Communication

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Stereocontrolled Polymerization of Racemic Lactide with Chiral Initiator: Combining Stereoelection and Chiral Ligand-Exchange Mechanism

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Polymerization of lactides (LA) and other cyclic aliphatic esters provides an excellent model system for fundamental studies of thermodynamics, kinetics, and mechanism of the ring-opening polymerization (ROP) of heterocyclic monomers. The best control of LA polymerization, with regard to molar masses and end-group structures in the resultant poly(lactide) (PLA), has been achieved with multivalent metal (e.g., Ca, Zn, Sn(II), Al, La, Y, Sn(IV), Ti) alkoxides as initiators and catalysts.1 A concept of a “single-site” initiator/catalyst in LA polymerization has thoroughly been explored2–7 to avoid the mechanistic complexity resulting from the aggregation equilibria, in which “multiple-site” alkoxides are usually engaged.

Stereochemical microstructure of PLA macromolecules formed in the ROP of LA, can be controlled by the monomer composition in the feed (proportion of (R,R)-, (S,S)-, and (R,S)-LA diastereoisomers) and/or by the stereochemical preference of the initiating/catalytic system. The idea of a single-site, enantioselective (or enantioelective) catalyst for polymerization of racemic lactide (rac-LA) has been realized by Spassky, who applied aluminum alkoxides of general structure SBO₂Al−OR, bearing Schiff’s base ligands.3

The method originally developed by Spassky was then followed by methods by Baker,4 Coates,5,6 Feijen,6 and Nomura.7 It has been revealed that polymerization of rac-LA mediated with either achiral (R′ = −(CH₂)₉−) or chiral racemic (R: (R,S)-(1,1′-binaphthyl-2,2′)-diyl) catalyst SBO₂Al−OR led to the multiblock stereopolymers [(S)-PLA-b-(R)-PLA]₈ (Scheme 1), due to a chain-end control or enantiomorphous site control of the monomer addition, respectively.

[(S)-PLA-b-(R)-PLA]₈ copolymers are able to form a stereocomplex due to van der Waals interactions between homochiral PLA sequences of opposite configuration, and therefore, they show enhanced thermal stability compared to the homochiral PLAs.8 The highest melting temperatures (Tₘ) of a stereocomplex obtained by the stereoelective polymerization of rac-PLA were equal to 191–192 °C.3–7

The present communication aims at a new approach to the chiral Schiff’s base/aluminum alkoxide/rac-LA system, based on a consecutive addition of homochiral (S)- and (R)-Schiff’s bases to the Al(OPr)₃/rac-LA polymerization mixture, employing a chiral ligand-exchange mechanism.

Two-step polymerization of rac-LA was initiated by 2,2′-[1,1′-binaphthyl-2,2′-diylbis(nitrylomethyldiene)]diphenol (SB(OH)₂)/aluminum isopropoxide trimer (A₃)⁹ mixture in which the actual initiator (SBO₂Al−OPr) was formed in situ. First, (S)-SB(OH)₂/Al(OPr)₃ mixture was reacted for 24 h in THF as solvent at 80 °C, and then rac-LA was introduced. Progress of the polymerization was followed using polarimetry (Figure 1) and size exclusion chromatography (SEC) (Table 1, entries 1 and 4).

Optical rotation (or) readings increased with polymerization time and eventually leveled off. SEC measurement revealed approximately 50 mol % consumption of LA (α). In the second step, an equimolar quantity of (R)-SB(OH)₂, with regard to (S)-SB(OH)₂, was introduced (Table 1, entries 2 and 5). Further polymerization was accompanied by a gradual decrease of or, and finally (α > 90 mol %) the polymerization product precipitated out.

Mₘ values of PLAs obtained in the first and second polymerization steps were controlled by the concentration ratios of the reacted LA and OPPr groups in the feed (Table 1, entries 1, 2, 4, and 5).

Low polydispersity indexes (PDI = Mₘ/Mₚ) (1.0−1.12) suggested the living polymerization mechanism, accompanied by a dynamic chain transfer to (macro)alcohol.

