

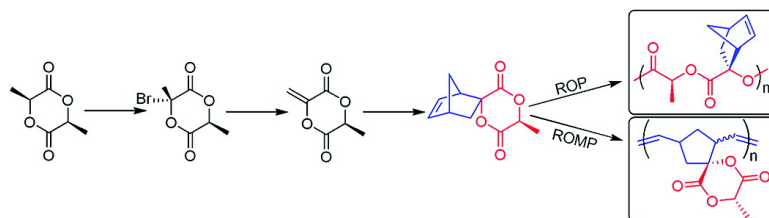
Communication

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A Bifunctional Monomer Derived from Lactide for Toughening Poly lactide

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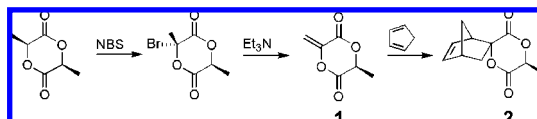
Poly lactide (PLA) is a biorenewable, biocompatible, and biodegradable polyester derived from the cyclic ester lactide. While the properties of PLA are attractive for many applications,¹ there has been much effort on rendering its properties to be more competitive with those of traditional, petroleum-based polymers. Among those approaches, the preparation and polymerization of lactide derivatives have been explored to enhance thermal, barrier, and mechanical properties in these related polyesters. For example, functionalized lactides have been prepared, in general, from the corresponding α -hydroxyacids and subsequently polymerized with varying degrees of success.^{2,3} Given that lactide is a well-established renewable monomer, we explored its derivatization to give new monomers that could be utilized to improve the properties of the PLA. In this communication, we report the synthesis and polymerization of a bifunctional cyclic ester derived from lactide. We utilize the resultant polymers to enhance the toughness of PLA through a reactive grafting approach to create novel polymeric alloys of PLA that exhibit much improved toughness compared to PLA homopolymer.

Modification of lactide without concomitant ring opening is rare.⁴ In 1969, Scheibelhoffer et al. demonstrated that 3-methylene-6-methyl-1,4-dioxane-2,5-dione could be prepared from lactide using a bromination/elimination approach.^{4a} Shown in Scheme 1 is an approach starting from L-lactide, with (3*R*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione and (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione (**1**, 95% ee) as the bromination and elimination products, respectively (see Supporting Information). The captodative alkene (i.e., an alkene substituted with both electron-withdrawing and electron-donating groups)⁵ in **1** can be used as a dienophile in a Diels–Alder reaction to construct a new tricyclic compound (**2**). We prepared cycloadduct **2** on a multigram scale in good yield from L-lactide and explored its ring-opening polymerization (ROP) behavior.

The reaction of **1** with cyclopentadiene gives **2** as four diastereomers (Scheme S1) due to the endo and exo forms of the tricycle. Using 1D NOE, ¹H–¹H COSY, and ¹H NMR spectroscopy of the mixture of isomers (and their diol derivatives,⁶ Figures S6–S9), the stereoisomer depicted in Scheme 1 was identified as the preferred cycloadduct (74%; all isomers were assigned in Figure S10). The observed diastereofacial selectivity (85:15) was consistent with the methyl group on dienophile **1** being positioned opposite the approaching cyclopentadiene to minimize steric repulsion. In addition, we observed exo selectivity (85:15) consistent with the preference for anti-Alder addition.^{6,7}

Compound **2** has two polymerizable rings, a substituted norbornene and a substituted lactide. To effect the ROP of the lactide ring (100 equiv) we used 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)⁸ as the catalyst (0.5 equiv) and benzyl alcohol (1 equiv) as the initiator. We achieved 81% conversion of **2** ($[2]_0 = 1.0$ M in CH₂Cl₂) after 3 h at RT and 84% conversion after 24 h (reactions were quenched by adding at least 10 equiv of benzoic acid). The M_n (SEC, PS std) of the poly**2-L** (the **L** denotes ring opening

Scheme 1. Synthesis of **1** and **2** from L-Lactide



Scheme 2. Polymerization of **2** by Two Different Mechanisms

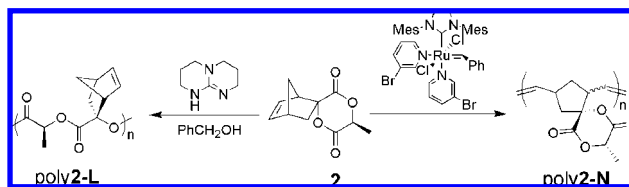


Table 1. ROMP of **2** by Third Generation Grubbs' Catalyst (Ru)^a

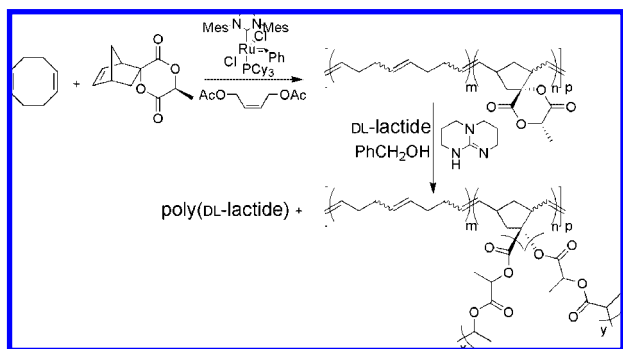
$[2]_0/[Ru]_0$	yield (%) ^b	M_n (kg mol ⁻¹)	M_w/M_n	T_g (°C)
50	83	14.0	1.04	168
100	86	27.2	1.09	191
200	88	48.5	1.10	191
300	89	62.8	1.16	191
500	93	91.6	1.12	189
1000 ^c	96	154	1.22	192

