

## Polymerization of $\epsilon$ -caprolactone assisted by trinuclear titanium(IV) alkoxides

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In the past few years, polynuclear alkoxides began to be employed as initiators of the polymerization of cyclic esters and lactones, demonstrating an improvement on control over the ring-opening polymerization (ROP) process. In this work, we described the synthesis of the trinuclear complex  $[\text{Ti}_3(\text{O})(\text{Cl})(\text{ONep})_9]$  (**B**) through the reaction of  $[\text{Ti}_3(\text{O}^i\text{Pr})_{11}][\text{FeCl}_4]$  (**A**)<sup>3</sup> with neopentanol. Alkoxide **B** shows titanium centers in distorted octahedral geometry connected by bridging neopentoxide ligands (ONep). The  $\mu_3\text{-O}$  and  $\mu_3\text{-Cl}$  occupy opposite sides of the  $\text{Ti}^{\text{IV}}$  triangular plane. The  $^1\text{H}$  NMR spectrum of **B** in toluene- $d_8$  at variable temperature revealed 3 signals of non-equivalent ONep in the 1:1:1 integration ratio, pointing to the maintenance of the solid state structure in solution. Polymerization of  $\epsilon$ -caprolactone ( $\epsilon\text{-CL}$ ) was carried out in toluene at various temperatures, monomer/initiator molar ratios, and reaction times. Initiators **A** and **B** were active in all conditions, producing PCL in high yields, with  $M_n(\text{GPC})$  values ranging from 3400 to 10300  $\text{g mol}^{-1}$ . Similar  $M_n$  values were found for both alkoxides, with slight advantage for **B**, which rendered a more controlled process. At 30 °C, complex **B** produced PCL with molecular weights ranging from 8600 to 9400  $\text{g mol}^{-1}$  and PDI values from 1.4 to 1.5 with high yields, while the parent alkoxide, **A**, required 24 h to achieve PCL with lower molecular weight (3400  $\text{g mol}^{-1}$ , 35% yield). Initiator **B** was shown to be independent of temperature in all conditions evaluated.  $^1\text{H}$  NMR molar masses are in agreement with those determined by GPC. The  $M_n(\text{theor})/M_n(\text{GPC})$  ratio ( $N_n$ )<sup>3</sup> was calculated, attempting to determine the average number of active ONep groups in the ROP process for each initiator. Initiator **A** showed a large range of  $N_n$  values (7.2 to 12.0) indicating breakage of the trinuclear structure into a number of unknown active species able to initiate a new polymer chain. On the other hand, the average  $N_n$  values of 5.9 for **B** are compatible with the maintenance of the polynuclear structure, with 6 terminal ONep groups being more active than the 3 bridging ( $\mu_2\text{-ONep}$ ). Kinetic studies of polymerization in bulk suggested a first order polymerization rate with monomer consumption in both cases. The estimated activation energy of 57.9  $\text{kJ mol}^{-1}$  followed in the same range as reported for **A**<sup>3</sup> (30.5  $\text{kJ mol}^{-1}$ ). The reactivity enhancement of **B** was also associated to the stronger Lewis basicity character of ONep as compared to  $\text{O}^i\text{Pr}$  and to the methylene spacer group of the ONep ligand when compared to  $\text{O}^i\text{Pr}$ , which facilitates access of the monomer to the active sites.

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<sup>2</sup>Egevardt, C.; *et al.* *J. Polym. Sci. Part A: Polym. Chem.* **2014**, 52, 2509

<sup>3</sup> Save, M.; *et al.* *Macromol. Chem. Phys.* **2002**, 203, 889