Correlative characterization of stereocomplex formation in aliphatic polyester P(PCL-*b*-PLLA) block-copolymers.

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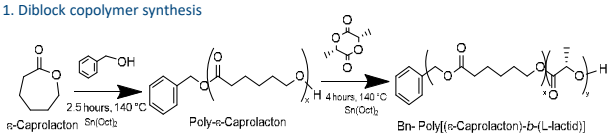
Introduction

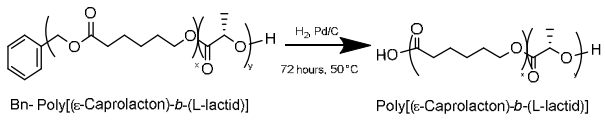
Quantifying the relationship between molecular structure and macroscopic properties in phase-separating semicrystalline block copolymers is a complex challenge, yet crucial for their processing and biomedical applications. In this work, I am studying a polymer system consisting of block copolymers of L-lactide (PLLA) and ε-caprolactone (PCL) that are blended with Poly(D-lactid) (PDLA). PLLA and PDLA sequences can form co-crystallites, referred to as stereocomplexes (SC). Stereocomplexation is faster and more reliable than homocrystallization of PLLA or PDLA alone, and the formed stereocomplexes are more resistant to mechanical deformation and hydrolysis than the corresponding homocrystallites, while furthermore displaying higher melting temperatures. Here, we aim to quantify the relationship between molecular structure and macroscopic properties in this class of copolymers, by combining correlative characterization techniques at different scales. P(PCL-*b*-PLLA) and PDLA with defined block lengths and molar masses were prepared to elucidate minimum block lengths for crystallization and stereocomplexation (SC), to characterize the size and spatial distribution of crystallites and their impact on physico-chemical properties. Our study showcases the precise control of stereocomplex formation and fine-tuning in high-performance PLA-based materials through strategic polymer synthesis and blending.

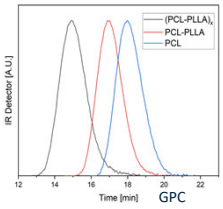
Methods

1. Diblock copolymer synthesis

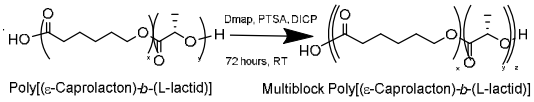


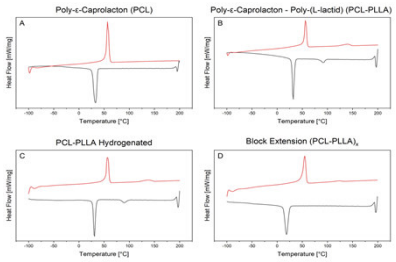
2. Hydrogenation



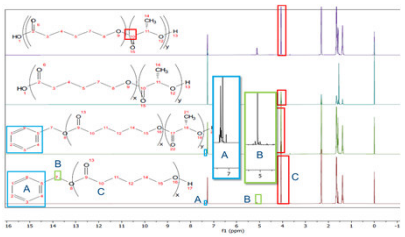


3. Multiblock copolymer (MBC) synthesis



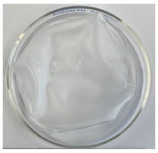


DSC



^{1}H-NMR

4. Film preparation



P(CL65-b-LLA13) 90 % + PDLA12 10 % polymer film.

P(CL-*b*-LLA)	GPC M_n	GPC M_w	GPC Đ
PCL65-PLLA30	71.000	130.000	1.8
PCL115-PLLA13	100.000	190.000	1.9
PCL120-PLLA48	120.000	230.000	1.9
PCL65-PLLA15	75.000	98.000	1.3

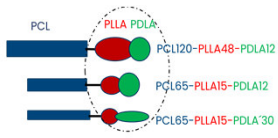
MBC´s

blended together

Poly(D-lactide)	GPC M_n	GPC M_w	GPC Đ
PDLA12	2550	2600	1.0
PDLA16	2700	3600	1.3
PDLA30	2120	2510	1.1
PDLA60	5750	7410	1.2

