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Synthesis of ArOTiCl$_3$ complexes and their application for ethylene polymerization and copolymerization

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Abstract. In this article, novel olefin polymerization catalyst with lower cost and simple synthetic process were developed, ArOTiCl$_3$ complexes [(2-OMeC$_6$H$_4$O)TiCl$_3$(**C1**), (2,4-Me$_2$C$_6$H$_3$O)TiCl$_3$(**C2**), TiCl$_3$(1,4-OC$_6$H$_4$O)TiCl$_3$ (**C3**), TiCl$_3$(1,4-OC$_6$H$_2$O-Me$_2$-2,5) TiCl$_3$(**C4**)] and corresponding (ArO)$_2$TiCl$_2$ complexes [TiCl$_2$(OC$_6$H$_4$-OMe-2)$_2$(**C5**) and TiCl$_2$(OC$_6$H$_3$-Me$_2$-2,6)$_2$(**C6**)] have been synthesized by the reaction of TiCl$_4$ with phenol, all these complexes were well characterized with ^{1}H NMR,^{13}C NMR, MASS and EA. When combined with methylaluminoxane (MAO), the ArOTiCl$_3$/ MAO system shows high activity for ethylene copolymerization with 1-octene and copolymer was obtained with broaden molecular weight distribution (MWD). The ^{13}C NMR result of polymer indicates that the 1-octene incorporation in polymer reached up to 8.29 mol%. The effects of polymerization temperature, concentration of polymerization monomer and polymerization time on the catalytic activity have been investigated.

Keywords: ArOTiCl$_3$ complex; catalyst; ethylene/1-octene; copolymerization

1. Introduction

Linear Low density polyethylene (LLDPE) has been widely used in industry because of its good performance. In generally, LLDPE is produced by copolymerization of ethylene and α-olefins. Due to the huge market demand of LLDPE, catalyst for olefin copolymerization attracts more and more research interest. At present, the copolymerization catalyst systems include metallocene (Delferro and Marks 2011), supported metallocene (Severn and Chadwick 2013), Constrained Geometry Catalyst (CGC) invented by Dow Corp. (Chum and Swogger 2008), FI Catalysts (Makio *et al*. 2011), Tandem system (Guo *et al*. 2015) and solid state bimetallic system (Sun *et al*. 2017 and Fu *et al*. 2017). Today, novel copolymerization catalyst systems and polymerization processes are still the research focus in the field of catalysts, such as dissymmetric ansa zirconocene complexes (Rimkus and Alt 2017), novel CGC (Lee *et al*. 2017), rare-earth

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complexes (Yao *et al*. 2013), supported ionic liquid system (Ochędzan-Siodłak and Bihun 2017), reversible addition-fragmentation chain transfer copolymerization (Dommanget *et al*. 2014) and coordinative chain transfer copolymerizations (Valente *et al*. 2013). However, LLDPE is still mainly manufactured by supported Ziegler-Natta catalysts (Baier *et al*. 2014), and heterogeneous Ziegler-Natta catalysts have multiple active centers, the obtained LLDPE has a wide molecular weight distribution (MWD) and chemical composition; on other hand, polyethylene obtained with metallocene catalysts often has a narrow MWD and chemical composition, which leads to difficult processing, the processing by injection molding and blow molding as well as extrusion requires shear thinning resulting from broad MWD. And so, the satisfactory combination of good flow ability and improved mechanical properties is achieved by tailoring MWD or by incorporating long-chain branches into PE chain (Sturzel *et al*. 2016). In the field of polyolefins, it is of great industrial significance to find LLDPE catalysts with simple synthesis process and relatively low cost. In 2000, Nielson *et al*. (2000) developed mono phenoxy titanium complexes $ArOTiCl_3$, the result of density functional calculations shows the lone pairs on oxygen donate electron density to titanium but O(2p)-to-C = C (π*) donation weakens the Ti–O interaction in the phenoxide complex. In 2010, Kong *et al*. (2010) found that, compared with the conventional catalysts, $(BzO)TiCl_3/MgCl_2$ system provide an improved copolymerization activity and stability, a good incorporation of 1-octene into the polyethylene main chain (7.60 mol% at 80℃) and produce random copolymer with high molecular weight. They attributed it to the steric hindrance of aryl oxygen, which is not conducive to the tight loading of Ti on the surface of the carrier, while the aryl oxygen has an electron donating effect and reduces the Lewis acidity of the Ti atom (Kong *et al*. 2010). In 2012, Xia *et al*. (2012) synthesized $TiCl_3(OC_6H_5)$ and immobilized it on $MgCl_2$, they found that the aryloxy-containing catalysts showed higher activity than $TiCl_4/MgCl_2$ when the $(i\text{-}Bu)_3Al$ (TIBA) used as cocatalyst, furthermore, the TIBA activated aryloxy-containing catalysts was found to produce poly (ethylene-co-1-hexene) with more uniform chemical composition distribution. In summary, the study of phenoxyl titanium catalysts for olefin polymerization is of great importance in reducing costs and simplifying processes. However, the catalytic behavior of these compounds under homogeneous conditions has not been reported in the literature, in this article, mononuclear phenoxyl titanium complexes and corresponding binuclear titanium complexes are prepared; their catalytic behavior is also investigated in detail.

