



Synthesis and characterization of Zr, Ti, Al-phthalate and pyridine-2-carboxylate compounds and their use in ring opening polymerization

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ABSTRACT

Zirconium, titanium and aluminum phthalate (PH, C₈H₄O₄) and pyridine-2-carboxylate (Pyca, C₆H₄NO₂) compounds were prepared by reaction of Zr, Ti and Al-alkoxides with phthalic acid (PHA) and pyridine-2-carboxylic acid (PycaH) in alcohol. All new complexes were characterized by a combination of elemental analysis, NMR and FTIR spectroscopy and used in polymerization of 3-glycidyloxypropyltrimethoxysilane (GPTS) in order to see their catalytic activity over epoxides. Especially, Al, Ti and Zr-phthalate catalysts were more effective in ring opening of GPTS when compared to Al, Ti and Zr-pyridine-2-carboxylate catalysts. Poly-GPTS were characterized by ¹H, ¹³C NMR and gel permeation chromatography (GPC).

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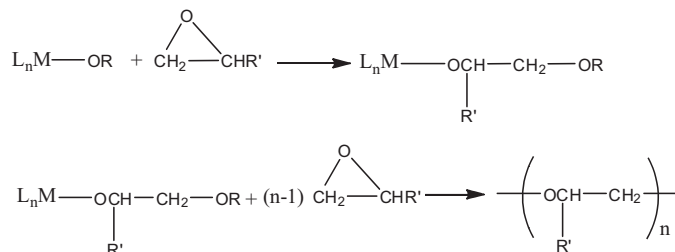
1. Introduction

Mono and dicarboxylate anions and their derivatives are useful ligands for the construction of new interesting complexes that possess oligomeric or polymeric structures [1–6]. One of the carboxylate derivatives is pyridine-2-carboxylate. Its complexes are gaining increasing attention because of their biochemical and physiological applications [7]. A great number of coordination compounds containing pyridine-2-carboxylate anions have been reported so far [8]. It has been recently demonstrated that the reactions of pyridine-2-carboxylic acid and 2,6-pyridinedicarboxylic acid with Bu₂Sn(IV)²⁺ and ^tBu₂Sn(IV)²⁺ cations result in the formation of polynuclear complexes [9–11]. In the carboxylate complexes, carboxylate groups were coordinated to the metal centers in monodentate or bridging bidentate manner [12–14]. However, the chemistry and structural properties of phthalate and pyridine-2-carboxylate zirconium(IV), titanium(IV) and aluminum(III)alkoxide complexes have not been studied yet. In the present work, the preparation and characterization of new series of metal alkoxide derivatives with the phthalic acid and of pyridine-2-carboxylic acid were reported. In addition to their synthesis and characterization, their catalytic activities over GPTS were investigated. There are a few reports that mention the use of L_nM(OR) compounds as catalysts for the polymerization of epoxides or lactides [15–19]. The chemistry of the complexes of Al,

Ti and Zr-(OR)(phthalate) and (pyridine-2-carboxylate) where OR[−] is a potentially active ligand for polymerization catalysis remains unknown.

3-Glycidyloxypropyltrimethoxysilane is one of the most commonly used epoxides for the preparation of inorganic–organic hybrid polymers which are used in several applications such as hard coatings of organic polymers, contact lens materials in the optical industry, electronics, proton exchange membrane fuel cells, membranes, nano-imprinting and waveguide [20–23]. So far, there is not enough knowledge concerning the effect of different catalysts on the epoxide ring-opening and the polymerization degree of GPTS in polymerization reactions.

Perfluoroheptanoate complexes of Zr, Ti and Al have been synthesized and characterized recently in our laboratory and used in the polymerization of GPTS [24]:



M = Zr, Ti, Al; L_n = perfluoroheptanoate

R = ⁿBu, ⁱPr, ^sBu, R' = CH₂O(CH₂)₃Si(OCH₃)₃

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