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Synthesis and characterization of Ti-/Zr-diphenylpropanedione complexes and their application in the ring opening polymerization of Ɛ-caprolactone

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Abstract: The purpose has been to achieve a controlled ring-opening polymerization of ε-caprolactone, resulting in polymers with desirable properties such as high molecular weight, low polydispersity index, and highly regio-/stereo regular forms. Therefore, it is important to synthesize single site or reduced number of active site metal alkoxide compounds as catalysts. Ti(IV)/Zr(IV) diphenylpropanedione complexes were synthesized by reactions of titanium or zirconium alkoxides with diphenylpropanedione (dion) ligand. The obtained complexes were characterized by nuclear magnetic resonance (^{1}H-, ^{13}C-NMR), high resolution mass (HRMS), Fourier transform infrared (FTIR) spectroscopies and elemental analysis. These compounds were tested as catalysts for the ring opening polymerization of Ɛ-caprolactone. The structure of poly-caprolactone (PCL) was analyzed by some spectroscopic techniques (NMR, FTIR) and gel permeation chromatography (GPC). In this work, all Ti-/Zr-complexes were effective over polymerization of Ɛ-caprolactone in solventless environment. Consequently, Ɛ-caprolactone polymers were obtained different average molecular weights between 7000-34000 Da with the PDI values of 1.14-1.60.

Keywords: Metal alkoxide, catalyst, ring opening, diphenylpropanedione.

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INTRODUCTION

The reactions between tetraalkoxy titanium or zirconium precursors and β-diketones and β-diketoesters have been known for over 30 years. Structures of titanium and zirconium β-diketonate complexes for the ethoxide, *n*-propoxide and other derivatives were prepared by different research groups (1-4). The allylacetoacetate and other derivatives were later prepared by Hoebbel, Schubert and co-workers (5-7). However, it is still unclear whether the complexes are monomeric, dimeric or oligomeric. For example, [Ti(acac)(OMe)$_3$]$_2$ compound is binuclear, centrosymmetric structures with asymmetric alkoxide bridges (8). In the reactions of titanium or zirconium alkoxides with β-diketonates, β-diketoesters and carboxylates the third or fourth alkoxy groups are not replaced with these organic chelate ligands because of a preferred coordination number of six or higher for metals (9,10).

It is important to stabilize the titanium or zirconium center with β-diketone ligand and also important to reduce the number of active alkoxy groups to prepare single-site or double-site titanium or zirconium complexes for catalytic activity. There are many examples of the use of metal-alkoxides based catalytic systems in polymerization reactions for manufacturing polymeric substances such as polyether, polylactone, and poly-lactides (11-

14). Due to their biocompatibility and biodegradability, these polymers have a lot of potential usage in medical, agricultural, and packaging areas (12-15).

Catalysts including single-site or reduced number of alkoxide groups stabilized with β-diketone have had a breakthrough impact in polymer synthesis. With the aim of these catalysts' molecular weights, molecular weight distributions and stereochemistry of polymers and copolymers can be controlled (15). The general formula of these catalysts are LnMOR or LnM(OR)2 (M:Metal, Ln: β-diketone) where the OR is an alkoxy group that initiates the polymerization (16,17).

In this study, our main objective is to prepare single site or double sites active catalysts by using different mole ratio of metal alkoxides and diphenylpropanedione and to characterize their structure by a combination of FTIR, ^{1}H-NMR, ^{13}C-NMR, HRMS spectroscopies and elemental analysis technique. The second objective is to see their catalytic efficiency on the ring opening polymerization of Ɛ-caprolactone. Finally, it is also important to characterize poly-ε-caprolactone by gel permeation chromatography (GPC), ^{1}H-NMR and ^{13}C-NMR, and FTIR spectroscopies.

EXPERIMENTAL

Materials and Instrumentation

Zirconium(IV) butoxide ($C_{16}H_{36}O_4Zr$, %80, Aldrich), zirconium(IV) propoxide ($C_{12}H_{28}O_4Zr$, %70, Aldrich), titanium(IV) butoxide ($C_{16}H_{36}O_4Ti$, %97), titanium(IV) isopropoxide ($C_{12}H_{28}O_4Ti$, %97, Aldrich), 3-diphenyl-1,3-propanedione ($C_{15}H_{12}O_2$, %98, Aldrich), and Ɛ –caprolactone ($C_6H_{10}O_2$, Alfa Aesar) were used as received. Solvents such as n-butanol (C_4H_9OH, 99%, Aldrich), isopropanol (C_3H_7OH, Aldrich), and others were dried over activated 4 Å molecular sieves before use. Polymerization reactions were carried out under nitrogen atmosphere.

The infrared spectra of synthesized compounds and PCL were recorded on a Bruker Tensor 27 FTIR spectrometer using single reflection ATR universal plate of diamond crystal. The Ti-/Zr-compounds, and PCL were scanned from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. ^{1}H and ^{13}C[^{1}H]NMR measurements were carried out with a Bruker 400 MHz spectrometers. The elemental analyses were carried out on a LECO CHNS-932 elemental analyzer.

Mass spectrometry (SCIEX 4000 QTRAP LC–MS/MS, HRMS) were used for measuring the molecular masses of complexes with electrospray ionization (ESI ±) method. 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 CTO10AS 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 10 mg/5mL and the injection volume was 50 µL. The calibration curve was made with polystyrene standards covering the molecular weight range from 162 to 34,300 Da.

