Kayan, JOTCSA. 2017; 4(1): 59-80. **RESEARCH ARTICLE**

Preparation and Characterization of TAMP/TIMP-Ti and Zr Compounds and Their Catalytic Activity over Propylene Oxide and ε-Caprolactone

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Abstract: Titanium and zirconium 2-((p-tolylamino/p-tolylimino)methyl)phenolate (TAMP and TIMP) were prepared by reaction of Ti- and Zr-alcoholates with 2-((p-tolylamino)methyl)phenol (TAMPH) and 2-((p-tolylimino)methyl)phenol (TIMPH) in ethyl alcohol. To characterize these compounds, ^{1}H, ^{13}C NMR, FTIR, mass spectroscopies, and elemental analysis were used. The TAMP and TIMP metal compounds can be formulated as $(TAMP)_3M_2(OR)O_2$ and $(TIMP)_4M_2O_2$, respectively. The catalytic activity of these compounds was checked in polymerization reactions with propylene oxide (PO) and ε-caprolactone (ε-CL) and Ti-TAMP was effective**.** Poly-propylene oxide (PPO) and poly-caprolactone (PCL) were identified by ^{1}H, ^{13}C NMR and gel permeation chromatography (GPC).

Keywords: Metal alkoxide, catalyst, Schiff base, ε-caprolactone, polymer.

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INTRODUCTION

Schiff-bases, carboxylate anions, and their derivatives are useful ligands for the construction of new interesting metal catalysts [1-7]. Metal alcoholate compounds modified by carboxylates, β-diketonates, and Schiff-bases have attracted much attention as catalysts for ring opening polymerization of oxirane derivatives, lactides, and ε-caprolactone [8-10]. The chemistry of the compounds of the type Ti- and Zr-(OR) (2-((p-tolylamino/p-tolylimino)methyl)phenolate) in which OR^- is a potentially active ligand for polymerization catalysis remains much less studied. Metal Schiff base compounds have used as catalysts for ring opening of ε-caprolactone and propylene oxide. Among those catalysts, some catalysts were low performance of ring-opening polymerization (ROP) of ε-CL and PO. ROP of ε-CL and PO has been gaining attention due to its wide range of applications such as production of nonionic surfactants, packaging materials, adhesives, plastics, and coating materials [10-13].

Therefore, it is important to synthesize new compounds containing single-site alcoholate group which is active in polymerization reactions. A major interest of this study is to synthesize and characterize zirconium and titanium catalysts containing both an active group of alcoholate and ligands (TAMP and TIMP) with nitrogen and oxygen as donor atoms. The second interest of this study is to compare the reactivity of ligands (TAMP and TIMP) against to metal alcoholates. Finally, seeing their catalytic activity over ring opening of PO and ε-CL in mild reaction conditions was also one of the interests of this study.

EXPERIMENTAL

Materials and instrumentation

Tetraisopropyl orthotitanate (98%, Merck), tetrapropyl zirconate (70% in propyl alcohol, Fluka), tetrabutyl zirconate (80% in *tert*-butanol, Fluka), salicylaldehyde (Sigma-Aldrich), *p*-toluidine (99%, Merck), sodium borohydride (98%, Merck), propylene oxide (99%, Alfa Aesar), ε-caprolactone (97%, Sigma-Aldrich), and tetrahydrofuran (THF) (99.9%, Merck) were used as received. *n*-Butyl alcohol (99%, Merck), n-propyl alcohol (99%, Sigma-Aldrich), chloroform

(99.8%, Sigma-Aldrich) and isopropyl alcohol (99.5%, Merck) were dried over activated 4A° molecular sieves before use. All syntheses were carried out in closed vessels under ambient atmosphere. TAMPH and TIMPH were prepared as in literatures [14,15].

^{1}H and ^{13}C{^{1}H}NMR experiments were performed on a Bruker 300 and 400 MHz NMR spectrometers. FTIR spectra of compounds were measured on a Shimadzu 8201/86601 PC spectrometer. The elemental analyses were performed on a LECO CHNS-932 elemental analyzer. Molecular mass measurements of compounds were performed on SCIEX 4000 QTRAP LC-MS/MS and Waters SYNAPT MS (HRMS, TOF/MS). Electrospray ionization (ESI ±) method was used in both mass spectrometers to produce ions. Gel permeation chromatography measurements (GPC) were carried out on a Shimadzu prominence GPC system including RID-10A refractive index detector, a LC-20AD solvent delivery unit, and two PSS SDV columns (50 and 1000 A°). The GPC was eluted with THF at 30 °C running at 1.0 mL/min and was calibrated using few polystyrene standards (162 -34300 Da).

Preparation of TIMPH (p-MeC$_6$H$_4$)N=CH(C$_6$H$_4$-2-OH) (1)

p-Toluidine (6.90 g, 0.064 mol) was added to the stirring solution of salicyl aldehyde (7.98 g, 0.064 mol) in ethanol (50 mL), which was let to react for 3 h at reflux temperature. After that, the solution was cooled to room temperature and an orange solid was formed. It was filtered and washed with ethanol and then dried by vacuum evaporator. Anal. Calcd. For $C_{14}H_{13}NO$ (%), (*Mw* = 211.26 g/mol): C, 79.59; H, 6.20; N, 6.63. Found: C, 79.35; H, 6.28; N, 6.42. MALDI-TOF MS (m/z): [$C_{14}H_{13}NO$] = 212.0 (100%) Da. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 6.94–7.40 (m, 8 H, PhO, PhN), 8.66 (s, 1 H, CH), 13.40 (s, 1 H, OH) ppm. Elemental analysis, $C_{14}H_{13}NO$ (211.26 g/mol): Calc. C 79.59, H 6.20, N 6.63% ; found: C 79.35, H 6.28, N 6.42. FTIR (KBr pellet, cm^{-1}): 3052, 3022, 2921, 2859, 1616 (C=C, Ar), 1597 (C=C, Ar), 1578 (C=N), 1509, 1498, 1459, 1414, 1367, 1282 (C-O, phenolic), 1181, 1159, 1118, 1033, 910, 851, 835, 816, 788, 750, 634.

Preparation of TAMPH (p-MeC$_6$H$_4$)NHCH$_2$(C$_6$H$_4$-2-OH) (2)

The reaction of salicylaldehyde with p-methylaniline yielded 2-((tolylimino)methyl)phenol. 2-((Tolylimino)methyl)phenol (2×10^{-2} mol) was dissolved in 50 mL of methanol and dioxane at 1: 1 ratio. NaBH$_4$ (2×10^{-2} mol) was added to this solution until the disappearance of yellow color of the Schiff base (1 h). Cold water was added to the solution to form precipitate. The precipitate was recrystallized with methanol to yield 2-((tolylamino)methyl)phenol. ^{1}H NMR (CDCl$_3$, ppm): δ 2.28 (s, 3H, CH$_3$), 3.87 (s, 1H, NH), 4.34 (s, 2H, CH$_2$-N), 6.7-6.75 (m, aromatic, 2H), 6.82-6.85 (m, aromatic, 2H), 7.02-7.04 (m, aromatic, 2H), 7.09-7.12 (m, aromatic, 1H), 7.16-7.22 (m, aromatic, 1H), 8.48 (s, 1H, OH). FTIR (KBr pellet, cm^{-1}): 3416 (OH), 3261 (NH), 3011, 2915, 2860, 1612 (C=C, Ar), 1591 (C=C, Ar), 1508, 1454, 1399, 1356, 1290 (C-O, phenolic), 1247, 1184, 1156, 1109, 1055, 975, 909, 862, 817, 751, 716, 704, 609.

