



## SYNTHESIZING PLA FOR A NEW APPROACH OF REACTIVE PROCESSING: RELATIONSHIP BETWEEN STRUCTURAL, THERMAL AND RHEOLOGICAL PROPERTIES

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The Polylactide (PLA) is an attractive biodegradable polymer that can be used in biomedical, packaging and pharmaceutical applications. The most efficient and usual way for the preparation of polylactides is the ring-opening polymerization (ROP) of lactide by coordination insertion. Significant progress to investigate thermal and mechanical properties of PLA has been obtained over the past decade. They depend especially on the variable optical purity on enantiomers L and D. However, few papers have been dedicated to the influence of polymerization route on the physical and the viscoelastic properties of the PLA.

This work deals to investigate the influence of catalytic polymerization on the properties of PLA. The original and robust chemistry has been developed and the relationship between structural and rheological properties was also investigated. Different PLA(s) with numerous L/D ratios have been obtained after polymerization of lactide initiated with different Metal-alkoxides in bulk at 120°C and under air. Meanwhile, Titanium (IV) alkoxide and Sn(Oct)<sub>2</sub> as no toxic catalyst have been used. The last catalyst is usually used by industrial companies under sophisticated conditions. We were able to develop a new experimental protocol to the polymerization under air using Titane as catalyst without any purification of monomer. Indeed, Poly (L, lactic-acide, PLLA), Poly (D, lactic-acide, PDLA) and the intermediate poly (DL-lactic acid) were obtained under our experimental conditions. Their stereochemistry has been controlled by the monomer composition and/or by the stereochemical preference of the initiating/ catalytic system. The molecular weights ( $\overline{M}_n, \overline{M}_w, \overline{M}_z...$ ) of the obtained PLA have been evaluated by Steric Exclusion Chromatography (SEC). The physicochemical properties of our new synthesized products were compared to those of commercially available PLA(s) used as a reference.

On the other hand, the viscosimetric properties of PLA (s) solutions have been characterized by the intrinsic viscosity. The radius of gyration of a polymeric macromolecule in a solvent were determined and compared to those of commercial PLA(s). Moreover, the structural properties (Tacticity, end of chains...) have been evaluated by NMR. The mechanical and thermal properties (T<sub>g</sub>, crystallization...) as well as their rates of degradation were also controlled depending on the catalyst system.

Finally, the rheological properties at different temperatures in linear viscoelastic regime were explored. The evolution of the viscous (i.e., loss modulus G'') and elastic (i.e., storage modulus G') properties as a function of (i) the molar mass and (ii) polydispersity for the different catalyst system were investigated. Indeed, the impact of the molar mass on the shear viscoelasticity of the PLA (s) was demonstrated. The plateau rubber value was deduced. Furthermore, relaxation times were found to increase with the molar mass despite the change of catalyst. The evolution of the zero shear viscosity ( $\eta_0$ ) for some PLAs as a function of their molar mass and stereo-regularities were reported. We have demonstrated that this evolution is not impaired by the stereo-regularity of PLA. In addition, the obtained results reveal that  $\eta_0$  is linked to Mw by a power relation with an exponent of 3.4, which is typical for linear flexible polymers.

Hence, the obtained results allowed making a clear relationship between structure and rheological properties. Our new and original approach used to synthesize PLA, with the organometallic catalyst under robust conditions, can be applied in the case of reactive processing.