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Poly(propylene succinate): A New Polymer Stereocomplex

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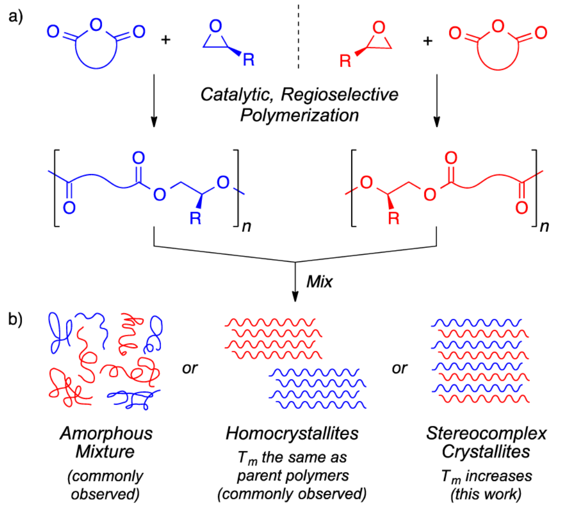
Supporting Information

ABSTRACT: Herein we show the formation of a polymer stereocomplex by mixing isotactic, regioregular chains of poly(propylene succinate) synthesized via the copolymerization of cyclic anhydrides and epoxides. The stereocomplex exhibits significantly improved thermal properties in comparison to the enantiopure parent polymers. We demonstrate that stereocomplexation is a route to a new class of semicrystalline polyesters with improved properties, produced from readily accessible starting materials.

Polyethylene and isotactic polypropylene are the two most widely produced polymers in the world, accounting for over half of the approximately 100 million pounds of plastic produced annually in the United States alone.[1] These semicrystalline polyolefins are ubiquitous because of their low cost and impressive physical and thermal properties, allowing for their use in a wide array of applications. Since the discovery of these materials, relatively few new classes of semicrystalline polymers have been commercialized, and even fewer where the monomers are nearly as readily available and inexpensive as ethylene and propylene.[2] One potential class includes polymers made from epoxides, isotactic versions of which were first synthesized around the same time as the first isotactic polyolefins.[3] As with olefins, epoxides are inexpensive and readily available, making them attractive monomers for large-scale polymers. However, unlike simple α-olefins, their corresponding epoxides contain stereogenic centers, which can be both an asset and a challenge for synthesizing polymers of controlled tacticity.[4]

Epoxides have also been studied in alternating copolymerizations with CO_2 to form polycarbonates[5] and with cyclic anhydrides to form polyesters.[6] In the case of the copolymerization of propylene oxide (PO) with CO_2, even the highly regio- and stereoregular poly(propylene carbonate) is amorphous.[7] However, we hypothesized that the copolymerization of PO with cyclic anhydrides could result in the formation of a new class of semicrystalline polyesters given the wide array of anhydride comonomers available. In general, polyesters are functionally diverse and bioresponsive, giving them advantages over polyolefins in the range of applications to which they can be applied.[8] Additionally, many commercial aliphatic polyesters, including polylactic acid (PLA), polyhydroxybutyrate (PHB), and polycaprolactone (PCL), can be decomposed in aerobic composting environments, and in vivo in the case of biomedical devices.[9] However, commercializing many of the current biodegradable polyesters for large-scale use challenges the existing industrial infrastructure because the processes required to produce them rely partially or fully on biotechnology.[10] In contrast, polyesters synthesized via the ring-opening alternating copolymerization (ROAC) of epoxides and cyclic anhydrides can be made by purely chemical means with a wide array of commercially available starting materials. A variety of metal-based complexes have been reported to catalyze this reaction.[6] We recently discovered that cobalt salcy complexes (salcy = N,N'-bis(salicylidene)-cyclohexanediimine) with a nucleophilic cocatalyst such as $[PPN][NO_3]$ ($[PPN] = [Ph_3P^+{-}N{=}PPh_3]$) can be used for the regioselective ROAC of various cyclic anhydrides and epoxides (Scheme 1a).[6m]

Scheme 1. (a) Regioselective Polymerization of Cyclic Anhydrides and Epoxides and (b) Stereocomplex Formation by Crystallization of Enantiomeric Polymer Chains