Preparation of (TAMP)$_3$Ti$_2$(O^{i}Pr)O$_2$ compound (3)

2-((p-Tolylamino)methyl)phenol (3.10×10^{-3} mol, 0.66 g) was added to the solution of tetraisopropyl orthotitanate (1.55×10^{-3} mol, 0.45 g) in 20 mL of isopropyl alcohol. The reaction mixture was stirred for 3 hours at room temperature. Then, the volatile parts were removed from the yellow-colored product by a vacuum evaporator at 30 °C. Then the compound was recrystallized from hexane. Elemental analysis ($C_{45}H_{49}N_3O_6Ti_2$, (TAMP)$_3$Ti$_2$(O^{i}Pr)O$_2$, M$_w$ = 823.62 g/mol): Calc. C 65.6, H 6.00, N 5.10%. Found: C, 65.8, H 6.03, N, 5.34%. MS (m/z, for (TAMP)$_3$Ti$_2$(O^{i}Pr)O$_2$): $[C_{45}H_{49}N_3O_6Ti_2{}^{48}Na]^+$ = 848.4 (16%), $[C_{45}H_{49}N_3O_6Ti^{48}]^+$ = 775.4, $[C_{45}H_{49}N_3O_6Ti^{47}]^+$ = 774.4, $[C_{45}H_{49}N_3O_6Ti^{46}]^+$ = 773.4, $[C_{42}H_{42}N_3O_3Ti^{48}]^+$ = 684.3 Da. ^{1}H NMR (CDCl$_3$, ppm): δ 1.23 (d, CH$_3$, O^{i}Pr), 2.30 (s, CH$_3$Ph), 4.05 (septet, OCH, O^{i}Pr), 4.43 (s, CH$_2$N), 6.3-7.4 (m, CH, aromatic). ^{13}C NMR (CDCl$_3$, ppm): δ 20.54 (CH$_3$Ph), 25.35 (CH$_3$, O^{i}Pr), 49.37 (CH$_2$N), 64.50 (OCH, O^{i}Pr), 116.24 (Ar), 116.70 (Ar), 119.90 (Ar), 122.91 (Ar), 128.61 (Ar), 129.17 (Ar), 129.67 (Ar), 130.46 (Ar), 144.8 (=CipsoN, Ar), 157.0 (=C-O, Ar). FTIR (KBr pellet, cm^{-1}): 3261 (NH), 3013, 2916, 2860, 1613 (C=C, Ar), 1593 (C=C, Ar), 1514, 1489, 1456, 1402, 1250, 822, 754.

Preparation of $(TIMP)_4Ti_2O_2$ compound (4)

2-((p-Tolylimino)methyl)phenol (3.12×10^{-3} mol, 0.66 g) was added to the solution of tetraisopropyl orthotitanate (1.56×10^{-3} mol, 0.45 g) in 20 mL of isopropyl alcohol. The reaction mixture was stirred for 3 hours at room temperature. Then, the volatile parts were removed from the yellow product by a vacuum evaporator at 30 °C. Then the compound was washed three times with n-heptane and dried under reduced pressure. Elemental analysis ($C_{56}H_{48}N_4O_6Ti_2$, $(TIMP)_4Ti_2O_2$, M_w = 968.74 g/mol): Calc. C 69.43, H 4.99, N 5.78%. Found: C 68.47, H 5.07, N 5.10%. MS (m/z): $[C_{56}H_{48}N_4O_6Ti_2^{48}]$ = 968.33 (100%), $[C_{56}H_{48}N_4O_6Ti]$ = 924.25 (16%) Da. ^1H NMR ($CDCl_3$, ppm): δ 2.39 (s, CH_3Ph), 6.94 (t, 1H, CH, aromatic), 7.02 (d, 1H, CH), 7.20 (m, 4H, CH), 7.38 (m, 2H, CH), 8.64 (s, CH=N). ^{13}C NMR ($CDCl_3$, ppm): δ 21.26 (CH_3Ph), 117.41 (Ar), 119.18 (Ar), 119.51 (Ar), 121.20 (Ar), 130.20 (Ar), 132.31 (Ar), 133.09 (Ar), 137.10 (Ar), 144.09 (=CipsoN, Ar), 161.32 (=C-O, Ar), 161.91 (CH=N). FTIR (KBr pellet, cm^{-1}): 3055, 3026, 2920, 2860, 1614 (C=C, Ar), 1601 (C=C, Ar), 1549 (C=N), 1502, 1471, 1446, 1379, 1310 (C-O, phenolic), 1184, 1150, 1122, 1016, 922, 864, 818, 754, 608.

Preparation of $(TAMP)_3Zr_2(O^nPr)O_2$ compound (5)

2-((p-Tolylamino)methyl)phenol (3.10×10^{-3} mol, 0.66 g) was added to the solution of tetrapropyl zirconate (1.55×10^{-3} mol, 0.73 g) in 20 mL of n-propyl alcohol. The reaction mixture was stirred for 3 hours at room temperature. Then, the volatile parts were removed from yellow product by vacuum evaporator at 30 °C. Then the compound was recrystallized with hexane. Elemental analysis ($C_{45}H_{49}N_3O_6Zr_2$, $(TAMP)_3Zr_2(O^nPr)O_2$, M_w = 910.34 g/mol): Calc. C 59.37, H 5.43, N 4.62%. Found: C 58.50, H 5.51, N 4.70%. MS (m/z): $[C_{45}H_{49}N_3O_6Zr^{92}Zr^{94}H]^+$ = 915.5, $[C_{45}H_{49}N_3O_4\ Zr^{90}Zr^{90}\ H]^+$ =876.6, $[C_{45}H_{49}N_3O_4Zr^{90}\ Zr^{91}H]^+$ = 877.6, $[C_{45}H_{49}N_3O_4\ Zr^{90}Zr^{92}H]^+$ = 878.6, $[C_{43}H_{45}N_3O_4Zr_2H]^+$= 850.4, and $[C_{42}H_{43}N_3O_4Zr_2H]^+$= 834.4 Da. ^1H NMR ($CDCl_3$, ppm): δ 0.98 (t, CH_3, O^nPr), 1.63 (m, CH_2, O^nPr), 2.34 (s, CH_3Ph), 3.65 (t, OCH_2, O^nPr), 4.42 (s, CH_2N), 6.81 (d, 2H, CH, aromatic), 6.94 (m, 2H, CH), 7.11 (d, 2H, CH), 7.19 (d, 1H, CH), 7.27 (t, 1H, CH). ^{13}C NMR ($CDCl_3$, ppm): δ 10.00 (CH_3, O^nPr), 20.67 (CH_3Ph), 26.00 (CH_2, O^nPr), 49.28 (CH_2NH), 64.85 (OCH_2, O^nPr), 116.26 (Ar), 116.73 (Ar), 120.07 (Ar), 123.22 (Ar), 128.76 (Ar), 129.23 (Ar), 129.99 (Ar), 130.38 (Ar), 144.85 (=C-NH, Ar), 157.03

(=C-O, Ar). FTIR (KBr pellet, cm^{-1}): 3259 (NH), 3013, 2916, 2860, 1614 (C=C, Ar), 1593 (C=C, Ar), 1511, 1484, 1451, 1400, 1357, 1289 (C-O, phenolic), 1249, 1184, 1155, 1109, 1056, 1041, 976, 903, 863, 819, 753, 710, 705.