Reaction of titanium(IV) butoxide with 1,3-diphenyl-1,3-propanedione in 1:1 mole ratio (1)

The reaction of 1,3-diphenyl-1,3-propanedione ($2.0x10^{-3}$ mol, 0.46 g) with titanium n-butoxide ($2.0x10^{-3}$ mol, 0.70 g) in 20 mL of n-butanol was carried out similarly to the preceding reaction. ^{1}H-NMR($CDCl_3$, ppm): δ 1.03 (t, CH_3, OBu), 1.53 (m, CH_3-$C\underline{H}_2$, OBu), 1.78 (pentet, $C\underline{H}_2$-CH_2O, OBu), 3.73 (t, J=6.40 Hz, CH_2O, OBu, *cis* to dion), 4.74 (t, J= 6.56 Hz, CH_2O, OBu, *trans* dion), 7.07 (1H, OC-$C\underline{H}$=, dion), 7.38 (2H, C_6H_5, dion), 7.46 (1H, C_6H_5, dion), 7.62 (3H, C_6H_5, dion), 7.94 (2H, C_6H_5, dion), 8.30 (2H, C_6H_5, dion). ^{13}C- NMR ($CDCl_3$, ppm): δ 14.10 (CH_3, OBu), 19.39 (CH_3-$\underline{C}H_2$, OBu), 35.30 ($\underline{C}H_2$-CH_2O , OBu) , 73.17 (CH_2O, OBu, *cis* to dion), 76.82 (CH_2O, OBu, *trans* to dion), 94.93 (OC-CH_2-CO, dion, keto-form, the ratio of keto to enol form is ~1/5), 96.13 (dyad, OC-$\underline{C}$H=, dion), 127.81-138.64 (C=C, C_6H_5, dion), 182.29 (CH=$\underline{C}$-O, dion, enol form), 184.84 (C=O, dion). FTIR (cm^{-1}): 3056, 2954, 2927, 2869, 2838, 1594, 1546, 1518, 1476, 1363, 1222, 1071, 745, 682, 617, 430. Mass spectrum: 529.184 Da for molecular ion $[Ti(OBu^n)_3(dion) +K]^+$ ($=TiC_{27}H_{38}O_5+K^+$) or $[Ti(OBu^n)_3(dion) +H]^+$ ($=TiC_{27}H_{38}O_5+H^+$).

Reaction of titanium(IV) butoxide with 1,3-diphenyl-1,3-propanedione in 1:2 mole ratio (2)

The reaction of 1,3-diphenyl-1,3-propanedione ($4.0x10^{-3}$ mol, 1.0 g) with titanium n-butoxide ($2.0x10^{-3}$ mol, 0.70 g) in 20 mL of n-butanol was carried out similarly to the preceding reaction. ^{1}H-NMR($CDCl_3$, ppm): δ 0.95 (t, CH_3, J=7.4 Hz, OBu), 1.54 (CH_3-$C\underline{H}_2$, OBu), 1.79 (pentet, $C\underline{H}_2$-CH_2O, OBu), 4.74 (t, CH_2O, J=6.58 Hz, OBu), 7.07 (2H, OC-$C\underline{H}$=, dion), 7.40 (4H, C_6H_5, dion), 7.49 (2H, C_6H_5, dion), 7.64 (6H, C_6H_5, dion), 7.95 (4H, C_6H_5, dion), 8.30 (4H, C_6H_5, dion). ^{13}C- NMR ($CDCl_3$, ppm): δ 14.14 (CH_3, OBu), 19.37 (CH_3-$\underline{C}H_2$, OBu), 35.31 ($\underline{C}H_2$-CH_2O, OBu) , 78, 60, 76.84 (CH_2O, OBu), 96.12 (dyad, OC-$\underline{C}$H=, dion), 127.83-137.97 (C=C, C_6H_5, dion), 182.28 (CH=$\underline{C}$-O, dion, enol form), 184.82 (C=O, dion). FTIR (cm^{-1}): 3055, 2954, 2926, 2885, 2837, 1592, 1542, 1517, 1470, 1451, 1366, 1313, 1299, 1226, 1071, 1022, 749, 714, 685, 550. Elemental analysis, $C_{38}H_{40}O_6Ti$ (640.59 g/mol): Calc. C 71.25, H 6.29% ; found: C 69.20, H 6.70%. Mass spectrum: 641.2386 Da for molecular ion $[Ti(OBu^n)_2(dion)_2 + H]^+$ ($=TiC_{38}H_{40}O_6+H^+$).

Reaction of titanium(IV) isopropoxide with 1,3-diphenyl-1,3-propanedione in 1:1 mole ratio (3)

The reaction of 1,3-diphenyl-1,3-propanedione ($2.0x10^{-3}$ mol, 0.46 g) with titanium iso-propoxide ($2.0x10^{-3}$ mol, 0.59 g) in 20 mL of isopropanol was carried out similarly to the preceding reaction. ^1H-NMR($CDCl_3$, ppm): δ 1.29 (d, J=6.12 Hz, CH_3, OPr^i), 5.05 (septet, J=6.15 Hz, OCH, OPr^i), 7.02 (H, OC-C$\underline{H}$=, dion), 7.38 (m, 2H, C_6H_5, dion), 7.46 (t, 1H, J= 6.92 Hz, C_6H_5, dion), 7.60 (m, 3H, C_6H_5, dion), 7.92 (d, 2H, J= 7.5 Hz, C_6H_5, dion), 8.25 (d, 2H, J= 7.0 Hz, C_6H_5, dion). FTIR (cm^{-1}): 3060, 2980, 2930, 2870, 1592, 1548, 1520, 1465, 1360, 1330, 1120, 1005, 940, 860, 618, 460. Elemental analysis, $C_{24}H_{32}O_5Ti$ (448.37 g/mol): Calc. C 64.29, H 7.19% ; found: C 62.90, H 6.65%.