Catalytic epoxide/anhydride copolymerization not only utilizes a large substrate scope, but also allows control over polymer microstructure. Additionally, by employing the regioselective ROAC of enantiopure epoxides with cyclic anhydrides, highly tactic polyesters can be synthesized, which increases the probability for crystallinity in the resulting materials. Because these polyesters are chiral, using enantiopure epoxides results in enantiomerically pure forms of each polymer. When these handed chains are mixed, they can result in an amorphous mixture, a semicrystalline material with segregated homocrystallites, or a semicrystalline material with stereocomplexed crystallites (Scheme 1b). Although we have observed many examples of the former two situations, we are

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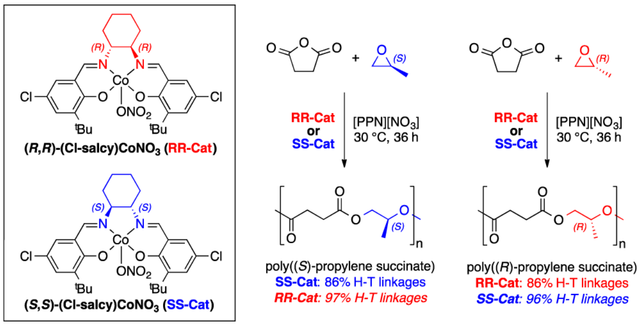
unaware of an example of stereocomplexation in polyesters formed from epoxides and anhydrides. Stereocomplexation is an attractive route to polymeric materials with improved thermal and mechanical properties compared to those of the individual enantiopure polymers.[11]

Stereocomplexation occurs when a stereoselective interaction takes place between two stereoregular complementary polymers in the crystalline state.[11a] Most commonly, stereocomplexes are formed between enantiomerically complementary polymer strands. One of the most widely studied stereocomplexes is a 1:1 mixture of poly(ʟ-lactic acid) (PLLA) and poly(ᴅ-lactic acid) (PDLA).[11b,12] From solution, PLLA and PDLA form helices that preferentially crystallize together when combined, creating a stereocomplex with a melting transition (T_m) approximately 50 °C higher than that of the parent polymers (230 vs 180 °C).[12] Stereocomplexation improves and allows for tunability of polymer properties, including crystallinity as well as biodegradability.[11]

In this report, we utilize cobalt salcy complexes with ionic cocatalysts for the synthesis of regioregular poly(propylene succinate). By polymerizing both (*R*)- and (*S*)-PO separately with succinic anhydride and subsequently mixing the resulting polyesters, we were able to investigate stereocomplex formation. This strategy resulted in the formation of a stereocomplex from enantiomeric strands of isotactic poly(propylene succinate), producing a material with an increased T_m and a greater level of crystallinity. Not only is poly(propylene succinate) formed from readily available monomers and likely to be biodegradable, but also the stereocomplex exhibits a T_m comparable to low density polyethylene.[2] In addition, succinic anhydride (SA) is an attractive monomer because its synthesis from biorenewable resources has expanded widely in recent years.[13]

To form the polyester stereocomplex, we first synthesized poly(*S*)- and poly((*R*)-propylene succinate) from (*S*)- and (*R*)-PO, respectively (Scheme 2). Poly(propylene succinate) regioregularity was analyzed by gas chromatography of the diol products that resulted from degrading the enantiopure polymers under basic conditions.[14] High regioregularity (96–97% head-to-tail linkages) was observed when a chloro group was present in the *para* position of the salicylidene moiety of the catalyst, (Cl-salcy)CoNO$_3$, and when enantiopure PO was polymerized using the catalyst of the opposite absolute stereochemistry (Scheme 2).[14] Copolymerization of (*S*)-PO with SA proceeded to full conversion in 36 h at 30 °C using enantiopure (*R*,*R*)-(Cl-salcy)CoNO$_3$ to give polymer with an M_n of 9.2 kDa, a PDI of 1.22, and a specific optical rotation of $[\alpha]_D^{20}$ −3.2°. Likewise, polymerization of (*R*)-PO proceeded using (*S*,*S*)-(Cl-salcy)CoNO$_3$ to give polymer with an M_n of 9.0 kDa, a PDI of 1.47, and a specific optical rotation of $[\alpha]_D^{20}$ +3.3°. These molecular weights are likely low because of the formation of cyclic polymer chains or transesterification of polymer chains by the catalyst.

