

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

Gamze Yalcin, Asgar Kayan*

Kocaeli University, Department of Chemistry, Kocaeli, 41380, Turkey

ARTICLE INFO

Article history:

Received 5 April 2012

Received in revised form 14 May 2012

Accepted 16 May 2012

Available online 24 May 2012

Keywords:

Metal alkoxides

Phthalate catalysts

Ring-opening

Pyridine-2-carboxylate catalysts

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).

© 2012 Elsevier B.V. All rights reserved.

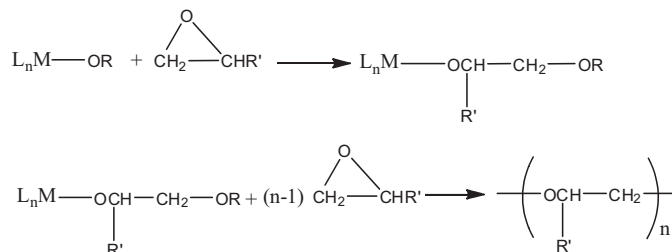
1. Introduction

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

* Corresponding author. Tel.: +90 262 3032018; fax: +90 262 3032003.

E-mail address: akayan@kocaeli.edu.tr (A. Kayan).

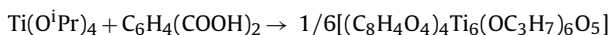
When these kinds of catalysts are used in ring opening polymerization, polymers result in controlled molecular weight and high yields at mild temperatures. Therefore, it is important to synthesize active and selective catalysts for ring opening of epoxides. It is also important to compare the activity of phthalate and pyridine-2-carboxylate-Ti, Zr and Al catalysts with published tetrafluorophthalate and perfluoroheptanoate metal catalysts [17,24]. A major interest of this study is to synthesize and characterize zirconium, aluminum and titanium phthalate and pyridine-2-carboxylate catalysts containing an active group of alkoxide. Furthermore, the activity of the Al, Ti, and Zr-phthalate and pyridine-2-carboxylate catalysts towards ring opening of GPTS constituted a major focus of this study.

2. Experimental

Aluminum(III) sec-butoxide (97%, Alfa Aesar), titanium(IV) isopropoxide (98%, Merck), zirconium(IV) n-butoxide (80%, Fluka), phthalic acid (100%, Aldrich), pyridine-2-carboxylic acid (98%, Merck) and 3-glycidyloxypropyltrimethoxysilane (97%, Alfa Aesar) were used as received. Tetrahydrofuran (THF) (99.9%, Merck), sec-butanol (99%, Merck), n-butanol (99%, Fluka) and isopropanol (99.5%, Meck) were dried over activated 4 Å molecular sieves before use. Polymer syntheses were carried out under a nitrogen atmosphere.

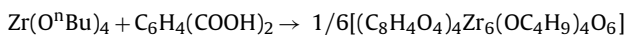
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR experiments were carried out with a Bruker 300 MHz Ultra shield TM spectrometer. Infrared spectra of complexes were recorded on Shimadzu 8201/86601 PC spectrometer. The elemental analyses were carried out on a LECO CHNS-932 elemental analyzer. Gel permeation chromatographic (GPC) analysis was performed at 30 °C on a Shimadzu prominence GPC system equipped with a RID-10A refractive index detector, a LC-20AD solvent delivery unit, a CTO-10AS column oven and a set of two columns, PSS SDV 5 μL 1000 Å and PSS SDV 5 μL 50 Å. THF (HPLC grade) was used as the mobile phase at 1.0 mL/min. The sample concentration was 2 mg/1 mL, and the injection volume was 10 μL . The calibration curve was made with seven polystyrene standards covering the molecular weight range from 162 to 34,300 Da.