Reaction of titanium(IV) isopropoxide with 1,3-diphenyl-1,3-propanedione in 1:2 mole ratio (4)

The reaction of 1,3-diphenyl-1,3-propanedione ($4.0x10^{-3}$ mol, 1.0 g) with titanium isopropoxide ($2.0x10^{-3}$ mol, 0.59 g) in 20 mL of isopropanol was carried out similarly to the preceding reaction. ^1H-NMR ($CDCl_3$, ppm): δ 0.94 (CH_3, OPr^i), 3.57 (CHO, OPr^i), 7.62 (OC-CH=, dion), 7.30-7.89 (CH=, C_6H_5 ,dion). Elemental analysis, $C_{36}H_{36}O_6Ti$ (612.53 g/mol): Calc. C 70.59, H 5.92% ; found: C: 69.08, H: 6.37%.

Reaction of zirconium(IV) butoxide with 1,3-diphenyl-1,3-propanedione in 1:1 mole ratio (5)

1,3-diphenyl-1,3-propanedione ($2.0x10^{-3}$ mol, 0.46 g) was added to a solution of zirconium(IV) butoxide ($2.0x10^{-3}$ mol, 0.96 g) in 20 mL of n-butanol. The reaction mixture was stirred for three hours at 35 °C over an oil bath. Then, the solvent was removed by rotary evaporator at 50 °C under vacuum. ^1H-NMR (DMSO, ppm): δ 0.709 (CH_3, OBu) , 1.14 (CH_3-C$\underline{H}_2$- , OBu), 1.25 (C$\underline{H}_2$-CH_2O , OBu), 4.1 (CH_2O, OBu), 7.3-7.7 (C_6H_5, dion) 7.9 (OC-CH=, dion). ^{13}C- NMR (DMSO, ppm): δ 13.8 (CH_3, OBu), 18.6 (CH_3-$\underline{C}H_2$, OBu), 34.6 ($\underline{C}H_2$-CH_2O, OBu), 70.7 (CH_2O, OBu), 95.05 (CO-$\underline{C}$H=, dion), 127-137 (C_6H_5, dion), 182.9 (C_6H_5-$\underline{C}$O, dion). FTIR (cm^{-1}): 3060 (CH=C, asym str), 3027 (CH=, Ph), 2953 (sp^3-CH, asym str), 2868 (sp^3-CH, asym str), 1594 (C=C, Ph), 1546 (C=O, asym), 1518 (C=C, Ph), 1476, 1363 (C-O, sym), 1222, 1071 (C-O, C-C), 745, 682, 617, 430.

Reaction of zirconium(IV) butoxide with 1,3-diphenyl-1,3-propanedione in 1:2 mole ratio (6)

The reaction of 1,3-diphenyl-1,3-propanedione ($4.0x10^{-3}$ mol, 1.0 g) with zirconium n-butoxide ($2.0x10^{-3}$ mol, 0.96 g) in 20 mL of n-butanol was carried out similarly to the preceding reaction. ^1H-NMR ($CDCl_3$, ppm): δ 1.0 (brd, CH_3, OBu), 1.46 (sextet, J= 7.55 Hz, CH_3-C$\underline{H}_2$, OBu), 1.62 (pentet, J=7.87 Hz, C$\underline{H}_2$-CH_2O, OBu), 3.69 (brd, CH_2O, OBu), 7.08 (2H, OC-C$\underline{H}$=, dion), 7.37 (brd, 2H, C_6H_5, dion), 7.44 (brd, 6H, C_6H_5, dion), 7.50 (d, J=6.8 Hz, 4H, C_6H_5, dion), 8.11 (d, J=6.3 Hz, 4H, C_6H_5, dion), 8.16 (d, J=6.3 Hz, 4H, C_6H_5, dion). ^{13}C- NMR ($CDCl_3$, ppm): δ 13.93 (CH_3, OBu), 19.01 (CH_3-$\underline{C}H_2$, OBu), 34.93 ($\underline{C}H_2$-CH_2O, OBu), 77.43 (CH_2O, OBu), 95.81 (OC-$\underline{C}$H=, dion), 128.04-138.73 (C=C, C_6H_5, dion), 182.88 (CH=$\underline{C}$-O, dion, enol form), 183.65 (C=O, dion). FTIR (cm^{-1}): 3059, 2953, 2868, 1593, 1519, 1476, 2365, 1319, 1220, 1068, 1024, 944, 719, 684, 617, 534, 454. Mass spectrum: 759.135 Da for $[Zr(OBu^n)_2(dion)_2 .C_4H_9OH+H]^+$, 683.195 Da for molecular ion $[Zr(OBu^n)_2(dion)_2+H]^+$.

Reaction of zirconium(IV) propoxide with 1,3-diphenyl-1,3-propanedione in 1:1 mole ratio (7)

The reaction of 1,3-diphenyl-1,3-propanedione ($2.0x10^{-3}$ mol, 0.46 g) with zirconium n-propoxide ($2.0x10^{-3}$ mol, 0.94 g) in 20 mL of n-propoxide was carried out similarly to the preceding reaction. ^1H-NMR($CDCl_3$, ppm): δ 0.80 (t, J=6.69 Hz, CH_3, OPr), 1.46 (m, CH_3-C$\underline{H}_2$, OPr), 3.48, 3.90 (brd, CH_2O, OPr), 7.13 (H, OC-C$\underline{H}$=, dion), 7.28 (t, J=7.53 Hz, 3H, C_6H_5, dion), 7.35 (d, J=7.33 Hz, 1H, C_6H_5, dion), 7.79 (d, J=7.22 Hz, 2H, C_6H_5, dion), 7.88 (t, J=7.56 Hz, 2H, C_6H_5, dion), 7.96 (d, J=7.22 Hz, 2H, C_6H_5, dion).

