Poly(lactide) (PLA) is an attractive polymer because it can be derived from renewable resources and provides a biodegradable alternative to polymers obtained from petrochemical sources. PLA is prepared by the ring opening polymerization (ROP) of lactide, the cyclic dimer of lactic acid. Commercial polylactides usually are synthesized from lactide monomers prepared from a single lactic acid enantiomer, and because the resulting polymers are stereoregular, they have high degrees of crystallinity. The mechanical properties of crystalline polymers are stable to near room temperature. Although L-lactide can be prepared with a melting transition near 180 °C and Tg ~ 67 °C, properties that make it useful for applications ranging from degradable packaging to surgical implants and matrices for drug delivery. In contrast, polylactide chains. Despite its improved mechanical properties, practical applications of the stereocomplex are prohibited by the requirement that separate pools of enantiopure lactide monomers must be polymerized to enantiopure polymers. If the same material could be prepared from the rac-lactide, it is conceivable that applications of the stereocomplex could be realized.

Scheme 1

An interesting effect of stereoregularity on lactide properties was first reported by Tsuji and co-workers. As shown in Scheme 1, D-PLA and L-PLA form a stereocomplex that has a Tm 50 °C higher than the Tm for the homochiral polymers. Preparation of this stereocomplex presently requires parallel ROP of D- and L-lactide with subsequent combination of the chiral polylactide chains. Despite its improved mechanical properties, practical applications of the stereocomplex are prohibited by the requirement that separate pools of enantiopure lactide monomers must be polymerized to enantiopure polymers. If the same material could be prepared from the rac-lactide, it is conceivable that applications of the stereocomplex could be realized.

Spassy’s and Coates’ results in stereoselective ROP of lactides suggests a strategy for the direct preparation of the polylactide stereocomplex from rac-lactide. Specifically, the racemic catalyst, rac-2, should lead to parallel syntheses of isotactic D-PLA and L-PLA chains since (−)-2 preferentially polymerizes D-lactide and (+)-2 preferentially polymerizes L-lactide. In contrast to kinetic resolution of rac-lactide with (−)-1, the D:L ratio in the monomer pool should remain constant at high conversion since polymerization by the racemic catalyst will remove D and L isomers at equal rates. Thus, the high enantioselectivity that is realized at low conversion in kinetic resolutions using chiral I should be maintained at high conversion with rac-1 to give a 1:1 mixture of isotactic chains (Scheme 2).

Polylactide of rac-lactide with rac-2 yields nearly monodisperse chains (Mw/Mn = 1.05) consistent with a “living” polymerization and the absence of transesterification. This is supported by the linear relationship between the monomer conversion to polymer and Mn~1.2–1.4 More importantly, the 'H NMR spectrum (Figure 1a) is consistent with formation of chains

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(6) In the kinetic resolution of rac-lactide by (−)-1, the enantiomeric excess at 20% conversion is 88%. By integration of the NMR spectrum in Figure 1a, we observe similar selectivity (~90%) for isotactic placement of D- and L-lactide units.
that are predominantly isotactic. Two separate control experiments were performed to confirm the tacticity. In the first control experiment, \( \text{L-lactide} \) was polymerized with the same catalyst batch used to generate the rac-PLA. The NMR spectrum of this sample (Figure 1b) demonstrates that epimerization of the lactide monomer does not occur under the experimental conditions. In the second control experiment, rac-lactide was polymerized with an achiral catalyst. The homonuclear decoupled spectrum of the methine region, shown in Figure 1c, is similar to that recently reported by Thakur et al. where assignments for various tetrad and hexad stereochemistries have been made.\(^{15}\) Comparable spectra of and \( \text{L-PLA} \) are shown in Figures 1a and 1b, respectively. Clearly, the spectrum of rac-PLA derived from rac-2 closely resembles the spectrum of L-PLA. This is significant since it confirms the formation of predominantly isotactic chains in the polymerization of rac-lactide by rac-2. The chemical shift for the methine resonance in spectrum b, Figure 1, is consistent with the chemical shift for the \( \text{III} \) tetrad in c, Figure 1. It is clear from the NMR data that the sample in Figure 1a has a small percentage of \( \text{III} \)ish hexads that are absent in the sample in Figure 1b.\(^{16}\) Thus, the stereoselectivity in the ROP of rac-lactide by rac-2 yields polymers that have enantiopurities slightly less than that of L-PLA.