2. Experimental

2.1 Chemicals and synthesis

Catalyst preparation and polymerization were carried out under dry argon using standard Schlenk techniques or in a glove box. $TiCl_4$ (Shanghai Mayer Chemical Comp.) and ArOH compounds (Ar = $2,4\text{-}Me_2C_6H_3$-, $2\text{-}MeOC_6H_4$-) , $1,4\text{-}C_6H_4(OH)_2$, and $2,5\text{-}(Me_3C)_2C_6H_2(OH)_2\text{-}1,4$ purchased from Sinopharm Chemical Reagent Co., L.td) were distilled under reduced pressure and stored in Ar atmosphere before use. Toluene, THF, diethyl and n-haxane (Sinopharm Chemical Reagent Co.Ltd.) was distilled over sodium/benzophenone ketyl under Ar atmosphere before use. Ethylene (polymerization grade, a product of Sinopec) was dried and purified by passing through columns of 4Å molecular sieves before use. 1-octene (97%) from ShangHai Chunyu Co. was purified by distillation over Na and stored in a Schlenk tube containing 4 Å molecular sieves. MAO (97%) from Azo.Co. and no was further processing prior to use.

2.2 Characterization of the catalysts and polymer

^{1}H NMR spectra and ^{13}C{1H} NMR were recorded on a Bruker ADVANCE DMX 400 spectrometer in CDCl$_3$ or d$_6$-DMSO (for complexes) and o-C$_6$D$_4$Cl$_2$ (for polymer samples) respectively. IR spectra were recorded on a Nicolet Nicolet E.S.P.560 FT-IR spectrometer as KBr pellets. Mass spectra were obtained using the direct insertion probe method on Micromass HP 5989A instrument operating at 70 eV. Elemental analyses were performed on an EA-1106. GPC was obtained on PL-GPC-220 at 135°C with polystyrene as standard.

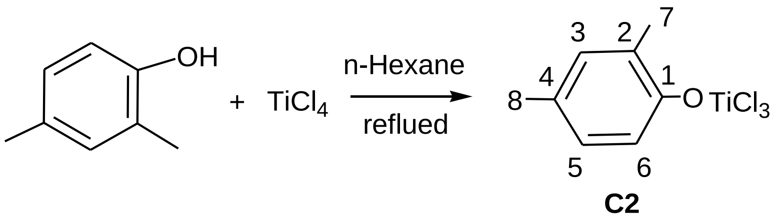
2.3 Synthesis of **C1-C6**

Synthesis of Complex **C1**

The procedures of synthesizing **C1** were as follows.

