



Preparation of Al, Ti, Zr-perfluoroheptanoate compounds and their use in ring opening polymerization

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ABSTRACT

Aluminum, titanium and zirconium perfluoroheptanoate (PFH) were prepared by reaction of Al, Ti and Zr-alkoxides with perfluoroheptanoic acid (PFHA) in alcohol. All compounds were characterized by NMR spectroscopy, FTIR, MS and elemental analysis and used in polymerization of 3-glycidyoxypropyltrimethoxysilane (GPTS) in order to see their catalytic activity over epoxides. These catalysts were effective in ring opening of epoxide. Poly-GPTS was characterized by ^1H , ^{13}C NMR and gel permeation chromatography (GPC).

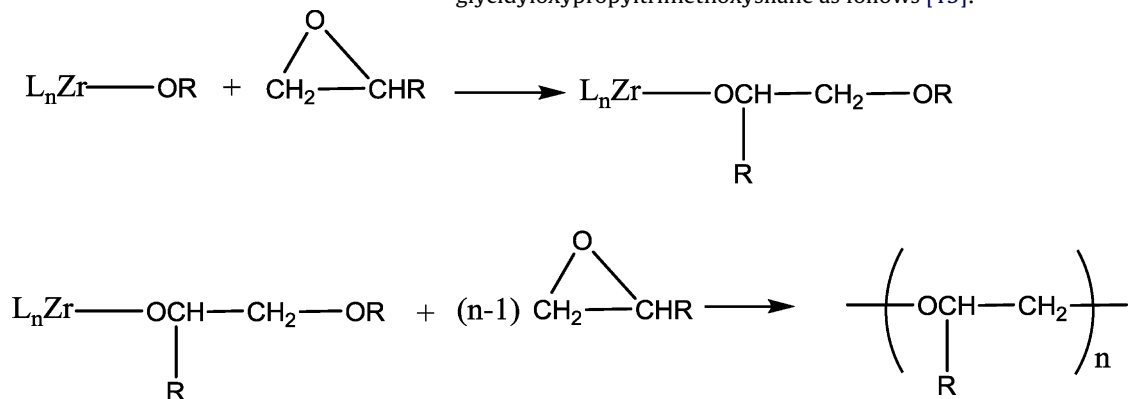
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1. Introduction

Carboxylate anions and their derivatives are useful ligands for the construction of new interesting supramolecular compounds [1–3]. Metal alkoxide complexes modified by carboxylates, β -diketonates and β -ketoesterates ligands have attracted much attention as coating materials for glasses [4,5]. Only a few reports mention the use of $L_n\text{M}(\text{OR})$ compounds as catalysts for the polymerization of epoxides [6–8]. The chemistry of the complexes of the type Al, Ti and Zr-(OR)(perfluoroheptanoate) in which OR^- is a potentially active ligand for polymerization catalysis remains unknown. Ring-opening polymerization of epoxide

monomers has been gaining much attention due to its wide range of applications [9,10]. 3-Glycidyoxypropyltrimethoxysilane is one of the most commonly used epoxides for the preparation of inorganic–organic hybrid polymers which are used, for instance, for hard coatings of organic polymers, adhesion promoters, derivatizing surfaces, contact lens materials in the optical industry, electronics, membranes, sensors, nano-imprinting and waveguide [11–15]. 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.

Tetrafluorophthalate zirconium complex was synthesized and characterized recently and used in the polymerization of 3-glycidyoxypropyltrimethoxysilane as follows [15]:



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Table 1
Data for GPTS polymers obtained from GPC measurements.

Catalyst	T (°C)	Time (h)	M _w	M _n	M _w /M _n	Conversion (%)
PFH-Ti	50	24	2300	1864	1.23	33
PFH-Ti	50	72	2438	1916	1.27	58
PFH-Ti	75	48	3764	2240	1.68	75
PFH-Al	50	24	874	719	1.22	19
PFH-Al	75	48	2909	1475	1.97	35
PFH-Zr	50	72	2833	1793	1.58	62
PFH-Zr	75	48	8672	4766	1.82	92

When these kinds of catalysts are used in ring opening polymerization, polymers result in controlled molecular weight and high yields at mild temperatures.