PDLA´s

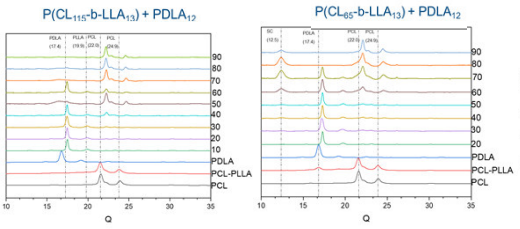
Formation Of SC



Mixed in different ratios 10-90 %

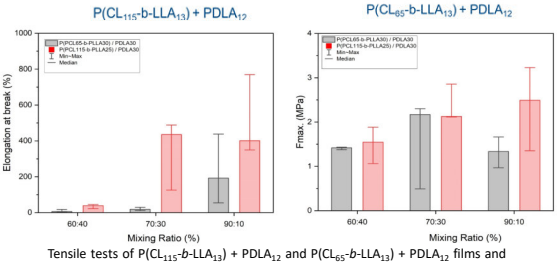
Results

1. Wide angle x-ray scattering (WAXS)



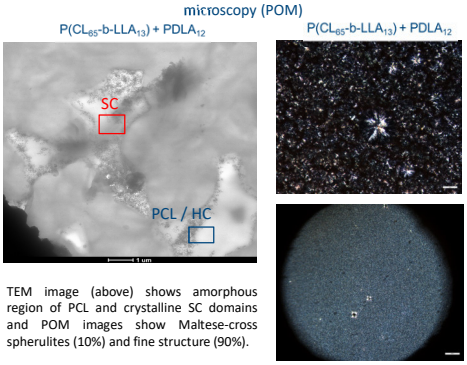
SC formation can be observed for P(CL_{65}-*b*-LLA_{13}) + $PDLA_{12}$ (right, Q = 12.5°). The crystallite size of the stereocomplexes could be controlled in the range between 1 and 8 nm. Co-crystallization of PCL occurred during the formation of SC.

3. Tensile testing



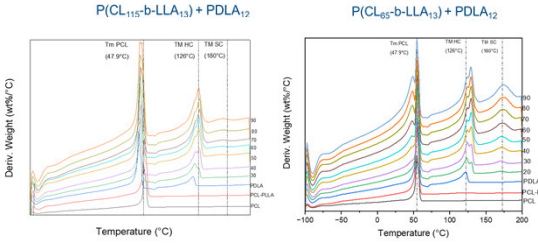
Tensile tests of P(CL_{115}-*b*-LLA_{13}) + $PDLA_{12}$ and P(CL_{65}-*b*-LLA_{13}) + $PDLA_{12}$ films and elongation at the break from 10% to 800% at room temperature.

5. Transmission electron microscopy (TEM) and Polarized optical microscopy (POM)



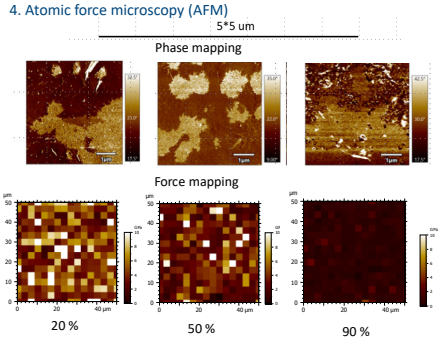
TEM image (above) shows amorphous region of PCL and crystalline SC domains and POM images show Maltese-cross spherulites (10%) and fine structure (90%).

2. Differential scanning calorimetry (DSC)



SC formation was indicated by the peak at 180°C. Crystallinities of 0-70 % (SC), 2-50 % (PCL) and 3-80 % (HC) were calculated.

4. Atomic force microscopy (AFM)



Microstructural hardness decreases significantly in P(CL65-b-LLA13) films. Phase composition changes in relation to the mixing ratio.

Conclusion

Stereocomplex (SC) formation could be shown by combining correlative characterization techniques at different scales. WAXS showed SC formation in short-chained MBCs mixed with poly(D-lactide) for seventy, eighty and ninety percent mixing ratios. The crystallite size of the stereocomplexes could be controlled depending on the mixture and chain length of the MBCs. SC formation in semi-crystallization block copolymers lead to hyperelastic material behavior under linear tension. These findings offer opportunities for the development of versatile materials with tunable mechanical and thermal properties.

References: Izraylit, Victor, et al. Biomacromolecules 21.2 (2019)
Neffe, Axel T., et al. European Polymer Journal (2021)

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