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

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A R T I C L E   I N F O

Article history:
Received 5 January 2012
Received in revised form 16 February 2012
Accepted 26 February 2012
Available online 5 March 2012

Keywords:
Catalyst
Metal alkoxides
Perfluoroheptanoate
Ring-opening

A B S T R A C T

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-glycidoxypropyltrimethoxysilane (GPTS) in order to see their catalytic activity over epoxides. These catalysts were effective in ring opening of epoxide. Poly-GPTS was characterized by \(^1H\), \(^13C\) 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, \(\beta\)-diketonates and \(\beta\)-ketoesters ligands have attracted much attention as coating materials for glasses [4,5]. Only a few reports mention the use of \(\text{LnM(OR)}\) compounds as catalysts for the polymerization of epoxides [6–8]. The chemistry of the complexes of the type \(\text{Al, Ti and Zr-(OR)}(\text{perfluoroheptanoate})\) 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-Glycidoxypropyltrimethoxysilane 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.

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

\[
\begin{align*}
\text{L}_n\text{Zr-OR} + \text{CH}_2=\text{CHR} & \rightarrow \text{L}_n\text{Zr-OCCH}_2\text{OR} \\
\text{L}_n\text{Zr-OCH}_2\text{OR} + (n-1)\text{CH}_2=\text{CHR} & \rightarrow (\text{OCH}_2\text{CH}_2)^n
\end{align*}
\]
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-PF 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-PF 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-glycidyloxypolytrimethoxysilane (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 13C1H[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 8200/86601 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 A and PSS SDV 5 μL, 50 A. THF (HPLC grade) was used as the mobile phase at 1.0 mL/min. The sample concentration was 2 mg/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)2COO)4Al2(OBu)2-δ(δ(ch3)δ(ch3))δ(ch3)]

Al(OBu)δ + 2CF2(CF2)3COOH → 1/2[(CF3(CF2)2COO)4Al2(OBu)2-δ(δ(ch3))δ(ch3)]

Perfluoroheptanoic acid (9.0 x 10⁻⁴ mol, 0.331 g) was added to the solution of aluminum sec-butoxide (4.5 x 10⁻⁴ mol, 0.114 g) in 10 mL sec-butoxyl. The reaction mixture was stirred for 3 h at room temperature. Then, the solvents sec-butoxyl and liberated sec-butoxide were removed from light yellow oily product by vacuum evaporator at 30 °C (MALDI-TOF: m/z = 1589.53), 1501.987, 1414.755, 1331.338, 1277.208, 1243.176, 1185.651. Elemental analysis (C23H20O11F52Zr2, Mw = 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, OBu). 13C NMR, CDCl3, ppm, 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), 69.77–67.81 (OCH, OBu), 34.3–32.29 (CH2), 24.54–23.03 (CH3), 10.14 (CH3). FTIR (NaCl cell, cm⁻¹): 1670.24 (vₛ,COO), 1473.51 (vᵢ,COO), 1363.58 (CH), 1240.14 (CF2), 1207.36, 1145.64, 1070.42, 669.25, 418.52.

2.2. Preparation of [(CF3(CF2)2COO)4Ti2(OiPr)4-δ(δ(ch3))δ(ch3)]

Ti(OiPr)3 + 2CF2(CF2)3COOH →

1/2[(CF3(CF2)2COO)4Ti2(OiPr)4-δ(δ(ch3))δ(ch3)]

The reaction of perfluoroheptanoic acid (9.0 x 10⁻⁴ mol, 0.331 g) with titanium isopropoxide (4.5 x 10⁻⁴ mol, 0.131 g) in 10 mL isopropanol was carried out under similar conditions to the preparation reaction. Elemental analysis (C36H20O11F52Zr2, Mw = 1682.12 g/mol): Calc. C, 24.28; H, 0.84%. Found: C, 24.90; H, 0.98%. 1H NMR (CDCl3), ppm, δ: 0.89 (t, 6H, CH3, OPr), 3.98 (d, 6H, CH3, OPr), 4.10 (septet, OCH, H, OPr), 5.37 (septet, OCH, H, OPr). 13C NMR (CDCl3), ppm, δ: 158.35 (br, COO), 125.25 (br, CF2), 110.94–110.65 (d, CF2), 108.82–108.22 (q, CF2), 106.8–106.70 (d, CF2), 73.87 (OCH, OPr), 21.47 (CH3), FTIR (NaCl cell, cm⁻¹): 1780.17 (medium band, vₛ,COO), 1664.45 (very strong band, vᵢ,COO), 1446.51 (vᵢ,COO), 1361.65 (CH), 1236.29 (CF2), 1209.28, 1145.64, 1068.49, 665.40.