2.1. Preparation of $[(\text{C}_8\text{H}_4\text{O}_4)_4\text{Ti}_6(\text{OC}_3\text{H}_7)_6\text{O}_5]$



Phthalic acid (3×10^{-3} mol, 0.50 g) was added to a solution of titanium isopropoxide (3×10^{-3} mol, 0.87 g) in 10 mL isopropanol. The reaction mixture was stirred for 3 h at room temperature. Then, the solvent isopropanol and volatile parts were removed by vacuum evaporator at 30 °C and again washed by isopropanol and dried. Elemental analysis (hexamer, $\text{C}_{50}\text{H}_{58}\text{O}_{27}\text{Ti}_6$, $M_w = 1378.18$ g/mol), $(\text{C}_8\text{H}_4\text{O}_4)_4\text{Ti}_6(\text{OC}_3\text{H}_7)_6\text{O}_5$, calcd.: C, 43.57; H, 4.24%. Found: C, 42.52; H, 4.13%. ^1H NMR, DMSO, ppm, δ : 1.04 (d, $J = 6.1$ Hz, gem-Me₂, OⁱPr), 3.76 (sept., $J = 6.17$ Hz, CH, OⁱPr), 7.58 (m, H, C₆H₄), 7.75 (m, H, C₆H₄). ^{13}C NMR, DMSO, ppm, δ : 25.95 (gem-Me₂, OⁱPr), 62.49 (OCH), 129.54 (CH=, C3, C6, C₆H₄), 131.15 (C=, C1, C2, C₆H₄), 133.68 (CH=, C4, C5, C₆H₄), 169.02 (COO). FTIR (KBr, cm^{-1}): 1700 (weak, ν_{as} C=O), 1554 (strong, ν_{as} CO₂), 1490 (C=C, Ph), 1448, 1414 (strong, ν_{s} CO₂), 1298, 1266, 1163, 1123, 1087, 1010, 946, 852, 750, 713, 692, 651, 592, 493 (Ti–O).

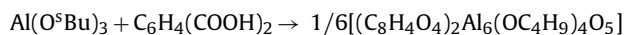
2.2. Preparation of $[(\text{C}_8\text{H}_4\text{O}_4)_4\text{Zr}_6(\text{OC}_4\text{H}_9)_4\text{O}_6]$



The reaction of phthalic acid (3×10^{-3} mol, 0.50 g) with zirconium n-butoxide (3×10^{-3} mol, 1.45 g) in 10 mL n-butanol was carried out similarly to the preceding reaction. Elemental analysis (hexamer, $\text{C}_{48}\text{H}_{52}\text{O}_{26}\text{Zr}_6$, $M_w = 1592.25$ g/mol,

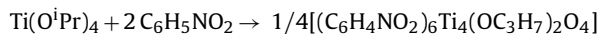
$(\text{C}_8\text{H}_4\text{O}_4)_4\text{Zr}_6(\text{OC}_4\text{H}_9)_4\text{O}_6$ calcd.: C, 36.21; H, 3.29%. Found: C, 35.63; H, 3.40%. ^1H NMR, DMSO, ppm, δ : 0.86 (t, $J = 7.2$ Hz, OⁿBu), 1.22–1.44 (m, CH₂CH₂, OⁿBu), 3.67 (t, $J = 6.3$ Hz, OCH₂, OⁿBu), 7.58 (m, H, C₆H₄), 7.71 (m, H, C₆H₄). ^{13}C NMR, DMSO, ppm, δ : 14.33 (CH₃, OⁿBu), 19.11 (CH₂CH₃, OⁿBu), 35.14 (OCH₂CH₂, OⁿBu), 65.36 (OCH₂), 129.26 (CH=, C3, C6, C₆H₄), 131.20 (C=, C1, C2, C₆H₄), 133.54 (CH=, C4, C5, C₆H₄), 169.10 (COO). FTIR (KBr, cm^{-1}): 1700 (weak, ν_{as} C=O), 1554 (strong, ν_{as} CO₂), 1492 (C=C, Ph), 1424 (strong, ν_{s} CO₂), 1298, 1264, 1149, 1085, 1039, 960, 879, 810, 752, 713, 692, 651, 474 (Zr–O).

2.3. Preparation of $[(\text{C}_8\text{H}_4\text{O}_4)_2\text{Al}_6(\text{OC}_4\text{H}_9)_4\text{O}_5]$



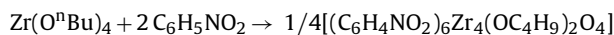
The reaction of phthalic acid (3.8×10^{-3} mol, 0.63 g) with aluminum sec-butoxide (3.8×10^{-3} mol, 0.97 g) in 10 mL sec-butanol was carried out similarly to the preceding reaction. Elemental analysis (hexamer, $\text{C}_{32}\text{H}_{44}\text{O}_{17}\text{Al}_6$, $M_w = 862.57$ g/mol), $(\text{C}_8\text{H}_4\text{O}_4)_2\text{Al}_6(\text{OC}_4\text{H}_9)_4\text{O}_5$, calcd.: C, 44.56; H, 5.14%. Found: C, 45.13; H, 5.23%. ^1H NMR, CDCl₃, ppm, δ : 0.83 (t, CH₃, O^sBu), 1.03 (d, CH₃, O^sBu), 1.32 (m, CH₂, O^sBu), 3.50 (m, CH, O^sBu), 7.57 (m, H, C₆H₄), 7.79 (m, H, C₆H₄). FTIR (KBr, cm^{-1}): 2968, 2935, 2876, 1568 (strong, ν_{as} CO₂), 1566, 1520, 1496, 1452, 1428 (strong, ν_{s} CO₂), 1295, 1263, 1149, 1110, 1091, 1029, 988, 916, 846, 818, 755, 717, 658, 614, 547 (Al–O).