^a Polymerization conditions: $[2]_0 = 0.2$ M in CH₂Cl₂, RT, 30 min. All reactions were quenched with ethyl vinyl ether. ^b All conversions are near quantitative (>99%). ^c Reaction time = 1 h.

through the lactide ring) produced after 24 h was 4.9 kg mol⁻¹, and the PDI was 1.85. Performing the same reaction at –20 °C gave 94% conversion after 24 h with $M_n = 12.2$ kg mol⁻¹ and PDI = 1.27.⁹ By controlling $[2]_0/[benzyl\ alcohol]_0$ we obtained controlled molecular weights of poly **2-L** as high as $M_n = 33.6$ kg mol⁻¹ (see Table S1). The structure of poly **2-L** shown in Scheme 2 was corroborated by NMR spectroscopy and MALDI mass spectrometry (Figures S12, S14). The increased conversion at low temperature is consistent with the bulky nature of the norbornene side group limiting the exothermicity of the polymerization reaction.¹⁰ By DSC, high molecular weight poly **2-L** exhibited a glass transition temperature of 113 °C, the highest T_g reported to date among all poly lactide derivatives.^{3c,d,11}

We also polymerized **2** by ring-opening metathesis polymerization (ROMP) using the third generation Grubbs' catalyst (Scheme 2).¹² As shown in Table 1, high molecular weight polymers with narrow PDIs were readily prepared, and the molecular weights were well-controlled by the $[2]_0/[Ru]_0$ ratio. The T_g of the high molecular weight poly **2-N** (where the **N** denotes ring opening through the norbornene ring) polymer was 192 °C.¹³ The structure of poly **2-N** shown in Scheme 2 was supported by NMR spectroscopy and MALDI mass spectrometry (Figures S13, S15).

With the aim of toughening PLA, we exploited the facile dual polymerizability of **2** to produce a lactide-substituted polybutadiene and utilized that reactive polymer for the formation of a PLA

Scheme 3. Preparation of a PLA-polyCOD Composite Using **2**

composite containing polybutadiene-PLA graft copolymer (Scheme 3).^{14,15} The ROMP of a mixture of 3 mol% of **2** and 97 mol% of 1,5-cyclooctadiene (COD) yielded a statistical copolymer (SEC, PS std: $M_n = 46.6 \text{ kg mol}^{-1}$, PDI = 1.69).¹⁶ This COD/**2** copolymer (20 wt%) was added to a TBD-catalyzed, benzyl alcohol-initiated polymerization of DL-lactide (80 wt%). The reaction product,¹⁷ **C1** (SEC: $M_n = 48.7 \text{ kg mol}^{-1}$, PDI = 2.89, Figure S18), was compression-molded into translucent films. In a separate reaction, polyCOD homopolymer (SEC: $M_n = 44.9 \text{ kg mol}^{-1}$, PDI = 1.70) was prepared (20 wt%) and added to a TBD-catalyzed, benzyl alcohol-initiated DL-lactide (80 wt%) polymerization. The reaction product, **C2** (SEC: $M_n = 34.5 \text{ kg mol}^{-1}$, PDI = 1.88, Figure S18), formed opaque films consistent with macrophase separation of polyCOD and PLA.

Analysis of the composites **C1** and **C2** by SEM revealed significant differences in morphology (Figures 1, S20–S21). As expected **C2** showed macrophase separated domains of PLA and polyCOD, whereas **C1** consisted of nanoscopic heterogeneities; TEM data confirmed the nanophase separation (Figure S22). In addition, small-angle X-ray scattering analysis of **C1** (Figure S23) showed a principal reflection with a domain spacing of $\sim 45 \text{ nm}$. Sample **C2** exhibited a lower strain at break, tensile strength, and modulus than PLA homopolymer (Figure S24). On the other hand, **C1** was characterized by an elongation at break of 65%, a tensile strength of 24 MPa, and a tensile toughness of 16 MJ m^{-3} ; these values for PLA homopolymer are ca. 5%, 44 MPa, and 2 MJ m^{-3} .¹⁸ We posit that the presence of the graft copolymer at the interface between PLA and the rubbery phase in **C1** reduced the interfacial tension and hence increased their interfacial adhesion thus leading to markedly improved toughness.¹⁸

In sum, we prepared **1** from L-lactide and used it as the dienophile to prepare **2** in a selective Diels–Alder reaction. Two distinct polymerizations of this bifunctional lactide derivative were successfully carried out to give high molecular weight and high T_g polymers. Furthermore, we demonstrated that by incorporating a small percentage of **2** into polyCOD and copolymerizing it with DL-lactide, a novel PLA composite with significant improvements

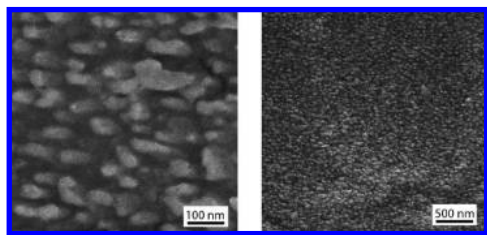


Figure 1. SEM backscattered electron images of composite **C1**. Samples were cryo-microtomed, stained by RuO_4 , and coated with platinum.

in toughness over PLA and the corresponding binary blend of PLA and poly(1,5-cyclooctadiene) can be prepared.

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Supporting Information Available: Experimental procedures, characterization data for monomers and polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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