Reaction of zirconium(IV) propoxide with 1,3-diphenyl-1,3-propanedione in 1:2 mole ratio (8)

The reaction of 1,3-diphenyl-1,3-propanedione ($4.0x10^{-3}$ mol, 1.0 g) with zirconium n-propoxide ($2.0x10^{-3}$ mol, 0.94 g) in 20 mL of n-propoxide was carried out similarly to the preceding reaction. ^1H-NMR($CDCl_3$, ppm): δ 0.94 (t, J=7.46 Hz, CH_3, OPr), 1.59 (sextet, J=7.18 Hz, CH_3-C$\underline{H}_2$, OPr), 3.57, 3.60 (brd, CH_2O, OPr), 7.03 (2H, OC-C$\underline{H}$=, dion), 7.33 (brd, H, C_6H_5, dion), 7.38 (brd, 3H, C_6H_5, dion), 7.44 (brd, 2H, C_6H_5, dion), 8.06 (brd, 2H, C_6H_5, dion), 8.10 (brd, 2H, C_6H_5, dion). FTIR (cm^{-1}): 2969, 2872, 2319,1738, 1593, 1538, 1518, 1476, 1454, 1376-1300, 1224, 1182, 1145, 1073, 1008, 969, 944, 785, 751, 618. Elemental analysis,

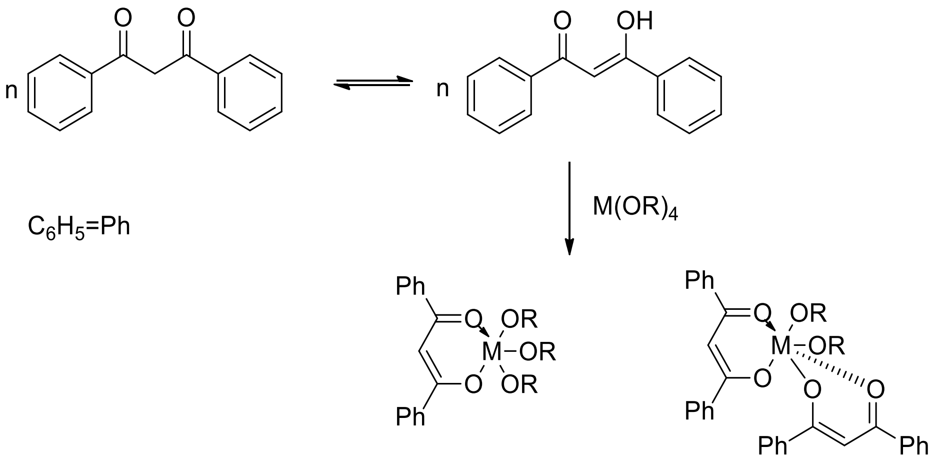
$C_{36}H_{36}O_6Zr$ (655.89 g/mol): Calc. H: 5.53% ; found: H 5.40%.

Polymerization of ε-caprolactone with Ti/Zr-dion complexes (9)

Ti/Zr-dion complexes (20 mg) were mixed with ε-caprolactone (1.5 mL) in a vial under nitrogen atmosphere. The mixture was stirred without solvent at 80°C for different times as indicated in Table 1. ^{1}H NMR ($CDCl_3$, ppm): δ 4.08 (t, *J* = 7.0 Hz, $^{e}CH_2$-O), 2.30 (t, *J* = 7.0 Hz, $^{a}CH_2$-C = O), 1.67 (m, *J* = 7.0 Hz, $^{b,d}CH_2$), 1.39 (m, *J* = 7.0 Hz, $^{g}CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 173.80 (C = O), 64.4 ($^{e}CH_2O$), 34.3 ($^{a}CH_2$), 28.6 ($^{d}CH_2$), 25.7 ($^{b}CH_2$), 24.8 ($^{g}CH_2$). [O = C-$^{a}CH_2{}^{b}CH_2{}^{g}CH_2{}^{d}CH_2{}^{e}CH_2O$-]. FTIR ($cm^{-1}$): 2940 ($CH_2$, asym str), 2864 ($CH_2$, sym str), 1720 (C=O), 1470 (CH_2, bending), 1365 (CH_2, bending), 1292 (C–C), 1240 (C–O–C, asym), 1165 (C–O–C, sym), 1046, 961,730.

RESULTS AND DISCUSSION

Stoichiometric reactions of 1,3-diphenyl-1,3-propanedione with zirconium or titanium alkoxides in 1:1 or 2:1 molar ratio in corresponding alcohols at 35 °C produced compounds (1-8). The formulation of compounds was based on combinations of ^{1}H, ^{13}C-NMR, FTIR, and mass spectroscopies, and elemental analysis. The structure of compounds can be drawn as seen in Scheme 1 for 1:1 mole ratio of 1,3-diphenyl-1,3-propanedione to $M(OR)_4$ and 2:1 mole ratio of 3-diphenyl-1,3-propanedione to $M(OR)_4$, [M-OR: Ti-OBu^n, Ti-OPr^i, Zr-OBu^n, Zr-OPr^n)], respectively.



n=1, A

n=2, B

Scheme 1. Structures of $[M(OR)_3(dion)]$ and $[M(OR)_2(dion)_2]$, (M=Ti, Zr; OR=OBu^n, OPr^n, OPr^i).