Scheme 2. Regioselective Alternating Copolymerization of Enantiopure Propylene Oxide and Succinic Anhydride with "Matched" and "Mismatched" Catalysts



Differential scanning calorimetry (DSC) was used to investigate the thermal properties of the enantiopure, regioregular polymers and of the mixed specimens. The DSC thermograms of both poly(*S*)- and poly((*R*)-propylene succinate) show no crystallinity, and only a glass transition (T_g) of −4 °C is observed (Figure 1a). Figure 1b shows that the parent polymers do slowly crystallize from the melt, with crystallinity first appearing after about 1 week and gradually increasing over time.[14] For poly((*R*)-propylene succinate), a relatively large amount of a low melting polymorph with a T_m around 50 °C and a Δ*H* value of 48 J/g is observed after 19 days, along with a very small amount of a higher melting polymorph (T_m around 70 °C). Some degree of crystallinity is

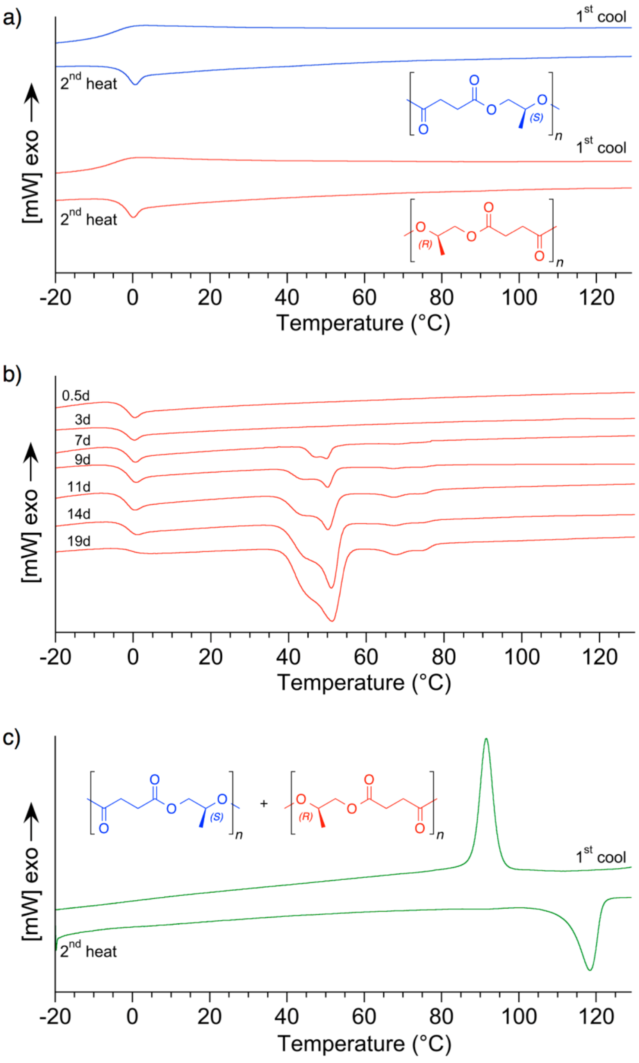


Figure 1. DSC thermograms of (a) isotactic poly((*S*)-propylene succinate) and poly((*R*)-propylene succinate), (b) crystallization of poly((*R*)-propylene succinate) over time, and (c) the stereocomplexed mixture of both polymers.

observed from precipitation of the enantiopure polymers with methanol, and a T_m of 79 °C along with ΔH values of 68−78 J/g can be obtained, although this method is not ideal for industrial applications as the resulting polymer is a fine powder and crystallinity disappears completely upon melting, and no T_m is seen on the second heat.[14]

To test for stereocomplex formation, dissolved solutions of poly((*S*)-propylene succinate) and poly((*R*)-propylene succinate) in dichloromethane were mixed and the solvent was allowed to slowly evaporate. The sample was then dissolved again in dichloromethane and precipitated by adding methanol dropwise with vigorous stirring. After drying, the resulting polymer was analyzed by DSC and the thermal properties of the poly(propylene succinate) stereocomplex were compared to the enantiopure polymers (Figure 1c). For the stereocomplex, not only does the melting point increase by approximately 40 °C (to 120 °C) on the first heat relative to the enantiopure polymers, but also recrystallization occurs upon cooling to approximately 92 °C, and the same T_m and ΔH value of 88 J/g are observed on the second heat. Both the rate of heating and cooling and the maximum temperature of heating affected the recrystallization of the stereocomplex, but had no effect on the enantiopure polymers. All polymers shown in Figure 1 were heated to a maximum temperature of 130 °C, but while the enantiopure polymers in Figure 1a,b were heated and cooled at a rate of 10 °C/min, the stereocomplex was heated at 2 °C/min to optimize the recrystallization temperature.[14]