2-MeOC$_6$H$_4$OH (0.62 g, 0.005 mol) in 40 mL toluene was added via a syringe to TiCl$_4$ (0.55 mL, 0.005 mol) in 10 mL toluene at 0°C, and the mixture was heated refluxed until the released gas passing over butyllithium no longer form white mist. The solvent was removed under vacuum until 30 Ml solution remaindered, brown solid precipitated at -20°C, the mixture was then filtered and the residue was washed with cool toluene (15 mL×3, 0°C), and dried under vacuum to give 1.09 g deep brown solide (79.5% yield) .^{1}H NMR (δ, ppm, CDCl$_3$, 400 MHz) : 7.04 (*t*, 1H, J = 7.6 Hz, Ar-*H*), 6.94 (*t*, 1H, J = 7.6 Hz, Ar-*H*), 6.86 (*d*, 1H, J = 7.6 Hz, Ar-*H*), 6.747 (*d*, 1H, J = 7.6 Hz, Ar-*H*), 4.04 (*s*, 3H, -OC*H*$_3$). ^{13}C NMR (δ, ppm, d$_6$-DMSO, 100 MHz) : 159.0 (1-*C*), 148.8 (2-*C*), 121.997 (5-*C*), 120.2 (4-*C*), 116.9 (6-*C*), 113.7 (3-*C*), 56.7 (-Me). HRMS (EI) : m/z calcd for [$TiC_7H_7Cl_3O_2^+$]: 275.8991; found : 275.8987. IR (KBr, cm^{-1}) : 3397 (w), 3045.2 (w), 2975 (w), 1642 (w), 1484 (w), 1459 (w), 1325 (w), 1278 (w), 1256 (w), 1249 (w), 1208 (w), 1171 (w), 1159 (w), 1155 (w), 1110 (w), 1028 (w), 997 (w), 922 (w) 882 (w), 857 (w), 804 (w), 775 (w), 749 (w), 664 (w), 642 (w), 586 (w), 574 (w), 474 (w), 453 (w), 412 (w).

Synthesis of **C2** TiCl$_3$(OC$_6$H$_3$-Me$_2$-2,4)

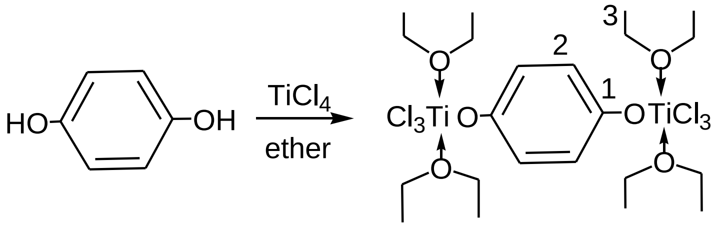


C2

((Equ 2))

The procedures of synthesizing **C2** was similar to that of **C1**, toluene was replaced by n-hexane used as a solvent, 2,4-Me$_2$C$_6$H$_3$OH (0.61 g, 0.005 mol), TiCl$_4$ (0.55 mL, 0.005 mol), brown solide 1.22 g (89.4% yield). ^{1}H NMR (δ, ppm, CDCl$_3$, 400 MHz) : 7.18 (*d*, 1H, J = 8 Hz, Ar-H), 6.96 (*m*, 2H, J = 8 Hz, Ar-H), 2.44 (*s*, 3H, p-CH$_3$), 2.32 (*s*, 3H, o-CH$_3$). ^{13}C NMR (δ, ppm, CDCl$_3$, 100 MHz) : 16.5 (7-*C*), 21.1 (8-*C*), 119.6 (2-*C*), 127.4 (6-*C*), 127.3 (3-*C*), 131.2 (4-*C*), 136.616(5-*C*), 170.3 (1-*C*). HRMS (EI) : m/z calcd for [$TiC_8H_9Cl_3O^+$]: 273.9198; found : 273.9197. IR (KBr, cm^{-1}) : 3385 (w), 3007 (w), 2971 (w), 2932 (w), 2861 (w), 2732 (w), 1605 (w), 1480 (w), 1440 (w), 1369 (w), 1255 (w), 1218 (w), 1151 (w), 1124 (w), 1093 (w), 1025(w), 944 (w), 881 (w), 814.0 (w), 784 (w), 719 (w), 607 (w), 524(w), 509 (w), 486 (w), 437 (w), 413 (w).

