

ON THE USE OF TI-POSS IN THE RING OPENING POLYMERIZATION OF L-LA

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Introduction

Among the metal salts and coordination compounds studied for the ROP of lactide, also titanium-based systems have been considered. Since the pioneer work of Kricheldorf *et al.*^[1] on the use of titanium alkoxides as initiators of the polymerization of lactones, several type of Ti complexes have been studied for the ring-opening polymerization of lactide to produce PLA. Indeed, some of the above systems were capable to give also stereoselective polymerization reactions.

Among the siliceous systems, metal-containing silsesquioxane derivatives represent novel catalysts in the field of both homogeneous and heterogeneous catalysis (such as alkene polymerization, metathesis or epoxidation)^[2,3] These molecules are generally prepared from incomplete condensed structures, *i.e.* open-corner polyhedral oligomeric silsesquioxanes (POSS) molecules which can react with transition metal compounds to form metal-silsesquioxanes (M-POSS). Together with the above mentioned application, M-POSS turned out to strongly affect thermo-oxidative degradation of polymer nanocomposites.

The present work has been focused on the use of a home-made Ti-based POSS (Figure 1), which is potentially capable of being active in the ring opening polymerization (ROP) of lactide. In particular, as shown in Figure 1, the titanium centers in these compounds retain one terminal alkoxide ligand, which is ideal for the ROP via the coordination-insertion mechanism established for known metal alkoxide initiators.

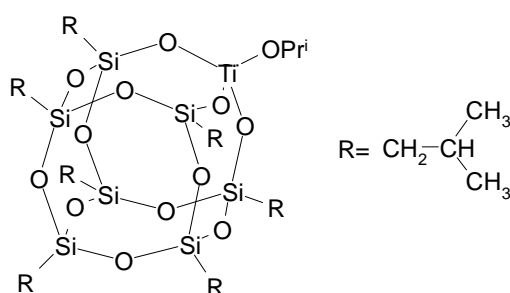


Figure 1 - Heptaisobutyl titanium-POSS (Ti-POSS)

Results and discussion

The results of bulk ROP of L-lactide (LLA), carried out at 130°C with different polymerization times (t_p) and [LLA]/[Ti] ratios, are shown in Table 1.

The linear correlation between the polymer molecular mass and monomer conversion, coupled with low PDIs, are indicative of a well controlled polymerization. Moreover, as the monomer-to-catalyst molar ratio [LLA]/[Ti] decreases from 300 to 75, the relative number-average molecular weight, M_n , decreases linearly while the PDI values of PLA remain unchanged under the conditions of the same

conversion (100%), implying the presence of a substantially controlled polymerization process. Thus, Ti-POSS turns out to have high reactivity in the controlled ROP of LA.

Table 1 - Polymerization of LLA using Ti-POSS

Entry	t_p (h)	[LLA]/[Ti]	conv. (%)	M_n	M_w	M_w/M_n	M_v
1	4	300	22	7840	9670	1.23	9000
2	6	300	48	16950	21020	1.24	19000
3	8	300	80	23500	29370	1.25	25000
4	12	300	100	28600	37180	1.30	33000
5	24	300	100	28200	38130	1.35	32000
6	24	75	100	10300	12355	1.30	11700

Moreover, $^1\text{H-NMR}$ measurements have demonstrated that POSS is chemically bound to PLA chains. On the basis of these results, it is possible to assume that the polymerization proceeds via a coordination-insertion mechanism. This process involves the insertion of lactide unit into Ti-O bond of a silsesquioxane molecule and the selective cleavage of the acyl-oxygen bond in lactide, which results in the formation of ester end group.

The evaluation of the thermal properties has evidenced that the crystallinity of the systems, prepared by using Ti-POSS as initiator, is much higher than that of commercial polymers with similar molecular masses.

Conclusion

The present work has demonstrated the possibility to use Ti-based POSS in the ROP of lactide, polymerization which occurs through a coordination-insertion mechanism. Moreover, the direct insertion of the silsesquioxane molecule to the polymer backbone, which was assessed by $^1\text{H-NMR}$ measurements, has evidenced that the M-POSS promotes not only the polymerization of L-lactide, functioning as initiator, but allows also the attainment of a hybrid system.

Another relevant aspect, which has been underlined by comparing the thermal behavior of the synthesized PLA with commercial samples, is the capability of POSS to enhance the polymer crystallinity. This finding has been ascribed to the local polymer chain deformation due to the tendency of POSS moiety, attached at one end of PLA chains, to aggregate.

References

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