Preparation of (TIMP)$_4$Zr$_2$O$_2$ compound (6)

2-((p-Tolylimino)methyl)phenol (3.12 × 10^{-3} mol, 0.66 g) was added to the solution of tetrapropyl zirconate (1.56 × 10^{-3} mol, 0.73 g) in 20 mL of n-propyl alcohol. The reaction mixture was stirred for 3 hours at room temperature. Then, the volatile parts were removed from the yellow product by a vacuum evaporator at 30 °C. Then, the compound was washed three times with heptane and dried under reduced pressure. Elemental analysis ($C_{56}H_{48}N_4O_6Zr_2$, (TIMP)$_4$Zr$_2$O$_2$, M_w = 1055.45 g/mol): Calc. C 63.73.12, H 4.58, N 5.31%. Found: C 63.30; H 4.67; N 5.37%. MALDI-TOF MS (m/z): [$C_{56}H_{48}N_4O_6Zr_2$] = 1029.82 (100%), [$C_{56}H_{48}N_4O_6Zr^{94}$] = 967.95(85%) Da. ^{1}H NMR (CDCl$_3$, ppm): δ 2.44 (s, C*H*$_3$), 7.0 (t, 1H, CH), 7.10 (d, 1H, CH), 7.26 (m, 4H, CH), 7.43 (d, CH, aromatic), 8.66 (s, CH=N). ^{13}C NMR (CDCl$_3$, ppm): δ 21.21 (CH$_3$Ph), 117.34 (Ar), 119.13 (Ar), 119.46 (Ar), 121.15 (Ar), 129.90 (Ar), 130.15 (Ar), 132.27 (Ar), 133.04 (Ar), 137.04 (Ar), 146.00 (=CipsoN, Ar), 161.27 (=C-O, Ar), 161.81 (CH=N). FTIR (KBr pellet, cm^{-1}): 3055, 3022, 2920, 2858, 1618 (C=C, Ar), 1599 (C=C, Ar), 1570 (C=N), 1540 (C=N), 1512, 1474, 1458, 1367, 1309 (C-O, phenolic), 1283, 1184, 1150, 1109, 908, 815, 752, 517.

Preparation of (TAMP)$_3$Zr$_2$(O^{n}Bu)O$_2$ compound (7)

2-((p-Tolylamino)methyl)phenol (3.10 × 10^{-3} mol, 0.66 g) was added to the solution of tetrabutyl zirconate (1.55 × 10^{-3} mol, 0.74 g) in 20 mL of n-butyl alcohol. The reaction mixture was stirred for 3 hours at room temperature. Then, the volatile parts were removed from yellow product by a vacuum evaporator at 35 °C. Then the compound was recrystallized from hexane. Elemental analysis ($C_{46}H_{51}N_3O_6Zr_2$, (TAMP)$_3$Zr$_2$(O^{n}Bu)O$_2$, M_w = 924.36 g/mol): Calc. C 59.77, H 5.56, N 4.55%. Found: C 58.89, H 5.83, N 4.74%. ^{1}H NMR (CDCl$_3$, ppm): δ 0.95 (t, CH$_3$, O^{n}Bu), 1.4 (m, CH$_2$, O^{n}Bu), 1.55 (m, CH$_2$, O^{n}Bu), 2.3 (s, CH$_3$-Ph), 3.65 (t, OCH$_2$, O^{n}Bu), 3.9 (s, NH), 4.40 (s, CH$_2$-N), 6.78 (d, CH), 6.78 (d, CH), 6.92-6.38 (m, CH), 7.07 (d, CH)), 7.16 (d, CH), 7.23 (t, CH). ^{13}C NMR (CDCl$_3$, ppm): δ 13.00 (CH$_3$, O^{n}Bu), 18.00 (CH$_2$, O^{n}Bu), 20.71 (CH_3Ph), 35.00 (CH_2, O^nBu), 49.44 (CH_2NH), 63.00 (OCH_2, O^nBu), 116.35 (Ar), 116.80 (Ar), 120.10 (Ar), 123.17 (Ar), 128.78 (Ar), 129.30 (Ar), 130.03 (Ar), 130.53 (Ar), 144.84 (=CipsoN, Ar), 157.12 (=C-O, Ar). FTIR (KBr pellet, cm^{-1}): 3261 (NH), 3022, 2920, 2859, 1616 (C=C, Ar), 1595 (C=C, Ar), 1510, 1451, 1365, 1281 (C-O), 1249, 1183, 1151, 1110, 1051, 975, 909, 857, 816, 751, 703.

Preparation of $(TIMP)_4Zr_2O_2$ compound (8)

2-((p-Tolylimino)methyl)phenol (3.12×10^{-3} mol, 0.66 g) was added to the solution of tetrabutyl zirconate (1.56×10^{-3} mol, 0.75 g) in 20 mL of n-butyl alcohol. The reaction mixture was stirred for 3 hours at room temperature. Then, the volatile parts were removed from the yellow product by a vacuum evaporator at 38 °C. Then, the compound was recrystallized from heptane. Elemental analysis ($C_{56}H_{48}N_4O_6Zr_2$, $(TIMP)_4Zr_2O_2$, M_w = 1055.45 g/mol): Calc. C 63.73, H 4.58, N 5.31%. Found: C 63.30, H, 4.80, N, 5.37%. MALDI-TOF MS (m/z): [$C_{56}H_{48}N_4O_4Zr_2^{94}$] =1029.74 (100%), [$C_{56}H_{48}N_4O_6Zr^{94}$] = 967.95 (38%), [$C_{56}H_{48}N_4O_5Zr^{90}$] = 945.80 (28%) Da. ^1H NMR ($CDCl_3$, ppm): δ 2.39 (s, CH_3-Ph), 6.94 (t, 1H, CH, aromatic), 7.03 (d, 1H, CH), 7.22 (m, 2H, CH), 7.38 (t, 2H, CH), 8.63 (s, CH=N). ^{13}C NMR ($CDCl_3$, ppm): δ 21.25 (CH_3Ph), 117.40 (Ar), 119.18 (Ar), 119.50 (Ar), 121.19 (Ar), 130.20 (Ar), 132.30 (Ar), 133.09 (Ar), 137.10 (Ar), 146.08 (=CipsoN, Ar), 161.31 (=C-O, Ar), 161.90 (CH=N). FTIR, cm^{-1}: 3053, 3022, 2922, 2859, 1617 (C=C, Ar), 1597 (C=C, Ar), 1570 (C=N), 1509, 1451, 1367, 1309 (C-O, phenolic), 1281, 1183, 1148, 1110, 1033, 909, 851, 816, 788, 751.

PPO and PCL prepared with $(TAMP)_3Ti_2(O^iPr)O_2$ (9)

The TAMP-Ti catalyst (40 mg) was taken in a vial and 1.5 mL of PO was added under nitrogen. The mixture was stirred at different temperatures and times as seen in Table 1. ^1H NMR ($CDCl_3$, δ, ppm): 3.60 (CH_2), 3.40 (CH), 1.10 (d, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 75.40 (CH), 73.30 (CH_2), 17.3 (CH_3).

The polymerization reactions of ε-CL (1.5 mL) with Ti-catalyst (20 mg) were carried out at 100 °C under solvent free condition. ^1H NMR ($CDCl_3$, ppm), δ: 3.46 (t, $^{\varepsilon}CH_2$-O), 2.31 (t, $^{\alpha}CH_2$-C=O), 1.66 (t, $^{\beta,\delta}CH_2$), 1.39 (t, $^{\gamma}CH_2$). ^{13}C NMR ($CDCl_3$, ppm), δ: 173.79 (C=O), 64.38 ($^{\varepsilon}CH_2O$), 34.34

($^{\alpha}CH_2$), 28.57 ($^{\delta}CH_2$), 25.75 ($^{\beta}CH_2$), 24.80 ($^{\gamma}CH_2$). [$O{=}C{-}^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2{}^{\delta}CH_2{}^{\varepsilon}CH_2O$-]. Full characterization of PCL and PPO prepared with different catalysts were given in the literatures [16,17].