Synthesis of **C3** $(Et_2O)_2$-$TiCl_3(OC_6H_4O)TiCl_3$-$(OEt_2)_2$

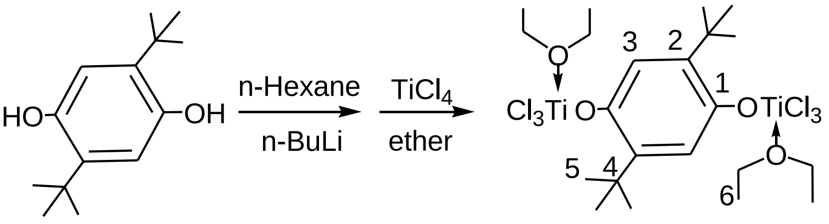


C3

((Equ 3))

The procedures of synthesizing **C3** was similar to that of C**1**, toluene was replaced by ethyl ether, 1,4-$(OH)_2C_6H_4$ (0.55 g, 0.005 mol), $TiCl_4$ (1.10 mL, 0.01 mol), brown solid 3.24 g (91.2% yield). ^1H NMR (*δ*, ppm, d_6-DMSO, 400 MHz) : 6.57 (*s*, 4H, Ar-H), 3.37 (*q*, 16H, *J* = 6.8 Hz, -CH_2-), 1.08 (*t*, 24H, *J* = 6.8 Hz, -CH_3). ^{13}C NMR (*δ*, ppm, d_6-DMSO, 100 MHz) : 162.3 (1-*C*), 120.6 (2-*C*), 64.8 (-OCH_2-), 15.1 (3-*C*). Anal. Calcd. For $[C_{22}H_{44}Cl_6O_6Ti_2]$: C, 37.06% ; H, : 6.22%, found : C, 37.11% ; H, 6.43%. IR (KBr, cm^{-1}) : 3337 (w), 2961 (w), 2928 (w), 2873 (w), 2366 (w), 1602 (w), 1484 (w), 1371 (w), 1213 (w), 1095 (w), 1011 (w), 893 (w), 837 (w), 758.5 (w), 736 (w), 693 (w), 564 (w), 495 (w).

Synthesis of **C4** Et_2O-$TiCl_3(OC_6H_2$-$^{t}Bu_2$-2,5-O)$TiCl_3$-OEt_2



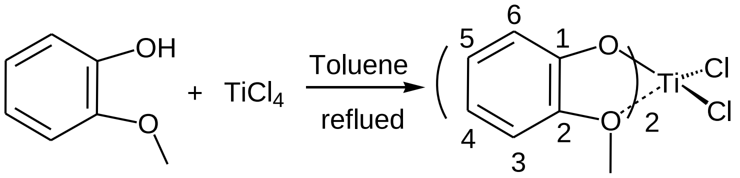
C4

((Equ 4))

To the solution of 2,5-$^{t}Bu_2C_6H_2$-(OH)-1,4 (2.05 g, 0.01 mol) in 60 mL hexane, solution of n-BuLi (1.5M, 7mL) in hexane was slowly added at 0°C, it can ben found a large amount white sediment produced, 30 minutes later, the mixture naturally warmed to room temperature and stirred for 10 hours, and then the mixture was filtered, the residue was washed with hexane (20 mL×3), the solvent was removed to obtain white powder 1,4-$C_6H_4O_2Li_2$.

To the solution of $TiCl_4$ (0.55 mL, 0.005 mol) in 20 mL ethylether, the suspend solution of 1,4-$C_6H_4O_2Li_2$ (0.59 g, 0.0025 mol) in 30 mL ethyl ether was added at 0°C, brown solid was produced immediately, the mixture was then heated to reflux until no HCl gas blow out, stop heating and cool to -20°C, brown solide precipitated and filtered and the residue was washed with cool ethyl ether (10 mL×3, -20°C), dried under vacuum to give 1.51 g deep brown solide filtered (89.6% yield). ^1H NMR (*δ*, ppm, d_6-DMSO, 400 MHz) : 6.67 (*s*, 2H, Ar-H), 3.44 (*q*, 8H, *J* = 6.8 Hz, -CH_2-), 1.34 (*s*, 18H, -$C(CH_3)_3$), 1.15 (*t*, 12H, *J* = 6.8 Hz, -CH_3). ^{13}C NMR (*δ*, ppm, d_6-DMSO, 100 MHz) : 160.9 (1-*C*), 147.5 (2-*C*), 114.6 (3-*C*) , 64.9 (-OCH_2-), 34.3 (4-*C*), 30.3 (5-*C*), 14.9 (6-*C*). Anal. Calcd. For $[C_{22}H_{40}Cl_6O_4Ti_2]$: C, 40.77% ; H, :6.56%, found : C,40.83% ; H, 6.82%. IR (KBr, cm^{-1}) : 3404 (w), 2959 (w), 2870 (w), 1609 (w), 1486 (w), 1398 (w), 1388.6 (w), 1364 (w), 1255 (w), 1196 (w), 1181 (w), 1121 (w), 1022 (w), 930 (w), 888 (w), 832 (w), 797 (w), 703 (w), 646 (w), 522 (w), 470 (w), 403 (w).