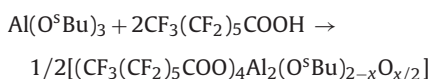
Therefore, it is important to synthesize selective and active catalysts for ring opening of epoxides. The aim of this work was to prepare and characterize aluminum, titanium and zirconium-PFH catalysts containing an active group of alkoxide by reaction of Al, Ti and Zr-alkoxides with PFHA in alcohol. Furthermore, the activity of the Al, Ti, and Zr-PFH catalysts toward 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), perfluoroheptanoic acid (99%, Aldrich), 3-glycidyoxypropyltrimethoxysilane (97%, Alfa Aesar) and tetrahydrofuran (THF) (99.9%, Merck) were used as received. Some syntheses and solvent purifications were carried out under nitrogen atmosphere.

¹H and ¹³C{¹H}NMR experiments were carried out with a Varian 500 MHz and Bruker 300 MHz Ultra shield TM spectrometer. Infrared spectra of complexes were recorded on a Shimadzu 8201/86601 PC spectrometer. The elemental analyses were carried out on a LECO CHNS-932 elemental analyzer. 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.

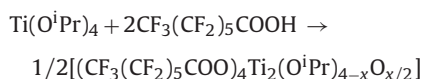
2.1. Preparation of [(CF₃(CF₂)₅COO)₄Al₂(O^sBu)_{2-x}(O)_{x/2}]



Perfluoroheptanoic acid (9.0 × 10⁻⁴ mol, 0.331 g) was added to the solution of aluminum sec-butoxide (4.5 × 10⁻⁴ mol, 0.114 g) in 10 mL sec-butanol. The reaction mixture was stirred for 3 h at room temperature. Then, the solvent sec-butanol and liberated sec-butoxide were removed from light yellow oily product by vacuum evaporator at 30 °C. MS (MALDI-TOF): (m/z = 1589.531), 1501.987, 1414.755, 1331.338, 1277.208, 1243.176, 1185.651. Elemental analysis (C₃₂H₉O_{9.5}F₅₂Al₂, M_w = 1587.29 g/mol): Calc. C, 24.21; H, 0.57%. Found: C, 24.40; H, 0.98%. ¹H NMR, CDCl₃, ppm, δ: 0.83 (t, 3H, CH₃), 1.02 (d, CH₃), 1.33 (m, CH₂), 3.48 (m, OCH, O^sBu). ¹³C NMR, CDCl₃, δ: 163.5 (broad, COO), 129.2–128.4 (d, CF₂), 125.52, 118.58 (t, CF₂), 116.32 (t, CF₂), 111.0 (t, CF₂), 108.7 (t, CF₂), 69.77–68.71 (OCH, O^sBu), 34.3–32.29 (CH₂), 24.54–23.03 (CH₃), 10.14 (CH₃). FTIR (NaCl cell, cm⁻¹): 1670.24 (ν_{as}COO),

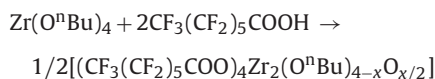
1473.51 (ν_sCOO), 1363.58 (CH), 1240.14 (CF₂), 1207.36, 1145.64, 1070.42, 669.25, 418.52.