2.3. Preparation of [(CF3(CF2)2COO)4Zr2(OBu)4-δ(δ(ch3))δ(ch3)]

Zr(OBu)δ + 2CF2(CF2)3COOH → 1/2[(CF3(CF2)2COO)4Zr2(OBu)4-δ(δ(ch3))δ(ch3)]

The reaction of perfluoroheptanoic acid (9.0 x 10⁻⁴ mol, 0.331 g) with zirconium n-butoxide (4.5 x 10⁻⁴ mol, 0.216 g) in 10 mL n-butanol was carried out under similar conditions to the preceding reaction. Elemental analysis (C36H20O11F52Zr2, Mw = 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), ppm, 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, OBu), 30.31 (CH2), 19.0 (OCH2CH2), 13.66 (CH3), FTIR (NaCl cell, cm⁻¹): 1784.03 (w band, vₛ,COO), 1683.74–1644.45 (s band, vᵢ,COO), 1444.58 (vᵢ,COO), 1359.72 (CH), 1257.50 (CF2), 1215.07, 1157.21, 1068.49, 663.47.

2.4. Polymerization of GPTS with [(CF3(CF2)2COO)4Zr2(OBu)4-δ(δ(ch3))δ(ch3)]

The catalyst ([(CF3(CF2)2COO)4Zr2(OBu)4-δ(δ(ch3))δ(ch3)], 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, CH2CH2CH2), 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).
Other signals: 73.70, 73.53 (CH$_2$ from O–(CH$_2$–CH$_2$–), 72.43, 72.20–72.23 (CH$_2$ from ring–CH$_2$–O), 50.49 (CH$_2$O), 22.84–22.94 (CH$_2$ from CH$_2$=CH$_2$CH$_2$), 7.19, 6.08 (CH$_2$–Si). Similar $^1$H, $^{13}$C NMR data were obtained for polymers prepared with Al and Ti-perfluoroheptanoate catalysts.

3. Results and discussion

Reactions of $\text{M}$(OR)$_m$ ($\text{M}$-OR: Ti-OiPr, Zr-OiPr, Al-OiPr, m: 4 for Ti and Zr, m: 3 for Al) with perfluoroheptanoic acid with 1:2 molar ratio in alcohol at room temperature gave the product of (C$_6$F$_{13}$COO)$_m$M$_2$O$_{2m/2}$(OR)$_{m-2-x}$, in accordance with the following reaction:

$$\text{M}$(OR)$_m$ + 2C$_6$F$_{13}$COOH → 1/2[(C$_6$F$_{13}$COO)$_m$M$_2$O$_{2m/2}$(OR)$_{m-2-x}$]

Some of the alkoxy groups undergo condensation reaction to form oxo group in the presence of strong acid like perfluoroheptanoic acid. The number of oxo group determined by elemental analysis and NMR measurements changes between zero and one (0 < oxo < 1.0) depending on the reaction time and temperatures. The structures of complexes can be drawn as seen in Scheme 1.

The FTIR spectrum of free perfluoroheptanoic acid exhibits intense band at 1775 cm$^{-1}$ corresponding to asymmetrical stretching vibrations of the carboxyl group [16]. After coordination of PFH to aluminum alkoxide, the band shifts to low wave numbers ~1670 and 1473 cm$^{-1}$. The carboxyl bands appear at 1670 cm$^{-1}$ for sCOO$_{\text{asym}}$ and 1473 cm$^{-1}$ for sCOO$_{\text{sym}}$. In the FTIR spectrum of perfluoroheptanoato-Al(III) complex the band at ~1670 cm$^{-1}$ indicates the existence of chelating carboxylic groups. In titanium and zirconium perfluoroheptanoate compounds, PFH groups bond to metals in both forms of monodentate at ~1780 cm$^{-1}$ and bidentate at ~1670–1680 cm$^{-1}$ (Fig. 1). All of these values are consistent with those detected in a number of carboxylate-metal compounds [17,18].

