributions. The linear relationship is evidence for a controlled polymerization process. Furthermore, by size exclusion chromatography, the molar mass distributions were all monomodal, and the polydispersity indices for the polymer products were all below 1.25 (Figure 3). In an effort to achieve high molar mass samples, we performed a room temperature polymerization with  $[\delta\text{-decalactone}]_0/[\text{BDM}]_0 = 638$  and  $[\delta\text{-decalactone}]_0/[\text{TBD}]_0 = 211$  and achieved an  $M_n$  for the poly( $\delta$ -decalactone) product by  $^1\text{H}$  NMR spectroscopy of  $83$  kg mol $^{-1}$ . By size exclusion chromatography, the  $M_n$  for this sample relative to poly(styrene) standards was determined to be  $80$  kg mol $^{-1}$  with  $M_w = 100$  kg mol $^{-1}$  (PDI = 1.25). We conclude that achieving high molar mass poly( $\delta$ -decalactone) from this bulk polymerization is feasible.

Given the equilibrium nature of this polymerization, we can expect the polydispersity index of the poly( $\delta$ -decalactone) samples to increase with polymerization time at fixed conversion of monomer due to the polymerization/depolymerization equilibrium.<sup>22</sup> To investigate this, we followed a room temperature polymerization of  $\delta$ -decalactone over 32 days, periodically removed (and quenched) aliquots, and analyzed

the poly( $\delta$ -decalactone) products by size exclusion chromatography. In a separate experiment, we determined that addition of a chloroform solution of benzoic acid (30-fold excess relative TBD) to the polymerization is an effective method to quench the polymerization as no further polymerization was observed.

Shown in Figure 4, the observed PDI initially decreases, reaches a minimum near PDI = 1.1, and then increases as the



**Figure 4.** Change in the polydispersity index for a room temperature reaction vs reaction time (top) and monomer conversion (bottom). In this reaction,  $[\delta\text{-decalactone}]_0 = 5.60$  M,  $[\text{TBD}]_0 = 29$  mM, and  $[1,4\text{-benzenedimethanol}]_0 = 95$  mM.

equilibrium conversion is approached. In terms of the reaction time, the minimum PDI (1.12) was observed after 8 h (74% conversion) and then broadens to 1.16 after 24 h (85% conversion). The possible reactions responsible for broadening of the molecular weight distribution (MWD) are (i) intermolecular chain-transfer, where the active chain-end of one polymer chain undergoes transesterification with a backbone ester of another chain redistributing the number of repeat units between the two resultant chains, and (ii) polymerization/depolymerization, where one repeat unit at a time is redistributed between chains in an equilibrium process. To investigate the contribution of these two mechanisms on the MWD evolution for our system we employed a computational method for determining the relative rate constants of depolymerization ( $k_d$ ) and intermolecular chain transfer ( $k_{tr}$ ) compared to the rate of polymerization ( $k_p$ ), as reported by Szymanski and co-workers.<sup>22,23</sup>

When the Szymanski method is used, a theoretical MWD can be simulated based on  $[M]_0/[I]_0$ ,  $k_{tr}/k_p$ , and  $k_d/k_p$ . The dependences of the PDI values on monomer conversion for each simulation were compared to the experimental data (see Supporting Information). The predicted PDI versus monomer conversion profile using the experimental monomer-to-initiator ratio  $[M]_0/[I]_0 = 5.6$  M/9.5 mM = 58.9 is in good agreement with the experimental results using  $k_{tr}/k_p = 5 \times 10^{-4}$  and  $k_d/k_p = 0.71$  (see Figure S3). Based on this, we conclude that the rate constant for intermolecular chain transfer is much smaller than

that for polymerization. Simulation results revealed that at 60 and 80% conversion only 2.5 and 8% of polymer chains had undergone intermolecular chain-transfer, respectively. As a result, polymers with a narrow MWD can be obtained from these bulk reactions to within about 5% of the equilibrium conversion. We note that extended reaction times and equilibration of chain lengths can be used to prepare materials with controlled molecular weight distributions.<sup>24</sup> The apparent low levels of chain transfer through transesterification facilitates the formation of block copolymers with high block fidelity, as we have demonstrated previously.<sup>3,11</sup>

The high molar mass sample of poly( $\delta$ -decalactone) described above was purified by precipitation and analyzed by differential scanning calorimetry (DSC). We observed a glass transition temperature at  $-51$  °C and no evidence of melting up to  $200$  °C. We determined a room temperature density of poly( $\delta$ -decalactone) of  $0.97$  g cm<sup>-3</sup> using a density gradient column. To demonstrate the utility of this new polymerization for the preparation of block copolymers, we simply added a solution of D,L-lactide (35 wt %) in methylene chloride to a TBD-catalyzed room temperature polymerization of  $\delta$ -decalactone after reaching equilibrium conversion ( $\sim 90\%$ ). The  $M_n$  and PDI determined by SEC prior to lactide addition were  $84$  kg mol<sup>-1</sup> and  $1.27$ , respectively. After  $1$  h, the lactide polymerization was quenched with excess benzoic acid. The conversion of  $\delta$ -decalactone did not change after the addition of lactide, however, 98% of the lactide had reacted. Prior to purification, SEC analysis showed an increase in  $M_n$  and PDI to  $100$  kg mol<sup>-1</sup> and  $1.4$ , respectively. Although the reaction was diluted upon the addition of lactide, the potential depolymerization of  $\delta$ -decalactone was not observed, indicating lactide effectively end-capped the poly( $\delta$ -decalactone) chain. Furthermore, the unreacted  $\delta$ -decalactone monomer did not participate in the lactide polymerization reaction consistent with clean formation of the triblock architecture.

Size exclusion chromatography analysis of the poly( $\delta$ -decalactone) prior to the addition of lactide and the reaction product after quenching was consistent with the formation of a triblock copolymer (see Supporting Information). Isolated and purified triblock was analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and DSC. The <sup>1</sup>H NMR spectrum is consistent with two lactide end groups per chain and block molecular weights of  $90$  and  $20$  kg mol<sup>-1</sup> for poly( $\delta$ -decalactone) and poly(lactide), respectively. Analysis of the polymer products by <sup>13</sup>C NMR spectroscopy did not show additional signals compared to the respective homopolymers, further supporting the triblock architecture and the absence of significant transesterification between the two blocks (i.e., the lactide propagating species does not "bite into" the previously formed poly( $\delta$ -decalactone) midblock). By DSC, the copolymer showed two glass transitions at  $-51$  and  $54$  °C, corresponding to domains of poly( $\delta$ -decalactone) and PLA, respectively. Taken together, these data support the formation of a microphase separated poly(lactide)-poly( $\delta$ -decalactone)-poly(lactide) triblock copolymer.

In summary, we have demonstrated the controlled ROTEP of  $\delta$ -decalactone, a monomer biologically produced from bio-oils that is available in large scale, in the absence of solvents, at moderate temperatures using a commercially available organocatalyst. We established kinetic and thermodynamic parameters for this polymerization and demonstrated control of the molar mass and polydispersity index of the product polymers. By sequential addition of monomers, we prepared poly(lactide)-

poly( $\delta$ -decalactone)-poly(lactide) triblock copolymers that were apparently microphase separated by DSC analysis. The low glass transition temperature of poly( $\delta$ -decalactone) makes it an attractive component for renewable triblock polymers with potential broad-based utility. We are actively exploring the self-assembly and mechanical properties of block copolymers that incorporate poly( $\delta$ -decalactone).

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details and detailed characterization data. This material is available free of charge 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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