2.2. Preparation of [(CF₃(CF₂)₅COO)₄Ti₂(OⁱPr)_{4-x}(O)_{x/2}]



The reaction of perfluoroheptanoic acid (9.0 × 10⁻⁴ mol, 0.331 g) with titanium isopropoxide (4.5 × 10⁻⁴ mol, 0.131 g) in 10 mL isopropanol was carried out under similar conditions to the preceding reaction. Elemental analysis (C₃₄H₁₄O₁₁F₅₂Ti₂, M_w = 1682.12 g/mol): Calc. C, 24.28; H, 0.84%. Found: C, 24.40; H, 0.98%. ¹H NMR (CDCl₃) ppm, δ: 1.25 (d, 6H, CH₃, OⁱPr), 1.39 (d, 6H, CH₃, OⁱPr), 4.10 (septet, OCH, H, OⁱPr), 5.27 (septet, OCH, H, OⁱPr). ¹³C NMR (CDCl₃) δ: 158.05 (br, COO), 125.52 (br, CF₂), 110.94–110.65 (d, CF₂), 108.82–108.22 (q, CF₂), 106.08–105.70 (d, CF₂), 73.87 (OCH, OⁱPr), 21.47 (CH₃). FTIR (NaCl cell, cm⁻¹): 1780.17 (medium band, νC=O), 1664.45 (very strong band, ν_{as}COO), 1446.51 (ν_sCOO), 1361.65 (CH), 1236.29 (CF₂), 1209.28, 1145.64, 1068.49, 665.40.

2.3. Preparation of [(CF₃(CF₂)₅COO)₄Zr₂(OⁿBu)_{4-x}(O)_{x/2}]



The reaction of perfluoroheptanoic acid (9.0 × 10⁻⁴ mol, 0.331 g) with zirconium n-butoxide (4.5 × 10⁻⁴ mol, 0.216 g) in 10 mL n-butanol was carried out under similar conditions to the preceding reaction. Elemental analysis (C₃₆H₂₀O₁₁F₅₂Zr₂, M_w = 1798.90 g/mol): Calc. C, 24.04; H, 1.12%. Found: C, 24.20; H, 1.17%. ¹H NMR (CDCl₃), ppm, δ: 0.95 (t, 6H, CH₃), 1.40 (m, 4H, CH₂CH₃), 1.75 (m, 4H, OCH₂CH₂), 4.40 (t, 2H, OCH₂), 4.35 (t, 2H, OCH₂). ¹³C NMR (DMSO-d₆), δ: 159 (broad (br), COO), 125.0 (br, CF₂), 110.9–110.6 (d, CF₂), 109.0–108.1 (br, CF₂), 106.08–105.60 (d, CF₂), 68.75 (OCH, OⁿBu), 30.31 (CH₂), 19.0 (OCH₂CH₂), 13.66 (CH₃). FTIR (NaCl cell, cm⁻¹): 1784.03 (w band, νC=O), 1683.74–1664.45 (s band, ν_{as}COO), 1444.58 (ν_sCOO), 1359.72 (CH), 1257.50 (CF₂), 1215.07, 1157.21, 1068.49, 663.47.

2.4. Polymerization of GPTS with [(CF₃(CF₂)₅COO)₄Zr₂(OⁿBu)_{4-x}(O)_{x/2}]

The catalyst ((CF₃(CF₂)₅COO)₄Zr₂(OⁿBu)_{4-x}(O)_{x/2}, 50 mg) was taken in a vial and 1.5 mL of GPTS was added under nitrogen. The mixture was stirred at different temperatures and time intervals as seen in Table 1. Data for 75 °C and 48 h: ¹H NMR (CDCl₃), ppm, δ: 4.06 (CH, br), 3.63–3.28 (CH₃O, CH₂, CH₂O, brs), 3.26 (CH₂CH₂CH₂Si), 1.60 (CH₂, m, CH₂CH₂CH₂Si), 0.57 (CH₂-Si, br). ¹³C NMR (CDCl₃), δ: for CH region: 71.42–71.38 (CH, diad, i/s), 70.81–70.78 (CH, diad, i/s), 59.08 (CH, diad, i/s). For CH₂ region: 74.49–74.45 (CH₂, diad, i/s), 73.80 (CH₂, diad, i/s).

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