The immediate stereocomplex crystallization upon cooling shows a vast improvement over any other polyester we have synthesized by the ROAC of propylene oxide and cyclic anhydrides. While we have observed the formation of other semicrystalline polyesters using this synthetic method, they only show crystallinity following isolation from solution, not from the melt after initial heating above the T_m.[6m] Additionally, none of these polyesters to date have shown stereocomplexation upon mixing of both enantiopure polymers. The $t_{1/2}$ of recrystallization at ambient temperature was calculated for both the enantiopure polymers and the racemate, and was found to be approximately 3 orders of magnitude faster for the stereocomplex than for the parent polymers.[14]

Powder X-ray diffraction (XRD) was used to confirm the formation of a stereocomplex via the presence of different crystalline diffraction peaks in comparison to the diffraction profiles of the parent polymers. Samples of both the enantiomerically pure, isotactic polymers and the stereocomplex were prepared by precipitation via dropwise addition of methanol into a dichloromethane solution of the polymer or polymer mixture to induce crystallization, especially important in the case of the parent polymers. Figure 2 shows the powder XRD profiles of both enantiopure forms of poly(propylene succinate) and of the poly(propylene succinate) stereocomplex. Both poly(*S*)- and poly((*R*)-propylene succinate) show five large crystalline diffraction signals at 10.2°, 18.5°, 19.4°, 21.8°, and 24.7° along with four smaller peaks at 9.2°, 15.4°, 16.8°, and 25.7°. In contrast, the polymer stereocomplex shows three large peaks at 17.9°, 20.8°, and 24.1° that are not present in the enantiopure polymer samples. Additionally, the stereocomplex shows one small shoulder at 16.2°.

In conclusion, we have discovered the formation of a new polymer stereocomplex from enantiomeric poly(propylene succinate) with vastly improved thermal properties compared to the enantiopure parent polymers. By optimization of the ring-opening alternating copolymerization of succinic anhydride with enantiopure propylene oxide and subsequent stereocomplex formation, a new class of semicrystalline biodegradable polyesters has been established. In addition, we have shown that a relatively high melting semicrystalline material with a T_m similar to low density polyethylene can be created from two very slow-crystallizing, low T_m aliphatic polyesters. With the wide range of cyclic anhydrides and epoxides available commercially, the current focus of our research is to widen the scope of biodegradable and biocompatible materials that can be improved via stereocomplexation. In addition, we are working to increase the molecular weights of polyesters formed via ring-opening alternating copolymerization, in particular poly(propylene succinate), so that we can investigate the relationship between molecular weight and stereocomplex formation. Finally, we are developing catalysts for the isoselective polymerization of racemic epoxides toward the goal of in situ stereocomplex formation so that we can further improve this process by eliminating the need for enantiopure starting materials.

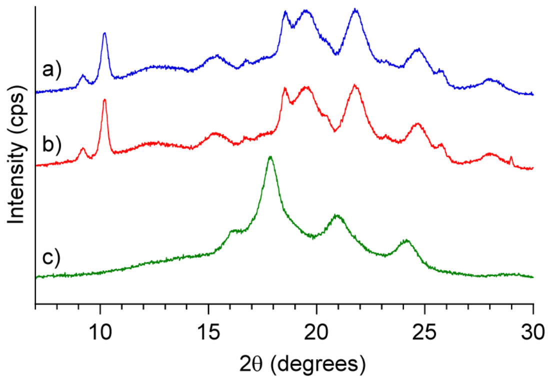


Figure 2. Powder XRD profiles of (a) poly((*S*)-propylene succinate), (b) poly((*R*)-propylene succinate), and (c) stereocomplexed poly(propylene succinate).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data and spectra of all new compounds. 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.

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