The $^1$H NMR spectra of perfluoroheptanoato-Al, Ti, and Zr complexes show expected peaks and peak multiplicities. For example, $^1$H NMR spectrum of Ti-complex showed doublet at 1.39, 1.25 ppm because of gem-dimethyl protons and septets at 5.27 (bridge OiPr), 4.10 (terminal or weak bridge OiPr) ppm for CH proton of isopropoxy groups in Ti-complex. The signal for the COOH proton is absent (Fig. 2). Lack of a carboxylic acid proton signal at around 11 ppm indicates that PFHA is completely coordinated to titanium.

The $^{13}$C NMR spectra of the metal complexes show shifts for the carboxylate carbon resonances compared with that of the free perfluoroheptanoic acid molecule. The peaks at δ = 163.5 and 158 ppm are attributed to the −COO$^-$ groups in Al-PFH and Ti-PFH complexes, respectively. The chemical shifts and coupling constants given in Section 2 are in agreement with reported values [18,19].

Polymer samples obtained from ring opening polymerization of GPTS were characterized by $^1$H, $^{13}$C NMR, FTIR and gel permeation chromatography (GPC). The data were consistent with previously published $^{13}$C NMR data for this polymer [15]. $^1$H NMR spectrum shows that main changes occur at the CH and CH$_2$ protons of epoxy when GPTS is polymerized. The CH and CH$_2$ protons shift to higher value 3.8–4.30 ppm from 2.30 and 2.96 ppm. These values are consistent with those in the literature [20]. The $^{13}$C NMR spectrum of pure GPTS shows seven peaks which are attributed to the seven carbon atoms as follows:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bonded to</th>
<th>Multiplicity</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$-O</td>
<td>H</td>
<td>s</td>
<td>54.3</td>
</tr>
<tr>
<td>CH$_2$O-CH$_2$</td>
<td>H</td>
<td>s</td>
<td>54.3</td>
</tr>
<tr>
<td>CH$_2$O-CH$_2$</td>
<td>H</td>
<td>d</td>
<td>53.9</td>
</tr>
<tr>
<td>CH$_2$-Si(OCH$_2$)$_2$</td>
<td>H</td>
<td>d</td>
<td>73.18</td>
</tr>
</tbody>
</table>

$^{13}$C NMR data of GPTS polymers were given in Section 2. Both regioisomers are formed due to the two directions of ring opening of epoxide but the major regioisomer –(OCHRCH$_2$)$_n$– predominates by ca. 0.80:0.20 (R=CH$_2$OCH$_2$CH$_2$Si(OCH$_3$)$_3$)

The methine and methylene signals in $^{13}$C NMR spectrum at ~71.40 (diad, i/s) and 74.49 (diad, i/s) ppm correspond to major regioisomeric polymer. The methine carbon peaks at 70.81–70.78 (diad, i/s) ppm region correspond to minor regioisomeric polymer. The methine carbon resonances at 71.40 ppm region appear as two signals readily assignable to the diads (i and s). This can be attributed to different stereosequences due to its asymmetric methine carbon. The peaks at 7.19, 6.08 ppm (from CH$_2$-Si) in $^{13}$C NMR spectrum also indicate that different regiosequences exist.

These data are consistent with the literature data for epoxide [23]. These data suggest that first GPTS attacks to metal-center and
Fig. 1. FTIR spectra of Ti and Zr-PFH complexes.

then the nucleophile OR⁻ ion attacks CH₂–O carbon atom in GPTS as seen in Scheme 2.

The side silyl group of 3-glycidoxypropyltrimethoxysilane has more stereoselective effect on stereosequences when compared to the methyl group of propylene oxide [24]. The perfluoroheptanoate-Ti, Zr and Al catalysts were very effective for the polymerization of GPTS with the maximum recovery rate of polymer. The maximum polymerization rate of GPTS occurred at 75 °C (mild temperatures). Even, they were effective for the polymerization of GPTS at room temperature. Mainly one regioisomer was formed due to the ring opening of epoxide from CH₂–O bond under reaction conditions. These new complexes were better catalysts than the known acid catalysts for ring opening of epoxide. The known acid catalysts were effective at high temperatures (90–120 °C) and caused regio and stereo irregular polymers [10]. The conversion of monomer GPTS to polymer was monitored by GPC measurements. The polymerization rate of GPTS decreases in the order of \(\left[(C_8H_6F_3COO)_2Zr_2O_4/2(OEtBu)^{m-2-x}\right]\) to \(\left[(C_8H_6F_3COO)_2Al_2O_4/2(OEtBu)^{m-2-x}\right]\) catalysts.