2.4. Preparation of $[(\text{C}_6\text{H}_4\text{NO}_2)_6\text{Ti}_4(\text{OC}_3\text{H}_7)_2\text{O}_4]$



Pyridine-2-carboxylic acid (9.4×10^{-3} mol, 1.18 g) was added to titanium(IV) isopropoxide complex (4.7×10^{-3} mol, 1.36 g) in 10 mL isopropoxide. The reaction mixture was stirred at room temperature for 3 h. Then, the solvent and volatile parts were removed from solid product at 30 °C under low pressure by vacuum pump. Product was washed again with solvent isopropanol-hexane and dried in vacuum. Elemental analysis ($\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{18}\text{Ti}_4$, $M_w = 1106.25$ g/mol) calcd. = C, 45.60; H, 3.46; N, 7.60%. Found = C, 45.76; H, 3.48; N, 7.83%. ^1H NMR, CDCl₃, ppm, δ : 1.23 (d, gem-Me₂, OⁱPr), 4.02 (sept., CH, OⁱPr), 6.8–8.8 (m, CH, pyca). ^{13}C NMR, DMSO-d₆, ppm, δ : 25.9 (CH, OⁱPr), 62.5 (CH₃, OⁱPr), 125.8 (C3, pyca), 129.4 (C5, pyca), 141.5 (C4, pyca), 147.6 (C2, 6, pyca), 167.5 (COO). FTIR (KBr, cm^{-1}): 3078, 2970, 2928, 2868, 1678 (strong, ν_{as} CO₂), 1605 (C=N), 1570 (C=C), 1474, 1448, 1377 (strong, ν_{s} CO₂), 1285, 1256, 1153, 1047, 1020, 860, 766, 715, 694, 461, 438.

2.5. Preparation of $[(\text{C}_6\text{H}_4\text{NO}_2)_6\text{Zr}_4(\text{OC}_4\text{H}_9)_2\text{O}_4]$



The reaction of pyridine-2-carboxylic acid (9.5×10^{-3} mol, 1.19 g) with zirconium(IV) n-butoxide complex (4.7×10^{-3} mol, 2.28 g) in 10 mL butanol was carried out similarly to the preceding reaction. Elemental analysis ($\text{C}_{44}\text{H}_{42}\text{N}_6\text{O}_{18}\text{Zr}_4$, $M_w = 1307.73$ g/mol) calcd. = C, 40.41; H, 3.24; N, 6.43%. Found = C, 41.32; H, 3.39; N, 6.94%. ^1H NMR, DMSO, ppm, δ : 0.86 (t, CH₃), 1.23–1.44 (m, CH₂CH₂, OⁿBu), 4.41 (t, OCH₂, OⁿBu), 7.89 (t, CH, pyca), 7.98 (d, CH, pyca), 8.21 (t, CH, pyca), 8.68 (d, CH, pyca). ^{13}C NMR, DMSO-d₆, ppm, δ : 14.3 (CH₃, OⁿBu), 19.1 (CH₂CH₃, OⁿBu), 35.14 (CH₂CH₂, OⁿBu), 60.8 (OCH₂, OⁿBu), 125.3 (C3, pyca), 129.5 (C5, pyca), 142.5 (C4, pyca), 147.1 (C2, pyca), 149.35 (C6, pyca), 167.9 (COO). FTIR (KBr, cm^{-1}): 3109, 2957, 2932, 2872, 1678 (strong, ν_{as} CO₂), 1603 (C=N), 1568 (C=C), 1474, 1439, 1321 (strong, ν_{s} CO₂), 1288, 1240, 1155, 1097, 1022, 856, 773, 763, 694, 642, 444.

Download English Version:

<https://daneshyari.com/en/article/40891>

Download Persian Version:

<https://daneshyari.com/article/40891>

[Daneshyari.com](https://daneshyari.com)