Synthesis of **C5** $TiCl_2(OC_6H_4\text{-}OMe\text{-}2)_2$

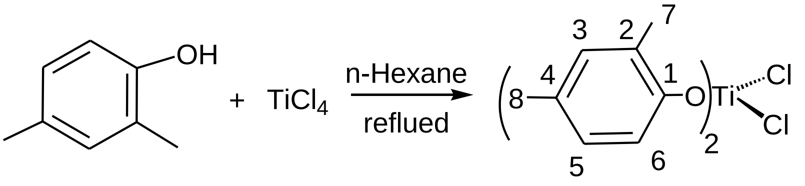


C5

((Equ 5))

The procedures of synthesizing **C5** was similar to that of C**1**, 2-$MeOC_6H_4OH$ (1.24 g, 0.01 mol), $TiCl_4$ (0.55 mL, 0.005 mol), red solide 1.67 g (91.8% yield). ^1H NMR (δ, ppm, $CDCl_3$, 400 MHz,) : 7.04 (*t*, 2H, *J* = 8.0 Hz, Ar-H), 6.94 (*t*, 2H, *J* = 8.0 Hz, Ar-H), 6.87 (*d*, 2H, *J* = 8.0 Hz, Ar-H), 6.73 (*d*, 2H, *J* = 8.0 Hz, Ar-H), 4.04 (*s*, 6H, -OMe). ^{13}C NMR (δ, ppm, $CDCl_3$, 100 MHz) : 152.3 (1-*C*), 149.5 (2-*C*), 124.0 (3-*C*), 122.5 (4-*C*), 113.3 (5-*C*), 110.1 (6-*C*), 59.5 (-Me). HRMS (EI) : m/z calcd for $[TiC_{14}H_{14}Cl_2O_2^+]$: 363.9749; found : 363.9753. IR (KBr, cm^{-1}) : 3412 (w), 3059 (w), 2942 (w), 1641 (w), 1482 (w), 1459 (w), 1325 (w), 1277 (w), 1249 (w), 1208 (w), 1162 (w), 1158 (w), 1154 (w), 1111 (w), 1027 (w), 997 (w), 921 (w), 881 (w), 856 (w), 813 (w), 769 (w), 750 (w), 662(w), 632 (w), 579 (w), 559 (w), 469 (w), 449 (w), 421 (w).

Synthesis of **C6** $TiCl_2(OC_6H_3\text{-}Me_2\text{-}2,4)_2$



C6

((Equ 6))

The procedure of synthesizing **C6** was similar to that of C**1**, toluene was replaced by n-hexane. 2,4-$Me_2C_6H_3$ (1.22 g, 0.01 mol), $TiCl_4$ (0.55 mL, 0.005 mol), red solide 1.59 g, (85.6% yield). ^1H NMR (δ, ppm, $CDCl_3$, 400 MHz,) : 7.18 (*d*, 2H, *J* = 8.0 Hz, Ar-H), 6.97 (*m*, 4H, *J* = 8.0 Hz, Ar-H), 2.44 (*s*, 6H, -Me), 2.32 (*s*, 6H, -Me). ^{13}C NMR (δ, ppm, $CDCl_3$, 100 MHz,) : 16.4 (7-*C*), 21.0 (8-*C*), 119.6 (2-*C*), 127.2 (6-*C*), 127.3 (3-*C*), 131.1 (4-*C*), 136.7 (5-*C*), 170.4 (1-*C*). HRMS (EI) : m/z calcd for $[TiC_{16}H_{18}Cl_2O_2^+]$: 360.0163; found : 360.0157. IR (KBr, cm^{-1}) : 3336.1 (w), 3014.3 (w), 2958.0 (w), 2920.8 (w), 2860.9 (w), 2732.3 (w), 1604.8 (w), 1486.7 (w), 1455.8 (w), 1378.7 (w), 1255.4 (w), 1217.7 (w), 1150.7 (w), 1123.8 (w), 1113.5 (w), 1034.9 (w), 944.3 (w), 881.3 (w), 814.0 (w), 784.1 (w), 716.5 (w), 600.8 (w), 528.0 (w), 503.3 (w), 483.8 (w), 432.7 (w), 406.5 (w).