RESULTS and DISCUSSION

Reactions of $M(OR)_m$ (M-OR: Ti-O^{i}Pr, Zr-O^{n}Bu, Zr-O^{n}Pr, m: 4 for Ti and Zr) with 2-((*p*-tolylamino)methyl)phenol or 2-((*p*-tolylimino)methyl)phenol with 1: 2 mole ratio in alcohols or chloroform at room temperature produced the compounds (3-8). The formulations of compounds were depended on mass measurements, elemental analysis results, ^{1}H, ^{13}C NMR and FTIR spectra. The masses of TAMP-M /TIMP-M compounds were determined by mass spectrometries (HRMS and MALDI TOF/TOF). The samples were analyzed under positive ionization conditions when HRMS (TOF/MS) was used. The ESI-MS method was chosen because of ions formed upon ESI under soft ionization condition [18]. In the mass spectra of TAMP/TIMP-metal compounds, isotopic patterns clearly identified metal containing ions, because there were a few relevant ions in spectra. For example, zirconium has four isotopes with significant natural abundance from 89.90 to 93.91 Da. The *m/z* spectrum of $(TAMP)_3Zr_2(O^{n}Pr)O_2$ compound showed ions at $[C_{45}H_{49}N_3O_6Zr^{92}Zr^{94}H]^+$ =915.5, $[C_{45}H_{49}N_3O_4Zr^{90}Zr^{90}H]^+$ =876.6, $[C_{45}H_{49}N_3O_4Zr^{90}Zr^{91}H]^+$ = 877.6, $[C_{45}H_{49}N_3O_4Zr^{90}Zr^{92}H]^+$ = 878.6, $[C_{43}H_{45}N_3O_4Zr_2H]^+$= 850.4, and $[C_{42}H_{43}N_3O_4Zr_2H]^+$ = 834.4 Da. (Figure 1). Especially the masses of TIMP compounds were determined by MALDI-TOF mass spectrometry. Although simple linear MALDI-TOF instrument is rather low resolution mass spectrometer, it gives a distribution of fragments of ions. For example, the MALDI-TOF *m/z* spectrum of $(TIMP)_4Ti_2O_2$ compound showed ions at $[C_{56}H_{48}N_4O_6Ti_2{}^{48}]$ =968.33 (100%) and $[C_{56}H_{48}N_4O_4Ti^{48}]$ = 924.25 (16%) Da (Figure 2). The suggested formula of ligands (TAMP and TIMP) and metal compounds (3-8) were consistent with elemental analysis and ^{1}H NMR results. MS measurements of TAMP and TAMP-metal compounds showed that compounds were dimeric by an oxo bridge in contrast to $ZrCl_2$-amino acid Schiff base compounds [19].

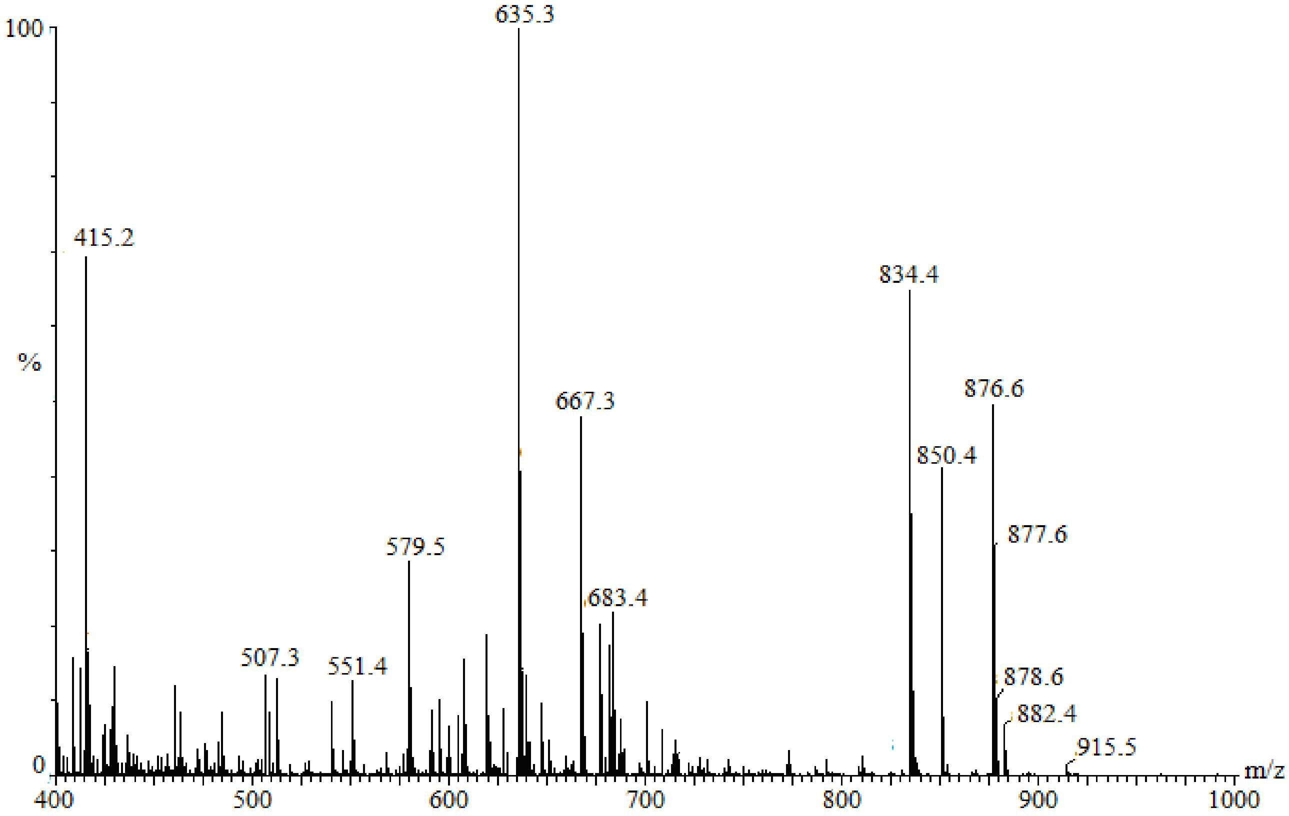


Figure 1. MS spectrum of $(TAMP)_3Zr_2(O^nPr)O_2$ compound under positive ionization conditions.

