

Nanostructure study of novel PLA block copolymers

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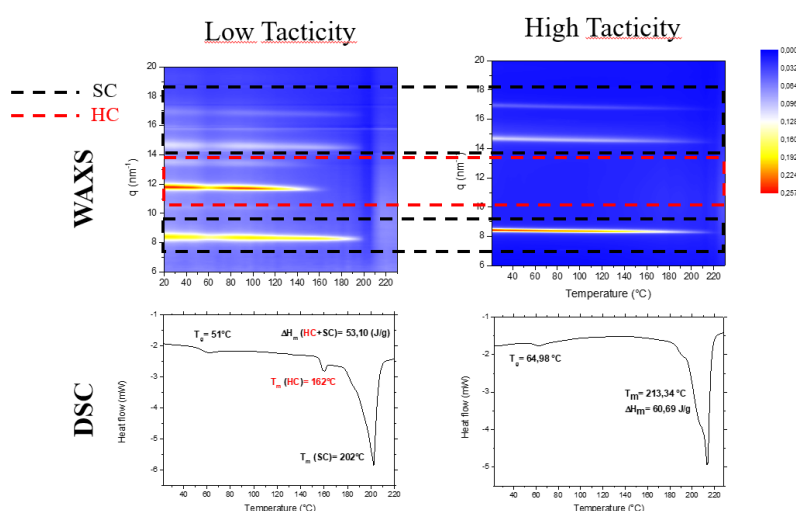
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Poly-lactide (PLA) is a well-studied bio-based polymer that is usually synthesized by Ring- Opening Polymerization (ROP), generating two enantiomers, poly (L-lactide) (PLLA) and poly (D- lactide) (PDLA) due to the presence of a carbon chiral centre in its backbone. PLA is the bio-based polymer most widely employed in diverse fields such as food handling, fibre manufacturing, textile industry or biomedical¹. However, the PLA applicability is slightly inferior to conventional petroleum- based polymers in terms of thermal resistance, mechanical properties and crystallinity kinetics. Different strategies have been evaluated to improve the physicochemical properties such as the use of plasticizers or nucleating agents. Moreover, the equimolar blend of PLLA and PDLA enantiomers is a strategy largely used to generate SC crystallites, which present a melting point 50 oC higher than its homocrystals (HC) counterparts due to the strong interactions between L- and D-lactyl unit sequences. SC crystallites can also be obtained through the synthesis of block copolymers by the one-pot sequential monomer addition to a truly living polymerization catalyst, what allows to retain the SC crystallization in High MW polymer².

Herein, a novel series of stereo-diblock-copolymers of PLA were synthesized by ring-opening polymerization (ROP) using a Zn organometallic catalyst. Molecular weight and tacticity of the final products were analysed through GPC and homodecoupled ¹H NMR spectra. Moreover, thermodynamic differences through DSC analyses were observed depending on the polymers tacticity. Finally, stereo- diblock-copolymer crystallization mechanism was investigated by time-resolved SAXS-WAXS and Raman spectroscopy to correlate the chain conformations evolution with the formation of the crystal precursors and establish the relationship with tacticity.



Références

- 1) Dechy-cabaret, O.; Martin-vaca, B.; Bourissou, D. Controlled Ring-Opening Polymerization of Lactide and Glycolide. **2004**, 20–23.
- 2) Tsuji, H. Poly(Lactic Acid) Stereocomplexes: A Decade of Progress. *Adv. Drug Deliv. Rev.* **2016**, 107, 97–135. <https://doi.org/10.1016/j.addr.2016.04.017>.