

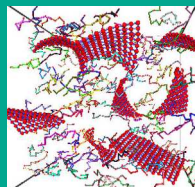


# Rheological and thermal behavior of nanocomposite PLAs with complex macromolecular architecture

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Different PLAs were synthesised from L-lactide in the presence of multifunctional comonomers and different nanoparticles; **silica and three Cloisites**



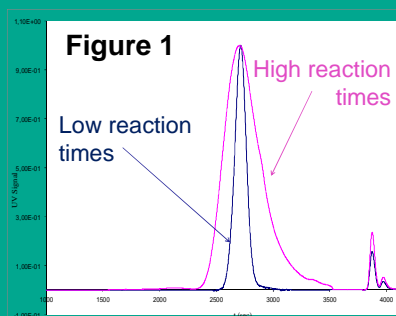
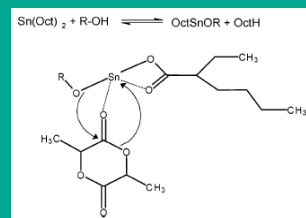
## SYNTHETIC CONDITIONS

**Bulk polymerisation at 190°C**

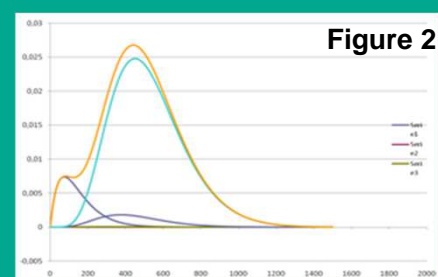
**Catalyst:** Sn(oct)<sub>2</sub>

**Comonomers and Cloisite introduced in the feed**

## PLA ROP MECHANISM



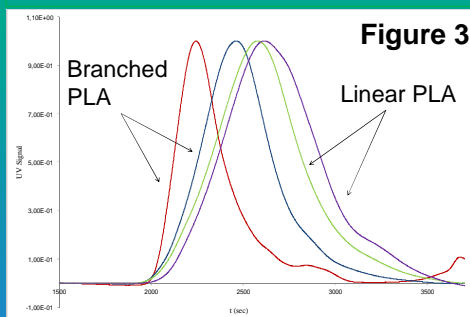
PLA ROP is like living anionic reaction; low dispersion index is observed. For longer reaction times backbiting processes can be activated; the final mixture of polymeric chains (figure 1) is similar to that predicted by equilibrium polycondensation (figure 2)



## SEC DATA (Mn, calibration in linear PLA)

Nanoparticle	0,5%	1,0%	2,0%
Nanosilice	50867	49172	24245
Cloisite Na <sup>+</sup>	55136	50569	37744
Cloisite 15A	50160	23050	16529
Cloisite 10A	39618	25600	15200

## BRANCHED PLAs



When branching comonomers are introduced, molecular weights increases (Figure 3)

Molecular masses are higher than observed in linear PLAs synthesized in the same experimental conditions.

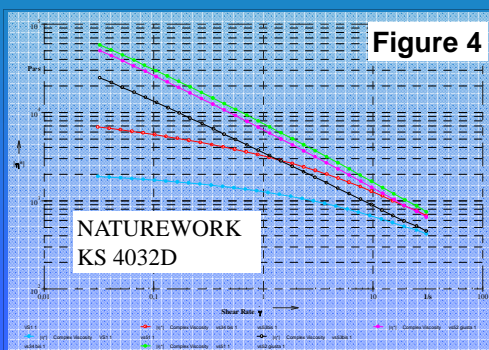


Figure 4 shows some rheological curves of our PLAs

The bottom curve refers to a linear commercial product

PLAs possessing lower melt viscosity are obtained when a pure star architecture is synthesized

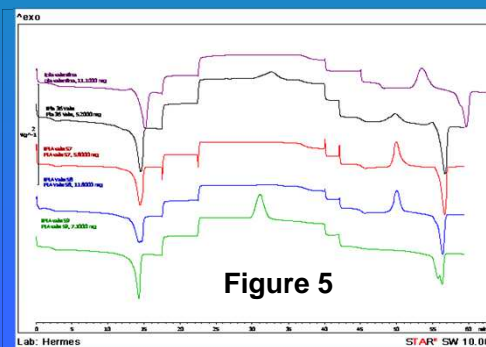


Figure 5 shows DSC curves of some PLA. Crystallization and in cold crystallization processes can be controlled

Also the thermal stability can be increased by the effect of macromolecular complexity and of the nanoparticle presence



**Figure 6**

Films cast from solution can be obtained (Figure 6)

These films possess a better gas permeability than films prepared from linear PLA

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