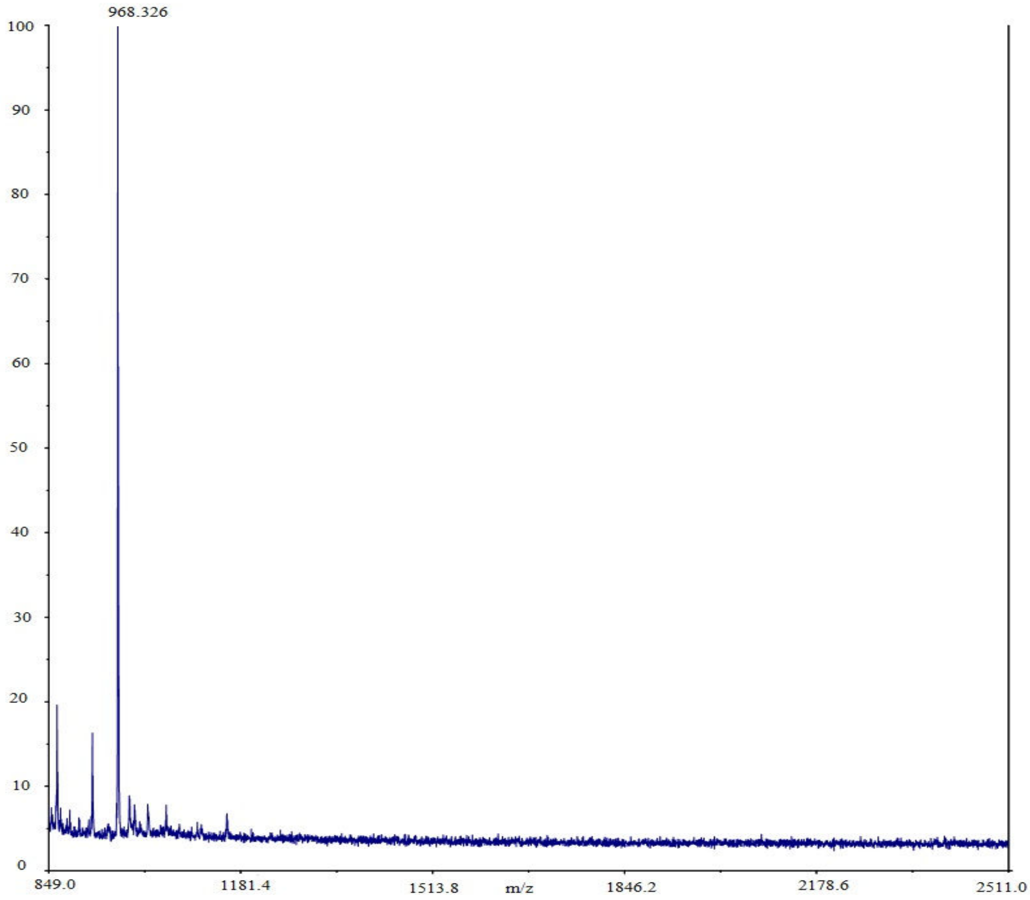
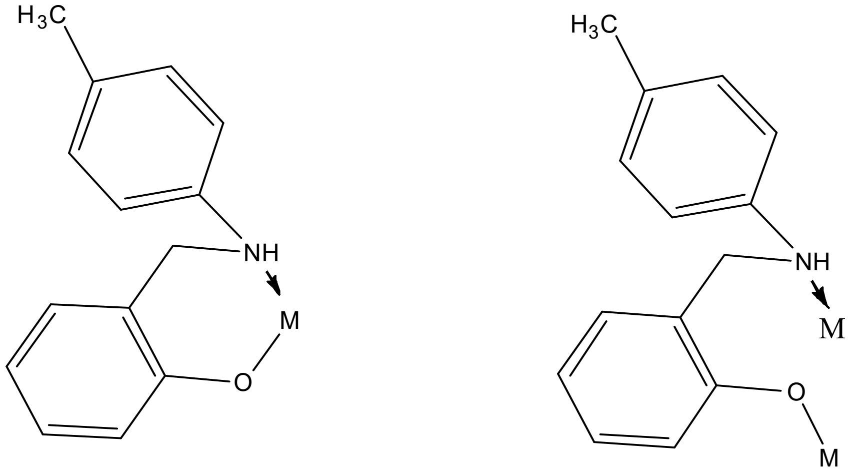


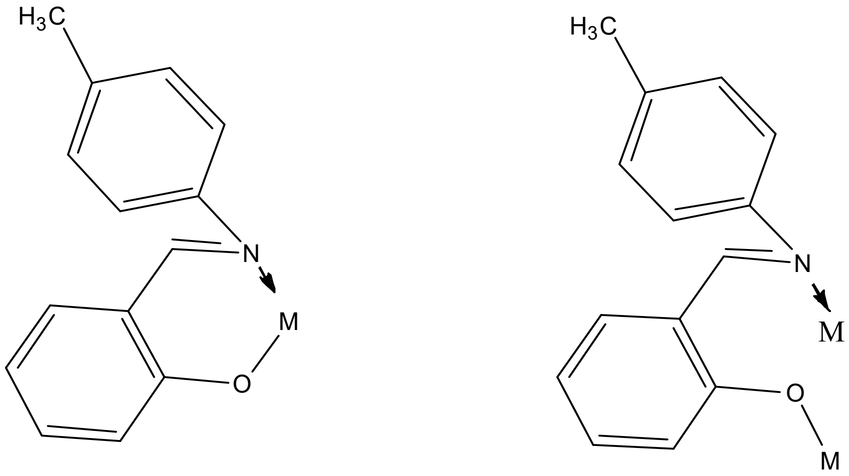
Figure 2. MALDI-TOF/MS spectrum of $(TIMP)_4Ti_2O_2$ compound.

TAMP and TIMP ligands were bound through both O and N atoms at the same time to one metal ion or two metal ions. These bindings are based on FTIR and NMR data of compounds and can be drawn as seen in Scheme 1.



TAMP-M
Chelate

TAMP-M_2
Chelate bridging



TIMP-M (M:Ti and Zr)
Chelate

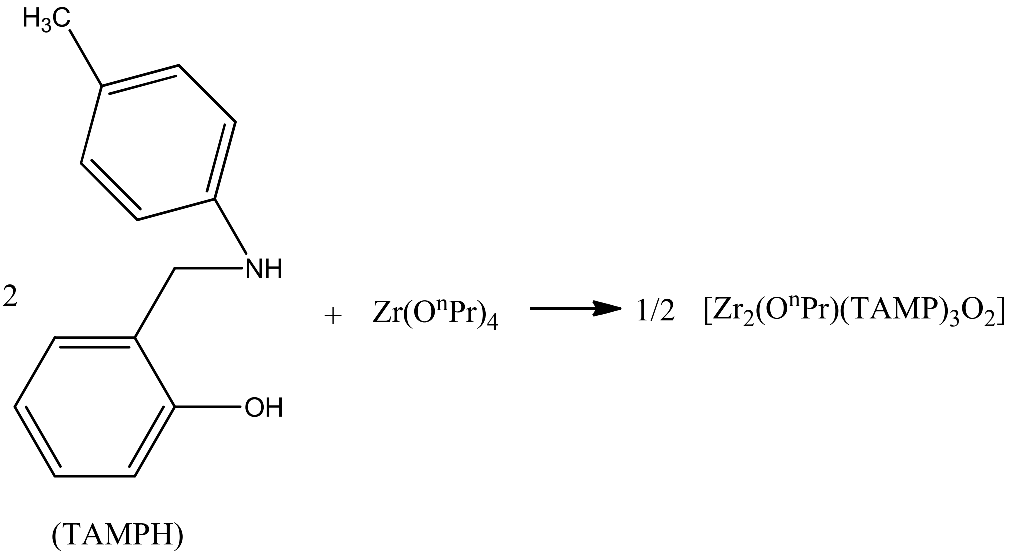
TIMP-M_2
Chelate bridging

Scheme 1. The structures of TAMP and TIMP-metal compounds.

FTIR spectrum of free 2-((*p*-tolylamino)methyl)phenol exhibited bands at ~3416 and 3261 cm^{-1} corresponding to stretching vibrations of the OH and NH groups, respectively [6,14]. After coordination of TAMP ligand to metal alcoholate, the broad OH band at ~3416 cm^{-1} disappeared and the NH band appeared at slightly different region. These FTIR measurements showed that the formations of metal compounds were stabilized by coordination of the phenoxido ligand and the amine functionality. TIMP ligand was also coordinated to metal centers by forming phenoxido-imino derivatives. A strong band is observed at ~1578 cm^{-1} for

C=N group in the FTIR spectra of TIMPH ligand. Coordination of nitrogen to the metals, the C=N band is shifted to the lower value (1570-1540 cm^{-1}) in the FTIR spectra. The shifting of this group to lower value in the metal compounds suggests the coordination of metal ion through nitrogen atom of C=N group. It is expected that coordination of nitrogen to the metal atom reduces the electron density in the C=N bond and lowers the value of C=N frequency [6,20]. The phenolic C-O stretch appears at ~1282 cm^{-1} in free ligand, whereas it appears at 1312-1308 cm^{-1} in the compounds. This is a sign of bonding through phenolic oxygen. These observations are consistent with literature data [6,20].