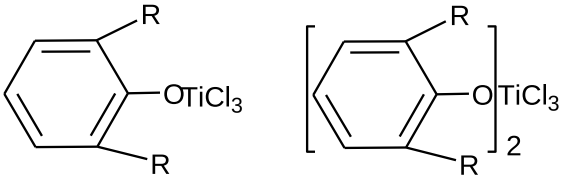
2.4 Polymerization procedure

Polymerization at 1.0 MPa ethylene pressure was carried out in a 250 mL reactor equipped with a mechanical stirring bar. At first, the reactor was filled with argon 3 times and replaced with ethylene, at 50℃, 40 mL toluene, certain amount of 1-ocetene and catalyst in toluene were then injected into the reactor, cocatalyst MAO in toluene was then added and control the whole valume equal 100 mL, ethylene was introduced into the reactor and kept 1.0 MPa pressure. The polymerization reaction was continued for 30 min under stirring and continuous supply of ethylene, then closed the ethylene, release the pressure of the reactor and put the slurry product into 200 mL ethanol containing 1 mL hydrochloric acid to terminate the reaction and 10 mL of 10% HCl in ethanol (volume fraction) was added to quench the polymerization. The mixture were transferred to a beaker and then separated from the solution by filtration. The collected polymer was washed to neutral with ethanol and then dried overnight in a vacuum oven at 60℃ to constant weight.

3. Results and discussion

3.1 Synthesis and characterization

In order to compare with the complexes in this paper, four complexes were synthesized according to literature (Päivi and Jukka 1994, Alan *et al*. 1986). (See Chart 1)



R = ^{i}Pr **3**
= ^{t}Bu **4**

R = ^{i}Pr **7**
= ^{t}Bu **8**

((Chart 1))

It is found that the reaction is reversible and the mainly product is monosubstituted $ArOTiCl_3$ when the $TiCl_4$ is excess. Actually, all the mono-substitution primary products contain trace amounts multisubstituted products, and recrystallization process must be carried out to obtain a pure mono-substitution product. Therefore, shortening the purification time and decreasing the purification temperature are the key step to obtain pure mono-substitution products, and so the solvent with low boiling point is chosen in order to get a pure product. And so in the process of synthesis of **C2** the toluene was replaced with hexane, although toluene has a much better solubility for reactants and products. Furthermore, in the process of synthesis of **C3** and **C4**, ethyl ether was used as solvent, the one benefit is that the boiling point of ethyl ether is relatively lower and easy to remove at lower temperature, the others is the product obtained is more stable because of the coordination of ethyl ether to titanium atom, which greatly avoid the side reaction. From the result of NMR and EA, it can be seen that the ethyl ether coordination number is related to the steric hindrance on the phenyl ring, in complex **C3** every titanium coordination two molecular ether, on the contrary, in complex **C4** only one molecular ethyl ether coordination to titanium atom because of the steric hindered of ortho tertiary butyl group.

As a derivative of tert-butylbenzene, Complex **C4** cannot be obtained by direct reaction of 2-tBu-phenol with $TiCl_4$, because the direct reaction could leads to an elimination reaction of tert butyl (Wu *et al*. 2007), and so tert-butyl phenol was treated with n-butyl lithium to obtain lithium salts, and then reacted with TiCl$_4$ followed by recrystallization at low temperature to give **C4**.