High resolution mass spectrometry (ESI-TOF-MS) was used to determine the masses of complexes. The samples were measured under positive and negative soft ionization conditions (ES+/ES-). The evaluation of the mass spectra which is based on isotopic patterns clearly showed metal-containing ions. For example, the mass spectrum of the product resulted from reaction between 1,3-diphenyl-1,3-propanedione and $Ti(OBu^n)_4$ in 1:1 molar ratio gave peaks at 529.184 Da for molecular ion $[C_{27}H_{38}O_5Ti + K]^+$ and at 491.228 Da for $[C_{27}H_{38}O_5Ti]^+$ (Figure 1).

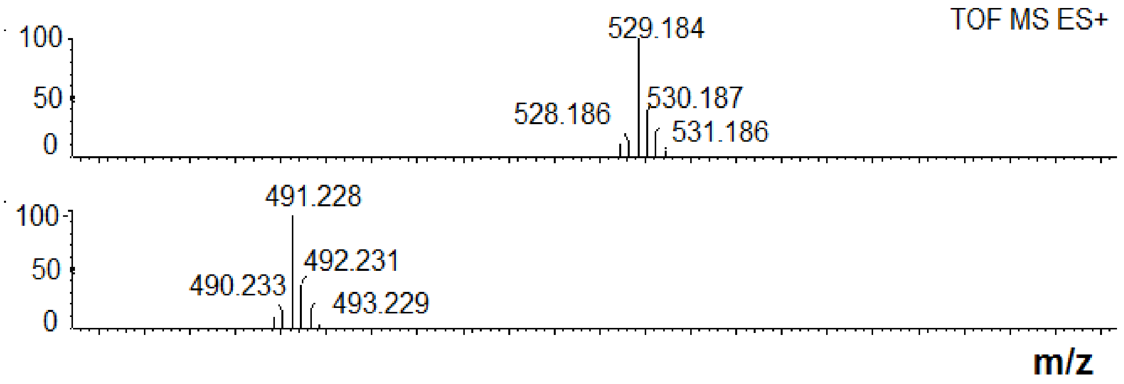


Figure 1. Mass spectrum of $[Ti(OBu^n)_3(dion)]$ compound.

The suggested formula of monomeric compound was consistent with elemental analysis and ^{1}H, ^{13}C-NMR and FTIR results. The FTIR spectra of the metal alkoxides $Zr(OBu^n)_4$, $Ti(OBu^n)_4$ and others are similar and show no absorption bands in the region of 1500–1800 cm^{-1}. The FTIR spectrum of $[Ti(OBu^n)_3(dion)]$ shows no free dion groups and but the two stretching vibrations (C=C and C=O) of the enolic form of the β-diketone at ~1615 and 1546 cm^{-1} show that all of dion is bonded to the Ti-butoxide. There was no stretching vibrations of υ(C=O) of the keto form of free β-diketone was at about 1740 cm^{-1}. These results were consistent with literature studies [5, 18]. ^{1}H and ^{13}C NMR spectra of compound supported the mass and FTIR spectra. For instance, The ^{1}H NMR spectrum of $[Ti(OBu^n)_3(dion)]$ complex showed the expected peaks and peak multiplicities. For example, ^{1}H NMR spectrum of $[Ti(OBu^n)_3(dion)]$ showed triplets at 0.95 ppm with J = 7.4 Hz for CH_3 protons, multiplet at 1.54 ppm with J = 7.4 Hz for CH_2 protons, triplets at 3.73 ppm with J = 6.4 Hz for OCH_2 protons of butoxide groups *cis* to dion and triplets at 4.74 ppm with J = 6.6 Hz for OCH_2 protons of butoxide groups *trans* to dion in titanium complex (Figure 2). The presence of very small CH_2 keto-form protons signal at around 2.35 ppm indicates that dion is predominantly coordinated to the titanium atom in the enolate form. The signal for the CH= proton of enol-form was at 7.64 ppm in the ^{1}H NMR spectrum. The integration of ^{1}H NMR spectrum indicated that very small amounts of the alkoxide groups underwent hydrolysis and condensation reactions. The deviation less than 2% in elemental analysis for carbon atoms also supported the presence of small amounts of hydrolysis and condensation reactions.

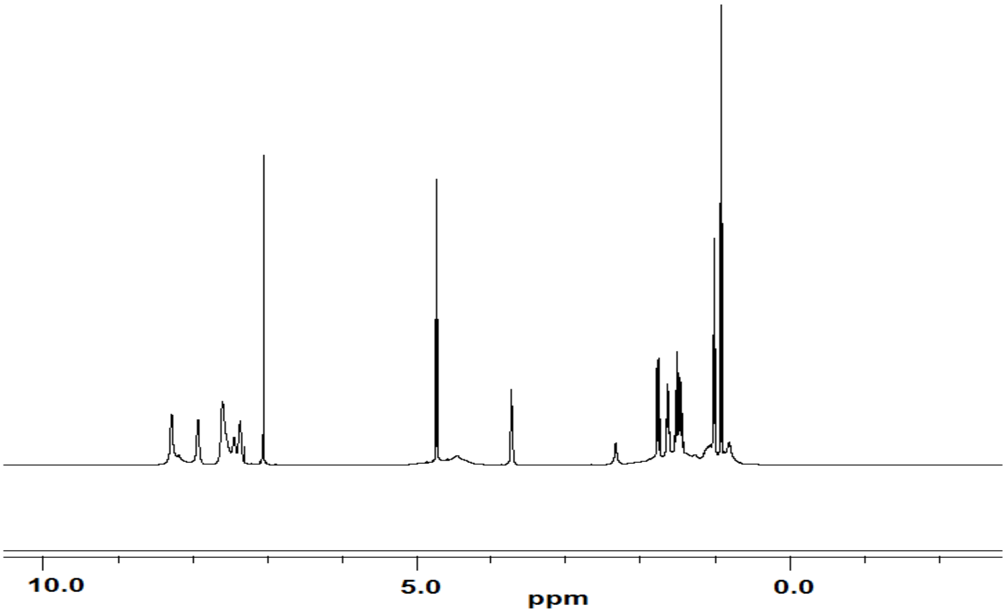


Figure 2. ^{1}HNMR spectrum of $[Ti(OBu^n)_3(dion)]$.