The ^{1}H NMR spectra of TAMP-Zr and TAMP-Ti compounds showed the expected peaks with peak multiplicities. The reaction between $Zr(O^nPr)_4$ and TAMPH can be shown in the Scheme 2.



Scheme 2. The reaction between $Zr(O^nPr)_4$ and TAMPH.

^{1}H NMR spectrum of TAMP-Zr compound showed triplets at 0.98 ppm for CH_3 protons, multiplets at 1.63 ppm for CH_2 protons and triplets at 3.65 ppm for OCH_2 protons of n-propylate groups in TAMP-Zr-O^nPr compound. The signals of TAMP groups appeared at 2.34 (s, CH_3), 4.42 (s, CH_2N), 6.81 (d, 2H, CH, aromatic), 6.94 (m, 2H, CH), 7.11 (d, 2H, CH), 7.19 (d, 1H, CH), 7.27 (t, 1H, CH), respectively (Figure 3). The signal for the C-OH proton is absent in the ^{1}H NMR spectrum. The lack of a hydroxyl proton signal at around ~8.50 ppm indicates that

TAMP is completely coordinated to zirconium. ^{13}C NMR spectrum of TAMP-Zr compound showed the expected peaks as given in the experimental section (Figure 4). The ^{13}C NMR data of compounds were consistent with literature data given for phenoxyimine/amine-$TiCl_2$, -CpTi, -CpZr compounds [15, 20-23].

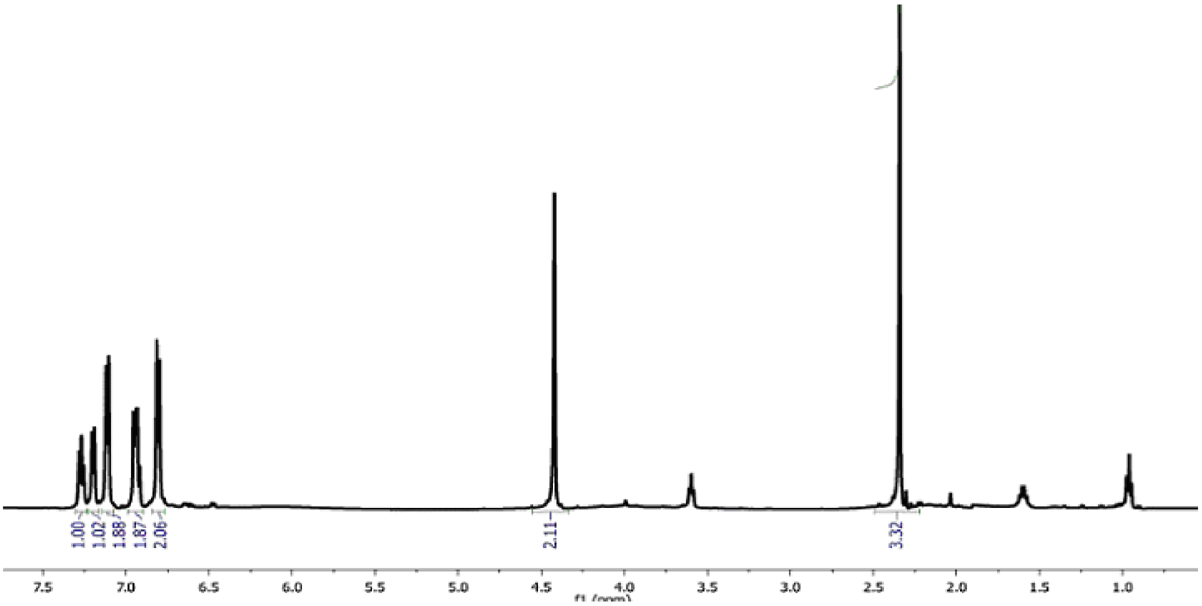


Figure 3. ^{1}H-NMR spectrum of $(TAMP)_3Zr_2(O^nPr)O_2$ compound

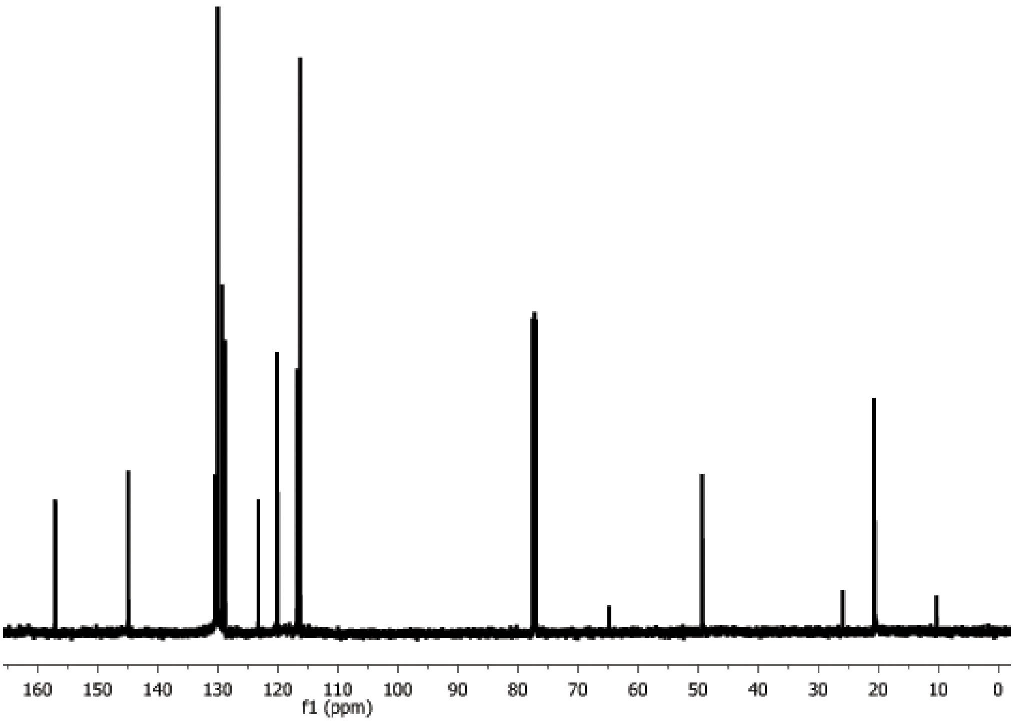
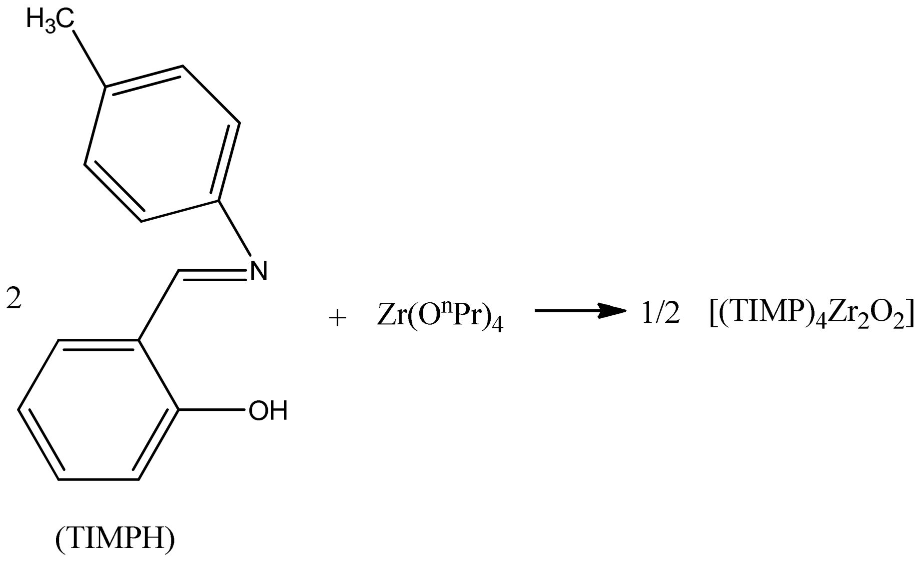