The polymers that correspond to the spectra in Figure 1 were characterized by differential scanning calorimetry (DSC). For L-PLA prepared by ROP of \( \text{l-lactide} \) by rac-2, the glass, melting, and crystallization temperatures (\( T_g = 55^\circ \text{C}, T_m = 170^\circ \text{C}, T_c = 91^\circ \text{C} \)) were comparable to those for samples described in the literature. In addition, the \( \Delta H_{\text{fus}} \) (65 J/g) indicates the sample has a degree of crystallinity of \( \approx 65\% \).\(^2\) rac-PLA prepared using rac-2 has a similar glass transition (\( T_g = 55^\circ \text{C} \)), but has significantly higher melting and crystallization temperatures (\( T_m = 191^\circ \text{C}, T_c = 101^\circ \text{C} \)). For rac-PLA the \( \Delta H_{\text{fus}} \) (42 J/g) indicates a significant degree of crystallinity (\( \approx 42\% \)).\(^{17}\) These results are remarkable. Normally amorphous materials result when rac-lactide is polymerized due to random placement of the d and l-lactide units in the individual PLA chains. Small amounts of a minor enantiomer can have deleterious effects on polymer properties when enantioenriched monomers are polymerized with achiral catalysts.\(^{18}\)

The surprisingly high crystallinity in the rac-PLA sample can be explained by two models for the crystalline phase of rac-PLA: the formation of the stereocomplex, or a 1:1 mixture of crystalline domains of \( \text{L-PLA} \) and \( \text{d-PLA} \). These two models can be easily distinguished by powder X-ray diffraction because of the large difference in the scattering profiles for the stereocomplex and for \( \text{L-PLA} \).\(^{11,19}\) The diffraction pattern of rac-PLA corresponding to the NMR spectrum in Figure 1a matches that of the stereocomplex, confirming that we directly obtained the stereocomplex from the polymerization.\(^{20}\) The difference between the \( T_m \) for the stereocomplex prepared from rac-lactide and rac-2 and the \( T_m \) for the stereocomplex prepared from enantiopure d- and l-PLA\(^2\) reflects a lower degree of isotactici in the individual chains in our rac-PLA sample.\(^{19,21}\) Improvements in the polymerization scheme for rac-PLA should lead to higher enantiopurities and melting points that approach those of stereocomplexes prepared by mixing enantiopure samples of \( \text{d-PLA} \) and \( \text{l-PLA} \).

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**Supporting Information Available:** Experimental details for catalyst synthesis, polymerization conditions, and polymer characterization (PDF). This material is available, free of charge, via the Internet at http://pubs.acs.org.

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\(^{16}\) The slight deviations in chemical shifts for the resonance for the \( \text{III} \) tetrad between our work and that reported by Thakur (\( \delta 5.14 \) vs \( \delta 5.17 \)) likely arise from deviations in field strength between spectrometers.

\(^{17}\) In polymerizations of lactide with an achiral Schiff’s base aluminum alkoxide, \( \Delta H_{\text{fus}} = 10 \) J/g for samples that are 40% enriched in a particular enantiomer. When rac-lactide was polymerized using the same catalyst, there was no evidence for crystalline domains and the melting point of the PLA (\( T_m \approx 150^\circ \text{C} \)) is considerably lower than we find for the stereocomplex: Wniewierski, M.; LeBorgne, A.; Spassky, N. Macromol. Chem. Phys. 1997, 198, 1227–1238.


\(^{19}\) X-ray powder diffraction is diagnostic for the formation of the lactide stereocomplex, as well as crystalline domains of d- or l-lactide.\(^{11,19}\) Peaks for the latter case are absent in Figure 2.

\(^{20}\) The powder pattern is available in the Supporting Information.

\(^{21}\) When rac-lactide is polymerized by rac-2 at higher temperatures, the NMR spectra reflect a degree isotacticity that is intermediate between that in Figures 1a and 1c. However, \( T_m \) and \( T_c \) were not observed for the resulting polymer. This highlights the sensitivity of \( T_m \) and \( T_c \) with respect to changes in tacticity.