

SI 01: FTIR spectra for L-lactide and poly(L-lactide) with weight average molar mass equal 87 kg/mol (PLLA-87). The others synthetic PLLA presented the same FTIR profile.



Supporting Information 02

SI 02: GPC chromatograms for homopolymers. [Top] PEO homopolymers, [Bottom] PLLA homopolymers.



SI 03: DSC curves for (a) 1st and (b) 2nd heating, and (c) cooling.

































Link for POM video of the crystallization of PEO-51/PLLA-46 80/20 blend:

[current] https://www.youtube.com/watch?v=Ms_v1F85f-8

or

[LINK OF THE VIDEO TO BE PROVIDED BY THE JOURNAL]

Figure SI 05 contains images of the surface of the PEO-51/PLLA-46 blends containing 40 wt % (images a, b and c) and 60 wt % of PEO (images d, e and f) before and after water-etching. Images (a) and (d) show no contrast between phase PEO and phase PLLA. As reported by Yang et $al.^{51}$, the electron density of crystalline and amorphous phases of PEO are too close, 406 and 345 e/nm³, respectively, while the electron density of the crystalline phase of PLLA is 410 e/nm³. Because of this, the phase contrast in the SEM or TEM images is poor. As reported previously for immiscible PEO/PLLA blends, there is no contrast enough for identifying phase separation²². However, SEM images also reflect the sample's topography. Thus, we subjected the blends to PEO etching with water during 5 min. After etching, SEM images revealed the topography of the samples with very well defined spherulites. The extraction of PEO resulted in empty spaces inside and around the PLLA spherulites, as can be seen in images (b), (c), (e), and (f). These results reinforce our conclusion that PEO is entrapped between PLLA lamellae and spherulites.



Figure SI 05: SEM images for PEO-51/PLLA-46 blends. (a-c) 40 wt % PEO, and (d-f) 60 wt % PEO. Images (a) and (d) before water-etching, and the others after water etching.

Link for POM video of the 2nd heating of PEO-51/PLLA-46 80/20 blend:

[current] <u>https://www.youtube.com/watch?v=9MKA7S_vNVA</u>

or

[LINK OF THE VIDEO TO BE PROVIDED BY THE JOURNAL]



SI 06: Zoom of XRD with demonstration of peak shifting.

Blend PEO-51/PLLA-46