Figure 4. ^{13} C-NMR spectrum of $(TAMP)_3Zr_2(O^nPr)O_2$ compound

The reaction between $Zr(O^nPr)_4$ and TIMPH can be shown in the Scheme 3. In contrast to ^1H and ^{13}C NMR spectra of TAMP-Zr compound, ^1H and ^{13}C NMR spectra of TIMP-Zr compound showed no peaks for n-propylate groups. In other words, in the presence of TIMP ligand the *n*-propylate groups were released from zirconium atom.



Scheme 3. The reaction between $Zr(O^nPr)_4$ and TIMPH.

^1H NMR and ^{13}C NMR (Figure 5) signals of TIMP groups appeared at 2.44 (s, CH_3), 7.0 (t,1H, CH), 7.10 (d, 1H, CH), 7.26 (m, 4H, CH), 7.43 (d, CH, aromatic), 8.66 (s, CH=), and 21.21 (CH_3Ph), 117.34, 119.13, 119.46, 121.15, 129.90, 130.15, 132.27, 133.04, 137.04, 146.0 (=CipsoN), 161.27 (=C-O, Ar), 161.81 (CH=N), respectively. ^1H NMR spectra of all TIMP-M compounds showed that no alcoholate groups remained as bonded to metals. However, ^1H NMR spectra of TAMP-M compounds showed expected peaks for alcoholate groups. TIMP ligand caused more condensation reactions than TAMP ligand as given in the experimental section. This can be attributed to the strong hygroscopic properties of metal-imine compounds. As written in the experimental section, all reactions (3-8) were conducted in atmospheric conditions instead of inert conditions (Ar, N_2). It was one of the purposes of this study to reduce the number of alcoholate groups of metal alcoholates to form single site catalysts for polymerization reactions. Therefore, some of the alcoholate groups underwent condensation reactions to form oxo groups in the presence of TAMPH and TIMPH ligands under atmospheric conditions. The presence of moisture was necessary to form oxo groups from metal alcoholates. The resulted oxo groups were bridged between metal atoms. This was the expected results as seen in literature data [24,25]. The number of oxo groups determined by both elemental analysis and ^{1}H NMR measurements. The ^{13}C NMR spectra of the metal compounds gave somewhat similar data for carbon resonances with that of the free TAMPH and TIMPH ligands. Because carbon atoms of TIMP and TAMP ligands (except for =C-O and =C-N carbons) were not affected too much when TAMP and TIMP were bonded to metals. The =CO and =C-N carbon peaks were shifted to somewhat different region when compared those of free ligands peaks in ^{13}C NMR spectra.

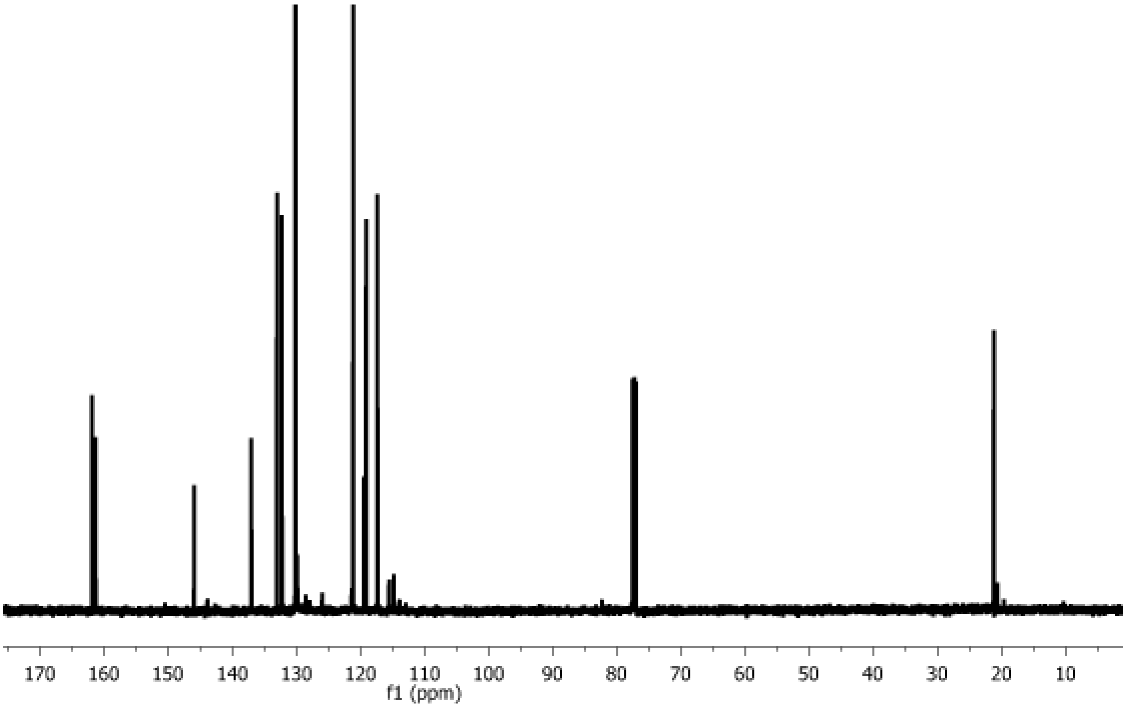


Figure 5. ^{13} C-NMR spectrum of $(TIMP)_4Zr_2O_2$ compound

Since TAMP-metal compounds have an active alcoholate group, TAMP-Ti compound was tested in the polymerization of PO and ε-CL. In order to characterize the PPO and PCL samples, GPC (gel permeation chromatography), ^{1}H NMR, and ^{13}C NMR instruments were used. The obtained data were consistent with the previously published ^{13}C NMR data for PPO [16] and PCL polymers [17]. ^{1}H and ^{13}C NMR spectra illustrated that main changes occurred at the CH and CH_2 protons of oxirane ring when PO was polymerized. For instance, there were shifts from 2.4-2.9 ppm to 3.4-3.7 ppm for the CH_2 and CH protons of PO. The maximum recovery rate of polymer and the maximum polymerization velocities of PO occurred at 75 °C for Ti catalyst.

The conversion of monomer PO and ε-CL to polymers was followed by GPC measurements. GPC was used to determine molecular weight of polymers. Changing the reaction time and temperature caused to obtained different weight average molecular weights (*Mw*) or number average molecular weights (*Mn*) polymers (Table 1). For polymers of PO prepared with TAMP-Ti stirring at 25 °C for 3 days, the main peak appeared at 2070 Da for *Mw* or 1912 Da for *Mn*. The ratio of *Mw/Mn* was 1.08. When the temperature was increased from 25 to 75 °C, the conversions of monomers to polymers increased from 28.6% to 100% and also molecular weight of polymer increased for titanium catalyst (Figure 6). However, as can be seen in Figure 6, the GPC chromatogram of the PO polymer prepared at 75 °C with Ti-TAMP showed bimodal molecular weight distribution. The first peak in Figure 6 has weight average molecular weight 5022 Da or number average molecular weight 3989 Da with the *Mw/Mn* value of 1.26. Ti-TAMP compounds were also tested in the polymerization of ε-caprolactone. The polymerization reactions were conducted without solvent at 100 °C. The conversion of ε-CL monomer as high as 99% was observed after polymerizing for 12 hours. The weight average molecular weight and the number average molecular weight of PCL were ~35000 Da and ~30000 Da, respectively, with the *Mw/Mn* value of ~1.15.

