

Zinc complexes supported by maltolato ligands : synthesis, structure, solution behavior, and application in ring-opening polymerization of lactides.

Autorzy

Rafał Petrus

Piotr Sobota

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Streszczenie

A series of novel zinc alkoxides supported by chelating maltolato (MalO; MalOH = maltol) ligands were successfully synthesized and characterized. Reaction of MalOH with ZnEt_2 (3:4) gives a trinuclear cluster $[\text{Zn}_3(\text{Et})_2(\text{MalO})_4]$ (**1**), which spontaneously disproportionates in solution to mononuclear species $[\text{Zn}(\text{MalO})_2]$ (**1a**) and $[\text{Zn}(\text{Et})(\text{MalO})]$ (**1b**); (**1a**) and (**1b**) form $[\text{Zn}(\text{MalO})_2(\text{py})]$ (**2**), $[\text{Zn}(\text{Et})(\text{MalO})(\text{py})]$ (**3**), $[\text{Zn}(\text{MalO})_2]_2$ (**(1a)₂**), $[\text{Zn}(\text{MalO})(\text{OBn})]_2$ (**(1c)₂**), and $[\text{Zn}_4(\text{Et})_2(\text{OEt})_2(\text{MalO})_4]$ (**4**) on addition of pyridine, benzyl alcohol (BnOH), or dry O_2 , respectively. Compounds **1**, **2**, **(1a)₂**, and **4** were characterized by elemental analysis, NMR, ESI-MS, and single-crystal X-ray structural analysis. Variable-temperature NMR experiments showed that **(1a)₂** and **(1c)₂** are in equilibrium with the monomeric form in solution. The addition of l-lactide (l-LA) to a combination of **1** and 2 equiv of BnOH in dichloromethane at room temperature in different molar ratios leads to rapid and efficient generation of poly(l-LA) with end-capped BnO groups. According to kinetic studies, propagation by $[\text{Zn}(\text{OBn})(\text{MalO})]$ (**1c**) is first-order with respect to both the monomer and **1c** concentrations; **1a** in ring-opening polymerization of l-LA shows no activity. These results suggest a single-site active species in the ring-opening polymerization of l-LA.

Adres publiczny

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Strona internetowa wydawcy

<https://www.acs.org/content/acs/en.html>