^{13}C NMR spectrum of $[Ti(OBu^n)_3(dion)]$ compound (Figure 3) gave the expected characteristic peak for enol-form of dion bonded to titanium at 96.13 ppm for OC-$\underline{C}$H=. As seen in the ^{13}C NMR spectrum, there was no peak for carbonyl carbon atom of free keto-form of 1,3-diphenyl-1,3-propanedione at ~ 190 ppm regions. The peaks at 182.28 and 184.82 ppm belongs to CH=$\underline{C}$-O (dion, enol form) and 184.82 (C=O, dion, enol form), respectively.

Reactions 1,3-diphenyl-1,3-propanedione with $M(OR)_4$ in 2:1 mole ratio resulted in the formation of $[M(OR)_2(dion)_2]$. All spectroscopic measurements given in the experimental parts support the suggested formulations. The studies of dion/$Ti(OBu^n)_4$ in 2:1 mole ratio showed that diones are completely coordinated to titanium atom just in enolate form as drawn in Scheme 1. The mass spectrum of $[Ti(OBu^n)_2(dion)_2]$ showed the molecular ion having a mass of 641.2386 Da (Figure 4). The molecular weight of 641.2386 Da confirmed the suggested formula for the compound prepared from $Ti(OBu^n)_4$ and 1,3-diphenyl-1,3-propanedione in 1:2 mole ratio.

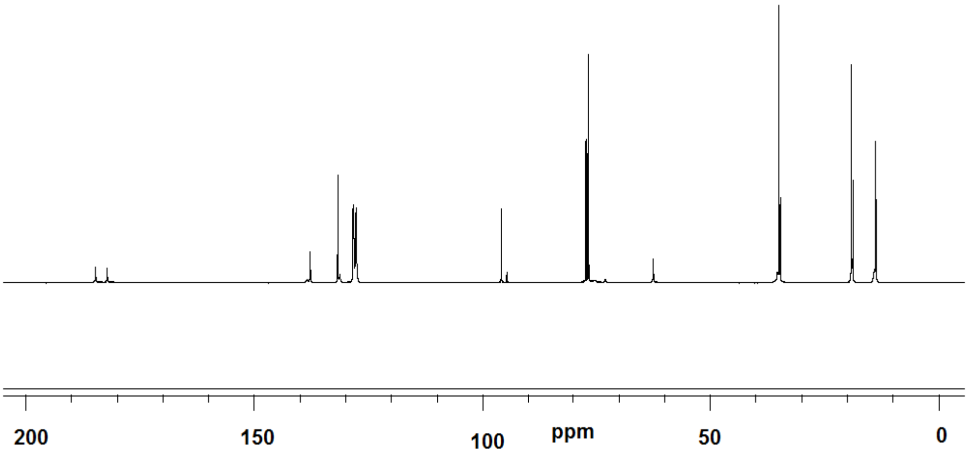


Figure 3. ^{13}C NMR spectrum of [Ti(OBu^n)$_3$(dion)].

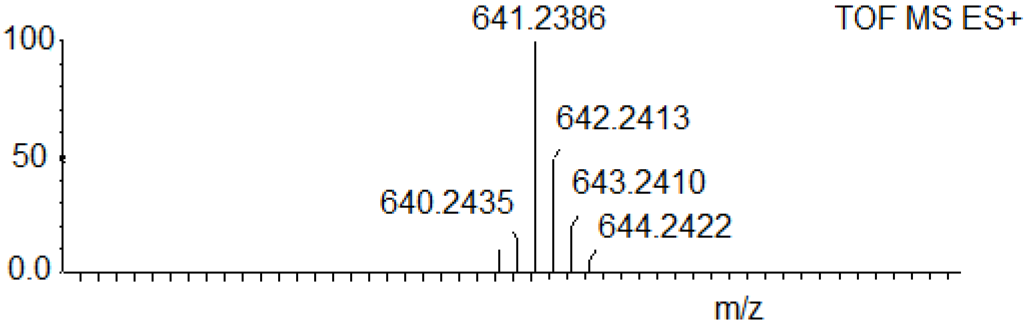


Figure 4. Mass spectrum of [Ti(OBu^n)$_2$(dion)$_2$].

As in titanium-dion compounds, the reaction between 1,3-diphenyl-1,3-propanedione and Zr(OBu^n)$_4$ in 2:1 mole ratio resulted in the formation of [Zr(OBu^n)$_2$(dion)$_2$]. The mass spectrum of [Zr(OBu^n)$_2$(dion)$_2$] showed the molecular ion having a mass of 683.1950 Da for (=$ZrC_{38}H_{40}O_6+H^+$) (Figure 5). The molecular weight of 683.1950 Da confirmed the suggested formula with the presence of one mole of n-butanol.

In contrast to β-diketone metal alkoxide compounds, the imine, amine, and carboxylate metal alkoxide compounds were resulted in oligomeric structures like tetramer or hexamer structures (19-21). The degree of oligomerization is affected by the acidity or basicity of ligands, stirring times and temperatures of reactions, the freshness of metal alkoxides, solvent types, *etc*.

