Sequential crystallization and morphology of triple crystalline biodegradable PEO-\textit{b}\-PCL-\textit{b}\-PLLA triblock terpolymers

Jordana K. Palacios\textsuperscript{1}, Agurtzane Mugica\textsuperscript{1}, Manuela Zubitur\textsuperscript{2}, Amaia Iturrospe\textsuperscript{3}, Arantxa Arbe\textsuperscript{3}, Guoming Liu\textsuperscript{4}, Dujin Wang\textsuperscript{4}, Junpeng Zhao\textsuperscript{5}, Nikos Hadjichristidis\textsuperscript{*5} and Alejandro J. Müller\textsuperscript{*1,6}

\textsuperscript{1}POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain.

\textsuperscript{2}Chemical and Environmental Engineering Department, Polytechnic School, University of the Basque Country UPV/EHU, 20018 Donostia-San Sebastián, Spain

\textsuperscript{3}Materials Physics Center (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain.

\textsuperscript{4}Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China.

\textsuperscript{5}King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, KAUST Catalysis Center, Thuwal, Saudi Arabia

\textsuperscript{6}IKERBASQUE, Basque Foundation for Science, Bilbao, Spain.

*corresponding authors: alejandrojesus.muller@ehu.es and Nikolaos.Hadjichristidis@kaust.edu.sa
S1. Differential scanning calorimetry (DSC)

Several tests, at different cooling rates, were carried out to establish the ideal rate to achieve the crystallization of the blocks.

Figure S1.1. a) DSC cooling scans at several cooling rates (CR) after melting at 160 ºC for 3 min and b) Subsequent DSC heating scans at 20 ºC min\(^{-1}\) for PEO\(_{29}\)PCL\(_{42}\)PLLA\(_{29}\)\(^{16.1}\).
Figure SI.2. a) DSC cooling scans at several cooling rates (CR) after melting at 160 ºC for 3 min and b) Subsequent DSC heating scans at several heating rates (HR) for PEO$_{29}$PCL$_{42}$PLLA$_{29}$.$^{16,1}$.
Figure SI.3. a) DSC cooling scans at several cooling rates (CR) after melting at 160 ºC for 3 min and b) Subsequent DSC heating scans at 20 ºC min⁻¹ for PEO₂₃PCL₃₄PLLA₄₃.¹⁹.⁹
Figure S1.4. a) DSC cooling scans at several cooling rates (CR) after melting at 160 °C for 3 min and b) Subsequent DSC heating scans at several heating rates (HR) for PEO<sub>23</sub>PCL<sub>34</sub>PLLA<sub>43</sub>19.9.
Table S.1. Crystallization and melting temperatures of PEO$_{29}$PCL$_{42}$PLLA$_{29}$ and PEO$_{23}$PCL$_{34}$PLLA$_{43}$ terpolymers compared to different linear diblock copolymers reported in the literature

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PLLA</th>
<th>PCL</th>
<th>PEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA12000bPEG5000</td>
<td>2.3</td>
<td>93.0</td>
<td>140.1</td>
</tr>
<tr>
<td>PLLA63000bPEG5000</td>
<td>6.3</td>
<td>105.2</td>
<td>153.8</td>
</tr>
<tr>
<td>PEO$<em>{5}$-b-PLLA$</em>{16}$</td>
<td>12.0</td>
<td>116.3</td>
<td>162.4</td>
</tr>
<tr>
<td>PEO$<em>{5}$-b-PLLA$</em>{30}$</td>
<td>30.0</td>
<td>100.0</td>
<td>142.1</td>
</tr>
<tr>
<td>2LPCL$<em>{50}$-b-PLLA$</em>{43}$</td>
<td>12.45</td>
<td>102.4</td>
<td>151.7</td>
</tr>
<tr>
<td>PEOCL56</td>
<td>6.24</td>
<td>30.4</td>
<td>55.4</td>
</tr>
<tr>
<td>PEOCL62</td>
<td>8.13</td>
<td>34.3</td>
<td>56.3</td>
</tr>
<tr>
<td>PEOCL62</td>
<td>8.13</td>
<td>34.3</td>
<td>56.3</td>
</tr>
<tr>
<td>PEG5000-PCL1000</td>
<td>1.0</td>
<td>5.0</td>
<td>34.7</td>
</tr>
<tr>
<td>PEG5000-PCL2900</td>
<td>2.9</td>
<td>5.0</td>
<td>30.0</td>
</tr>
<tr>
<td>PEG5000-PCL9200</td>
<td>9.2</td>
<td>34.6</td>
<td>56.7</td>
</tr>
</tbody>
</table>

### Table S.1 continued...
References of supporting information


S3. Polarized light optical microscopy (PLOM). Photographs videos

PLOM was performed on cooling from the melt in order to observe the sequential crystallization and superstructure formation of each block. Small videos made of PLOM photograps for each triblock terpolymer are presented.

TriblockTerpolymer 16.1.ppsx
TribloqueTerpolymer 16.1.ppsx
TriblockTerpolymer 19.9.ppsx
TriblockTerpolymer 19.9.ppsx