



(Ferrocenylpyrazolyl)zinc(II) benzoates as catalysts for the ring opening polymerization of ϵ -caprolactone



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ABSTRACT

The reaction of $\text{Zn}(\text{OAc})_2$ and $\text{C}_6\text{H}_5\text{COOH}$ or 3,5- NO_2 - $\text{C}_6\text{H}_3\text{COOH}$ with 3-ferrocenylpyrazolyl-methylenepyridine (**L1**), 3-ferrocenyl-5-methylpyrazolyl-methylenepyridine (**L2**), 3-ferrocenylpyrazolyl-ethylamine (**L3**) and 3-ferrocenyl-5-pyrazolyl-ethylamine (**L4**) afford the corresponding complexes $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2(\text{L1})]$ (**1**), $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2(\text{L2})]$ (**2**), $[\text{Zn}(3,5\text{-NO}_2\text{-C}_6\text{H}_3\text{COO})_2(\text{L1})]$ (**3**), $[\text{Zn}(3,5\text{-NO}_2\text{-C}_6\text{H}_3\text{COO})_2(\text{L2})]$ (**4**), $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2(\text{L3})]$ (**5**), $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2(\text{L4})]$ (**6**), $[\text{Zn}(3,5\text{-NO}_2\text{-C}_6\text{H}_3\text{COO})_2(\text{L3})]$ (**7**) and $[\text{Zn}(3,5\text{-NO}_2\text{-C}_6\text{H}_3\text{COO})_2(\text{L4})]$ (**8**). These complexes behave as catalysts for the ring opening polymerization of ϵ -caprolactone to produce polymers with molecular weight that range from 1480 to 7080 g mol^{-1} and exhibited moderate to broad PDIs. Evidence of these complexes acting as catalysts was obtained from both the polymerization data and kinetic studies. The polymerization data show that variation of the $[\text{CL}]/[\text{C}]$ from 100 to 800 produced PCL with relatively the same molecular weight indicative of a catalyst behavior. The appearance of induction period in kinetic plots strengthens the fact that these complexes are catalysts rather than initiators. MALDI-TOF MS and ^1H NMR data show di-hydroxy end groups, which support the coordination mechanism rather than insertion mechanism.

To understand the broad PDIs obtained for some of the polymer, the electronic properties of the zinc complexes were investigated using cyclic voltammetry. The results show that the zinc complexes containing amine based ligands are highly electrophilic therefore making them unstable, hence the broad PDIs observed for zinc complexes containing amine based ligands. Among the eight complexes investigated, complex **7** is the most active catalyst with k_p value of $1.18 \times 10^{-7} \text{ h}^{-1} \text{ mol}^{-1}$ at 110 °C.

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1. Introduction

One of the widely studied polymerization processes is ring opening polymerization (ROP) of cyclic esters. Polyesters prepared by the ROP process are used in a wide range of applications such as sutures, bone fracture fixation devices, controlled drug release, tissue engineering scaffolds, green plastic wrapping materials, disposal containers and fibers [1]. As a result of these applications, it is very important to synthesize polymers with targeted molecular weights for specific purposes.

Polycaprolactone is generally prepared *via* ROP of ϵ -caprolactone and initiated by compounds such as tin [2], aluminum [3], and zinc alkoxides [4]. Among these metal alkoxides, zinc is becoming the preferred choice due to its high Lewis acidity, low

cost, ease of synthesis and low toxicity [4]. In this regard, zinc-based initiators have been extensively used and are among the highly active metal-based initiators used to date for the controlled polymerization of ϵ -caprolactone. Most of these zinc initiators have nitrogen donor ligands due to the good σ -donor abilities to form very stable complexes. For example several (β -diketinate)zinc(II) complexes act either as initiators or catalysts for the ROP of ϵ -caprolactones and tuning of the donor ability of these ligands lead to improve activities compounds [5]. Also a recent report on β -diiminate zinc(II) complexes, has shown that these complexes initiate ROP of lactides with both control of polymer stereoregularity and excellent activity [6]. This control of polymer microstructure is largely influenced by the steric bulk of the ligand used, and as such careful design of the ligand motif can result in controlled ROP of the cyclic esters.

Despite such encouraging results issues such as controlling polymer structure still remains a challenge. Therefore, the need

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