From the result of synthesis of **C5** and **C6**, it is found that bi-substitution products are obtained by the reaction of small steric hindrance phenol with TiCl$_4$ in proportion to the amount of substance in 2:1. As for sterically hindered phenols, the reverse is true. As expected, complex **4** or **8** was obtained with higher yield through controlling the ratio of phenol to TiCl$_4$. Actually, we didn't find tri-substitution product, which may be caused by the two ortho bulky tert-butyl group, the steric hindrance prevents more ligands coordinating with Ti atom, nd so the synthesis of tri and tetra substituted complex must through other methods as the literature reported (Latesky *et al*. 1985, Prashant *et al*. 2007).

It is worth noting that the chemical shifts of methyl hydrogen of methoxy in **C1** appear at 4.04 ppm, lower 0.24 pm than that of ligand, which is attributed to the coordination of methoxy to titanium atom and the intramolecular chelate structure increase the complex's stability. From the result of MASS, it is found that molecular ion peak is the base peak; the result of MASS also confirms intramolecular chelate structure. The similar phenomenon is also found in the MASS reault of **C5**.

From the ^{1}H NMR result of **C2**, it is found the chemical shift of *ortho*-Me is 2.32 ppm and the *para*-Me is 2.44 ppm, however, in the ^{13}C NMR result, a similar situation appears again and become more obvious: the chemical shift of *ortho*-Me is 6.5 ppm and the *para*-Me is 21.1 pm, which implies that the electron induced effect of *para*-methyl group is larger than *ortho*-Me. Compared with mono-substitution **C2**, the Mass spectra of bi-substitution **C6** shows that the molecular ion peak is the base peak, which indicating that bi-substitution is beneficial to molecular stability.

3.2 Olefin polymerization

Combined with MAO, complexes **C1**-**C4** have been used for olefin polymerization, and the catalytic behavior was investigated carefully. The results were shown in Table 1. However, the TiCl$_2$(OAr)$_2$/MAO system almost has no activity for ethylene polymerization under our condition, therefore, no further investigation is conducted.

From Table 1, it is found that the catalytic activity of **C1**-**C4** was higher than that of Ref. complex **3** and **4**, we attribute this to the steric hindrance of 2,6-position ^{i}Pr and ^{t}Bu group. On other hand, the molecular weight of PE with ArOTiCl$_3$ complexes was higher than that of Cp$_2$TiCl$_2$, and the MWD of former was obviously broaden than that of Cp$_2$TiCl$_2$, which implies that there are more than one activated species in ArOTiCl$_3$-MAO system. It is also found that the α-olefin can be effectively inserted into the propagation polyethylene chain, and the incorporation of 1-ocetene reaches up to 8.29 mol%. It is different from our binuclear metallocene compounds (Xu *et al*. 2006, 2007, Mi *et al*. 2011, Xu and Huang 2013), the catalytic activity of mononuclear **C1** and **C2** is higher than that of binuclear, furthermore, as for **C3** and **C4**, both of the activity and molecular weight for copolymerization is lower than that of ethylene polymerization, all these results suggest that there are no cooperativity effects in binuclear (ArO)$_2$TiCl$_2$–MAO system. It is well known that the stronger the ligand's ability to donate electrons, the higher the catalytic activity. Compared with mononuclear ArOTiCl$_3$, it is clear that the charge density assigned to the central metal Titanium in the binuclear complexes **C3** and **C4** is lower than that of the mononuclear **C1** and **C2**, which leading to the low activity of the binuclear complexes; Furthermore, both of the ligand's steric and electronic effect affected the molecular weight of polymer greatly, and the molecular weight finally depends on the ratio of the chain transfer rate to the chain propagation rate. The

Table 1 The result of Olefin Polymerization with $ArOTiCl_3$-MAO

Run	Cat	Olefin	Activity[a]	M_η[b]	*Mn*[b]	*Mw*[b]	PDI	1-octene Incorporation[c]
1	**C1**	Ethylene	2.40	20.1	2.36	22.69	9.62	
2		E/O	2.20	12.2	1.39	12.82	9.25	6.69
3	**C2**	Ethylene	3.20	25.8	2.29	26.54	11.61	
4		E/O	2.08	11.6	0.82	11.98	14.61	6.18
5	**C3**	Ethylene	1.61	12.1	2.39	14.04	5.87	
6		E/O	1.12	4.50	0.96	4.60	4.79	6.87
7	**C4**	Ethylene	1.68	9.10	1.80	10.84	6.01	
8		E/O	1.30	6.55	1.39	6.89	4.97	8.29
9	**3**	Ethylene	0.44	10.0	1.49	10.2	6.80	
10	**4**	Ethylene	0.10	10.2	2.73	10.9	7.10	
11	Cp_2TiCl_2	Ethylene	4.51	2.52	1.60	2.86	1.79	