Moreover, the ²⁷Al NMR spectrum of the living polymerization mixture revealed the presence of one absorption band at δ ≈ 67 ppm,¹⁰ characteristic of the tetracoordinate SBO₂Al−O−PLA active...
Table 1. Polymerization of rac-LA Using SB(OH)2/Al(OPr)3 Mixture

<table>
<thead>
<tr>
<th>entry</th>
<th>[rac-LA]a</th>
<th>[Al]b</th>
<th>([S]-SB(OH)2)</th>
<th>([R]-SB(OH)2)</th>
<th>time (min)</th>
<th>M∞(calcld)</th>
<th>M∞×10−3 (SEC)b</th>
<th>PDI (SEC)c</th>
<th>Tm° (°C)d</th>
<th>ΔHmixf (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.54</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
<td>0</td>
<td>220</td>
<td>53</td>
<td>1.80</td>
<td>1.12</td>
<td>130 ± 5</td>
</tr>
<tr>
<td>2</td>
<td>1.54</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
<td>0</td>
<td>93.4</td>
<td>1.11</td>
<td>189 ± 3</td>
<td>70 ± 7</td>
<td>56 ± 0.5</td>
</tr>
<tr>
<td>3</td>
<td>1.54</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
<td>0</td>
<td>96.3</td>
<td>1.61</td>
<td>129 ± 14</td>
<td>14 ± 1</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>0.55</td>
<td>1.10</td>
<td>1.10</td>
<td>0</td>
<td>75.0</td>
<td>48</td>
<td>8.2</td>
<td>1.04</td>
<td>158 ± 50</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>0.55</td>
<td>1.10</td>
<td>1.10</td>
<td>1500</td>
<td>~90°</td>
<td>15.7a</td>
<td>12.3±b</td>
<td>1.1</td>
<td>210 ± 70</td>
</tr>
</tbody>
</table>

* See ref 10 for polymerization conditions. ** Conversion of rac-LA to PLA measured by SEC. ** M∞(calcld) = 144.13±1(rac-LA)/[Al] + 60.10. f The average molar mass measured by SEC (PLA standards, CH2Cl2). g Polydispersity index (Mw/Mn). h PLA melting temperature measured by DSC. i Enthalpy of PLA melting measured by DSC. j PLA partially insoluble in CH2Cl2.

Scheme 2

\[
\begin{align*}
(S)-SB(OH)_2 + Al(OPr)_3 & \rightarrow (S)-SB-OPr + 2 PrOH + 2 mrac-LA \\
\text{(a)} \\
(S)-SB(OH)_2 + Al(O)O- (S)-PLA & \rightarrow (S)-SB-AL-O-(S)-PLA (fast exchange) \quad \text{(b)} \\
(R)-SB(OH)_2 + (R)-LA & \rightarrow (R)-SB-AL-O-(R)-PLA-b-(R)-PLA \quad \text{(c)} \\
ROH + SB-AL-O-PLA & \rightarrow PLA-OL + SB-AL-OR \\
\text{(where R = Pr and/or PLA)}
\end{align*}
\]

\text{species, with an additional coordination of the Al atom by the acyl oxygen from the first repeating unit (Scheme 2).}

The independent kinetic measurements, carried out for the ([S]-SB(OH)2)/A/(S,S)-LA and ([S]-SB(OH)2)/A/(R,R)-LA systems, exhibited a 28:1 preference for the polymerization of ([S]-LA) over (R,R)-LA. Thus, for the final polymerization of ([S]-LA)-grad-(R)-LA, rather than the pure block copolymer structure, should have been expected. Indeed, decoupled 1H NMR spectra showed a presence apart from the strong signal of the isotactic mmn tetrad and also peaks of lower intensity, which could be ascribed to the mmn, rmm, and rmn tetrads, according to the reported stereoregular polymers to chemical shaft assignments.

Attempts to synthesize poly([S]-LA)-grad-(R)-LA from rac-LA, resulting in the stereocomplex formation with ([S]-SB(OH)2) only and without introducing the (R)-ligand in the second step, failed. PDI, DSC data (Table 1, entry 3), and 1H NMR spectra revealed an important role of transesterification during the very slow polymerization of ([R]-LA) on the ([S]-SB(OH)2)-... active centers.

In conclusion, we reported new opportunities provided by the SB(OH)2/Al(OPr)3/rac-LA polymerization system employing a combination of stereoelectron with (S) and (R) ligand exchange at Al-alkoxide active centers. Two-step polymerization of rac-LA was initiated by ([S]-SB(OH)2)-OPr and mediated in the second step by ([R]-SB(OH)2), adding to the reacting mixture. The stereoelectivity was close to that determined for the process with an additional synthetic step of isolation and purification of the SBO2—Al—OPr alkoxide. The resultant poly(rac-LA) had a gradient stereocopolymer structure and exhibited enhanced thermal stability due to a stereocomplex formation (Tm = 210 °C). This is the highest melting temperature reported until now for PLA prepared directly from rac-LA.

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Supporting Information Available: Experimental procedures, discussion of the polymerization mechanism, figures of 75 MHz 2H NMR spectra, DSC traces of PLA stereocopolymers, and kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


(10) See the Supporting Information.

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