Experimental data support that the alkoxide group bound to metal is active group to ring opening of epoxide. Zr-catalyst is more reactive than Ti-catalyst. The perfluoroheptanoate ligands bond to titanium alkoxide in both monodentate and bidentate forms. However, the PFH bonds to zirconium mostly in bidentate form. This chelate bond causes to decrease the strength of alkoxide bond and increases the formation of polymer. The other possibility is the size of zirconium ion which is large cation. Therefore, an epoxide can easily attack to zirconium center to form a polymer. These data are consistent with the data published by Hoebbels and his research group [25]. These new complexes were good catalysts for ring opening of epoxide when compared to the known acid catalysts. For example, when the compounds \(\text{Al}(\text{OEt}0\text{Bu})_3\), \(\text{Sn}(O^\delta\text{Bu})_4\), \(\text{Al}(O^\delta\text{Bu})_3\), \(\text{Ti}(O^\delta\text{Et})_4\) and \(\text{Zr}(O^\delta\text{Bu})_4\) were used as catalysts for ring opening of GPTS, they were only effective in higher metal alkoxide concentration (10 mol%) in the presence of HCl(aq) [25]. Besides, the known acid catalysts mentioned above were neither regio nor stereoselective in polymerization of epoxide because of many alkoxide groups bound to metals.

Gel permeation chromatography was also used to determine the conversion of monomers to polymers, molecular weight and the molecular weight distribution index of polymers. By varying the reaction time intervals and temperatures, the polymers with different weight average or number average molecular weights were obtained (Table 1). For the polymers of GPTS prepared with by PFH-Zr stirring at 50 °C for 3 days, the main peak appeared at weight average molecular weight \((M_w)\) 2833 Da or number average molecular weight \((M_n)\) 1793 Da. The ratio of the weight average molecular weight to the number average molecular weight \((M_w/M_n)\) was 1.58. When the temperature was increased from 50 to 75 °C, the conversion of monomers to polymers increased from 62% to 92% for zirconium catalyst (Fig. 3).

FTIR studies support the polymerization of GPTS. The monomer of GPTS shows characteristic bands at 2842–2950 \((\nu\text{ vibration of CH groups, } v_\text{c})\), 1461 \((\text{CH}_2\text{ due to stretching})\), 1250 \((\nu_\text{as})\), 810–950 \((\nu_\text{as})\), 750–840 \((\nu_\text{as})\), cm⁻¹ due to the symmetric and asymmetric vibrations of ring stretch of the epoxy group of GPTS \([15,21]\). When GPTS undergoes polymerization, the peak at 1250 cm⁻¹ disappears in the FTIR spectrum. This disappearance supports a ring opening reaction of GPTS \([21,26]\). GPTS exhibits a strong absorption at 1090 cm⁻¹ due to the Si(−O−C). For poly-GPTS, the Si(−O−C) absorption appears at 1100 cm⁻¹. All these data support the polymerization of GPTS.

4. Conclusions

As a conclusion, the findings of the present study indicated that perfluoroheptanoate was versatile ligand for modification of Al, Zr and Ti-alkoxides. These three new catalysts were characterized by spectroscopic methods and elemental analysis. The perfluoroheptanoate ligands were bonded to titanium and zirconium alkoxide in both monodentate and bidentate forms. The prepared catalysts were very effective for the polymerization of GPTS at room and mild temperatures. The polymerization of GPTS displays the highest polymerization rate at 75 °C. Mainly one regioisomer was formed due to the ring opening of epoxide from CH₂–O bond. Isotactic/syndiotactic polymers were obtained and characterized by NMR, FTIR and gel permeation chromatography (GPC). The polymerization rate of GPTS decreased in the order of Zr > Ti > Al-catalysts. This is due to the large size of zirconium and the chelate bond formation of PFH which decrease the strength of alkoxide bond and increase the formation of polymers. GPC measurements showed that the polymerization had a characteristic of living polymerization with perfluoroheptanoate metal catalysts. In summary, these complexes were good catalysts for ring opening of epoxide when compared to the known acid catalysts.

Acknowledgment

This work was supported by the research foundation of Kocaeli University (project No: 2009/034).

References