The development of "single-site" or "reduced number of active sites" catalysts has been a key goal for producing polymers with controllable molecular weights and low polydispersity index (22). The Ti/Zr-dion complexes were very effective in the polymerization reactions of ε-caprolactone when they were used as catalysts (Table 1). For example, ε-caprolactone polymers prepared with Zr(OBu^n)$_2$(dion)$_2$ by stirring at 80 °C for 18 hours, the main peak appeared at 21140 Da for weight average molecular weight (M*w*) with a conversion of 78%.

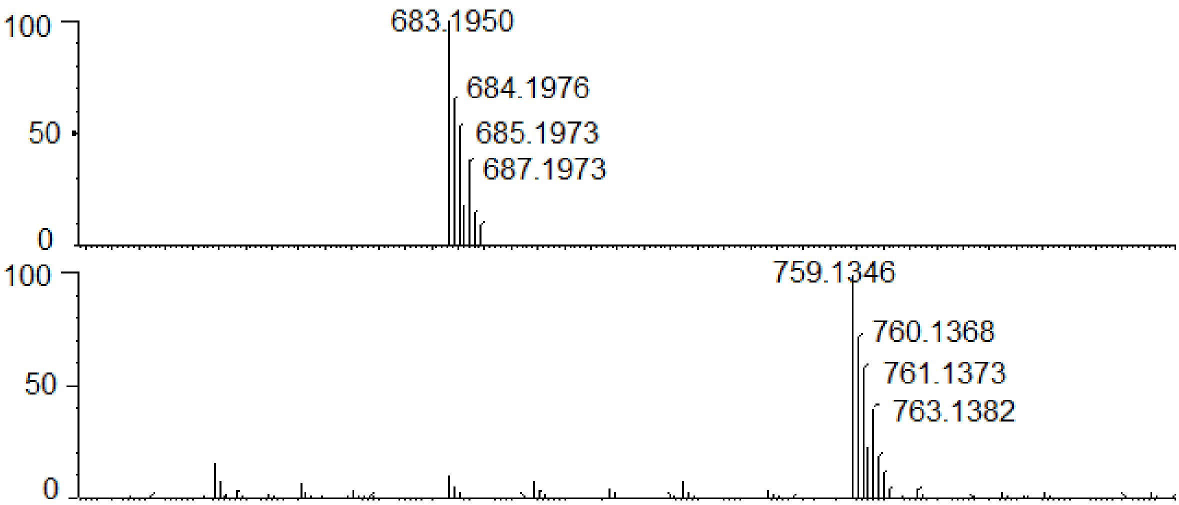
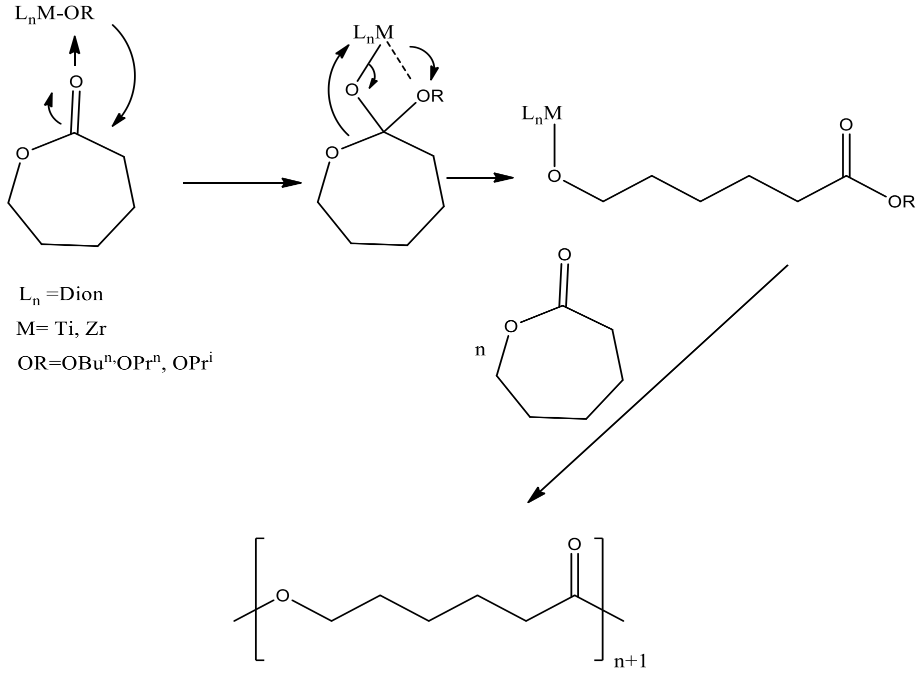


Figure 5. Mass spectrum of [Zr(OBu^n)$_2$(dion)$_2$] .C_4H_9OH.

Metal alkoxide compounds proceed through a coordination-insertion mechanism for the ring opening polymerization (ROP) of ε-caprolactone [23, 24]. In this mechanism (Scheme 2), the Ti/Zr-dion compounds first allow bonding of the ε-caprolactone to the metal center by oxygen atom of the carbonyl group. Then, the nucleophilic alkoxide group attacks the carbon atom of the activated carbonyl group, leading to ester cleavage. Subsequently, ε-caprolactone monomers incorporate to the metal center and insert into the metal-alkoxide bond. Consequently, polycaprolactone with an alkoxide end group is obtained.



Scheme 2. Polymerization of ε-caprolactone with Ti/Zr-dion catalysts.