Table 1. Data for PO and ε-CL polymers obtained from GPC measurements.

Catalyst	**T, °C**	**Time, h**	**M_w**	**M_n**	**(M_w/M_n)**	**Conversion (%)**
TAMP-Ti	25	72	2070 PO	1912 PO	1.08	28.6
TAMP-Ti	50	48	2385 PO	2175 PO	1.09	32.7
TAMP-Ti	75	48	5022 PO	3989 PO	1.26	100
TAMP-Ti	75	48	11400 ε-CL	10200 ε-CL	1.12	30
TAMP-Ti	100	12	35656 ε-CL	30835 ε-CL	1.15	99

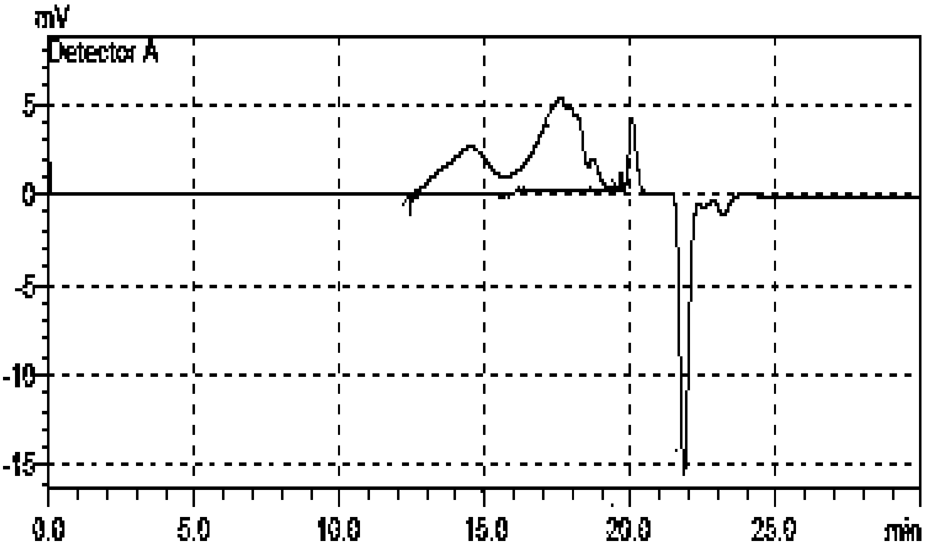
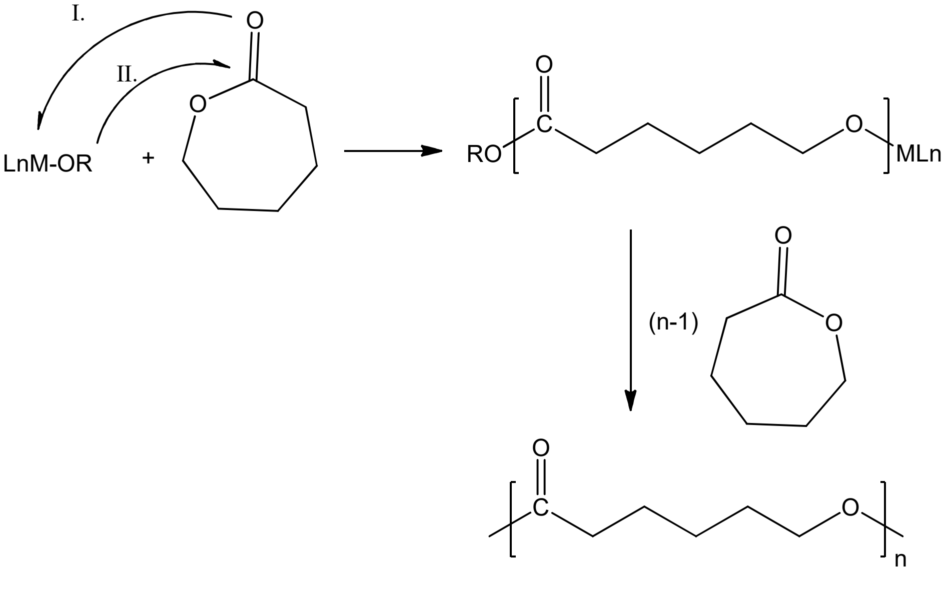


Figure 6. Gel permeation chromatogram of PO polymer prepared at 75 °C with $(TAMP)_3Ti_2(O^iPr)O_2$ compound.

Transition metal compounds carry out ROP of ε-CL and PO via a coordination-insertion mechanism [26-33]. For example, the polymerization mechanism of ε-CL can be shown in Scheme 4. The spectroscopic data suggest that ε-CL attacks the metal-center first and then the nucleophile OR- ion attacks C=O carbon atom in ε-CL.



Scheme 4. The attack of ε-caprolactone to metal center of metal-alcoholate compound (I.: first step, II.: second step).

CONCLUSIONS

The result of this study showed that TAMPH and TIMPH were good ligands for modification of Ti and Zr-alcoholates. These compounds were synthesized and characterized by elemental analysis, mass measurements and spectroscopic techniques including ^{1}H NMR, ^{13}C NMR and FTIR spectroscopy. Each product was formulated by combination of techniques mentioned above. The prepared Ti-compound having an active alcoholate group was effective as catalyst for the polymerization of PO and ε-CL at mild reaction conditions. The structures of polymers were characterized by spectroscopic techniques and gel permeation chromatography (GPC).

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Türkçe Öz ve Anahtar Kelimeler

TAMP/TIMP-Ti ve Zr Bileşiklerinin Hazırlanması ve Karakterizasyonu ve Propilen Oksit ile ε-Kaprolakton Üzerindeki Katalitik Aktivitesi

Asgar Kayan

Öz: Titanyum ve zirkonyum 2((p-tolilamino/p-tolilimino)metil)fenolat (TAMP ve TIMP), etil alkol içinde 2-((p-tolilamino)metil)fenol (TAMPH) ve 2-((p-tolilimino)metil)fenol (TIMPH) bileşiklerinin Ti- ve Zr-alkolatlarının tepkimesinden hazırlanmıştır. Bu bileşiklerin karakterizasyonu için ^{1}H, ^{13}C NMR, FTIR, kütle spektrometrisi ve elementel analiz kullanılmıştır. TAMP ve TIMP metal bileşikleri sırasıyla $(TAMP)_3M_2(OR)O_2$ ve $(TIMP)_4M_2O_2$ olarak gösterilebilir. Bu bileşiklerin katalitik aktivitesi propilen oksit (PO) ve ε-kaprolakton (ε-CL) bileşiklerinin polimerleşmesinde kullanılmıştır ve Ti-TAMP'ın aktif olduğu bulunmuştur. Poli-propilen oksit (PPO) ve poli-kaprolakton (PCL) ^{1}H, ^{13}C NMR ve jel geçirgenlik kromatografisi (GPC) ile tanımlanmıştır.

Anahtar kelimeler: Metal alkoksit, katalizör, Schiff bazı, ε-kaprolakton, polimer.
Gönderilme: 28 Haziran 2016. **Düzeltme:** 06 Ağustos 2016. **Kabul:** 6 Eylül 2016.