Each carbon atom of PCL appeared at only one region 173.80 (C = O), 64.4 ($^eCH_2O$), 34.3 ($^aCH_2$), 28.6 ($^dCH_2$), 25.7 ($^bCH_2$), 24.8 ($^gCH_2$) ppm in ^{13} C-NMR spectrum. These data are the evidence of regular polymerization of ε-CL and are consistent with the literature data (25).

The Mw, Mn, and PDI values for PCL prepared with metal(dion)alkoxide catalysts at 80 °C are summarized in Table 1.

Table 1. Data for PCL obtained from GPC measurements.

Catalysts	**Time (h)**	**M_w (Da)**	**M_n (Da)**	**PDI(M_w/M_n)**	**Conversion (%)**
$Ti(OBu^n)_3(dion)$	12	10640	9410	1.14	54
$Ti(OBu^n)_3(dion)$	24	12770	11000	1.16	92
$Ti(OBu^n)_2(dion)_2$	24	6990	5880	1.19	45
$Ti(OBu^n)_2(dion)_2$	36	8990	7300	1.21	90
$Ti(OPr^i)_3(dion)$	24	13720	11780	1.16	60
$Ti(OPr^i)_3(dion)$	36	15900	13475	1.18	92
$Ti(OPr^i)_2(dion)_2$	36	20260	16010	1.26	59
$Zr(OBu^n)_3(dion)$	4.0	30820	25710	1.20	44
$Zr(OBu^n)_3(dion)$	10	34000	27420	1.24	93
$Zr(OBu^n)_2(dion)_2$	18	21140	13290	1.59	78
$Zr(OPr^n)_3(dion)$	2	22420	17650	1.27	66
$Zr(OPr^n)_2(dion)_2$	10	17360	11970	1.45	60
$Zr(OPr^n)_2(dion)_2$	16	19800	13380	1.48	92

The PDI values for PCL produced using $[M(OR)_3(dion)]$ catalysts are noticeably smaller than that for PCL produced using $[M(OR)_2(dion)_2]$ catalysts. As seen from Table 1, the polymerization with $[M(OR)_2(dion)_2]$ catalysts exhibited a slower kinetic of reaction and the polymer synthesized lower weight average molecular weight than with $[M(OR)_3(dion)]$ catalysts.

The GPC curve of polycaprolactone displayed unimodal behavior with narrow distribution index indicating regular polymerization of ε-caprolactone (Figure 6).

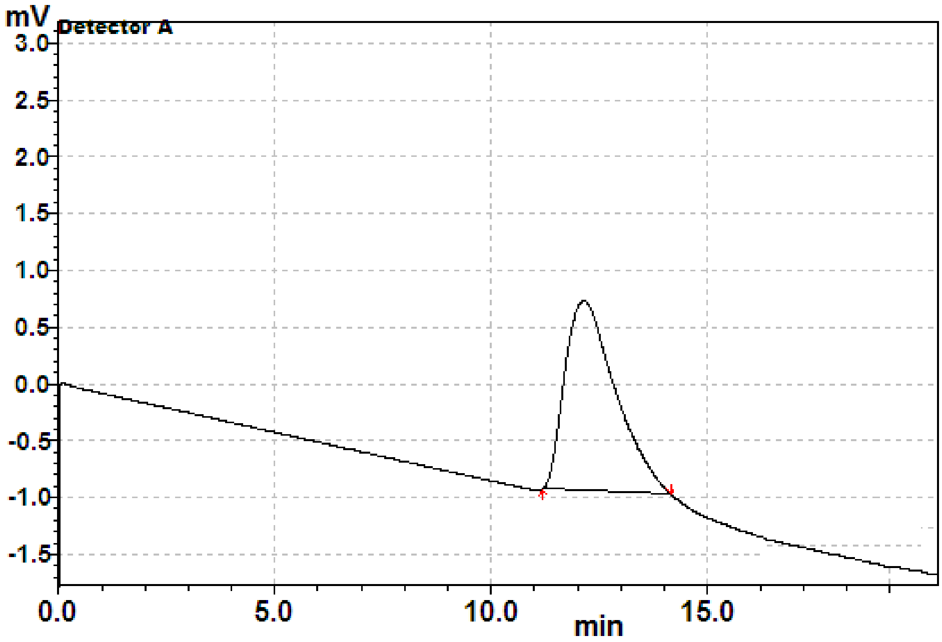


Figure 6. Gel permeation chromatogram of PCL prepared at 80 °C with the catalyst $[Zr(OPr^n)_3(dion)]$.

CONCLUSIONS

In this study, Ti/Zr alkoxide precursors were stabilized by diphenylpropanedione (dion) ligand using sol-gel process. It is interesting to note that the alkoxide groups are significantly more reactive than the β-diketonate ligands. The β-diketonate ligands are bidentate ligands and form stronger bonds with the coordinating Ti/Zr atom than monodentate (alkoxide) ligands. Therefore, the dion ligands displace the alkoxide groups bonded to Ti/Zr atoms. The synthesized Ti/Zr-dion compounds were characterized by elemental analysis and spectroscopic techniques such as ^1H-, ^{13}C-NMR, high resolution mass (HRMS), FTIR. These complexes were used as catalysts on the ring opening polymerization of ε-caprolactone. These results demonstrated that an alkoxide substituent on the diphenylpropanedione-Ti/Zr compounds acted as the initiator on Ɛ-caprolactone under solvent-free conditions. As expected, the changes in the number of alkoxide groups bonded to Ti/Zr atoms have a dramatic influence not only on the activity of the catalyst, but also on the degree of the polydispersity index and molecular weights of polymers. The aim of this work was to make a contribution to the research for catalyst systems on ROP of Ɛ-caprolactone.

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