Condition: 1-octene = 10 mL; MAO : 6.25 mL; [Cat] = 10 μmol, Al/Ti = 1000;
Time = 0.5 h; Pressure of ethylene = 1.0 MPa; Temperature = 50℃;
Soluvent = toluene, V = 100 mL.
[a] Activity: $\times 10^6$g Polymer / mol Ti· h; [b] $\times 10^4$ g/mol; [c] mol %.
E/O: ethylene/1-octene. Mn, Mw and PDI come from GPC

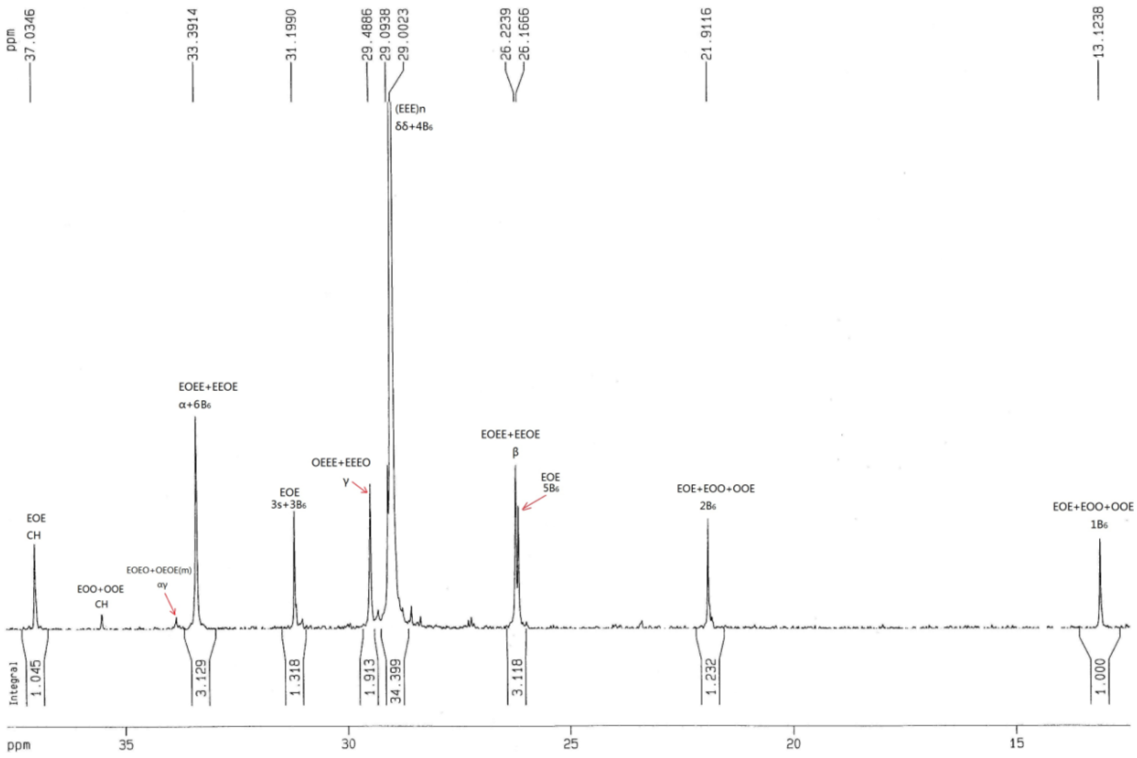


Fig. 1 The ^{13}C NMR characterization of ethylene/1-octene copolymer sample with **C1**

experimental results show that the weaker electron donating capacity of phenol in **C3** and **C4** is responsible for low molecular, it is also confirm by the follow result: in the four compounds, both of the activity and the molecular weight with **C1** is higher than that of the others complexes, which must be related to the coordination of methoxy oxygen with titanium and the extra stability of the central metal lead to high catalytic activity and molecular weight.

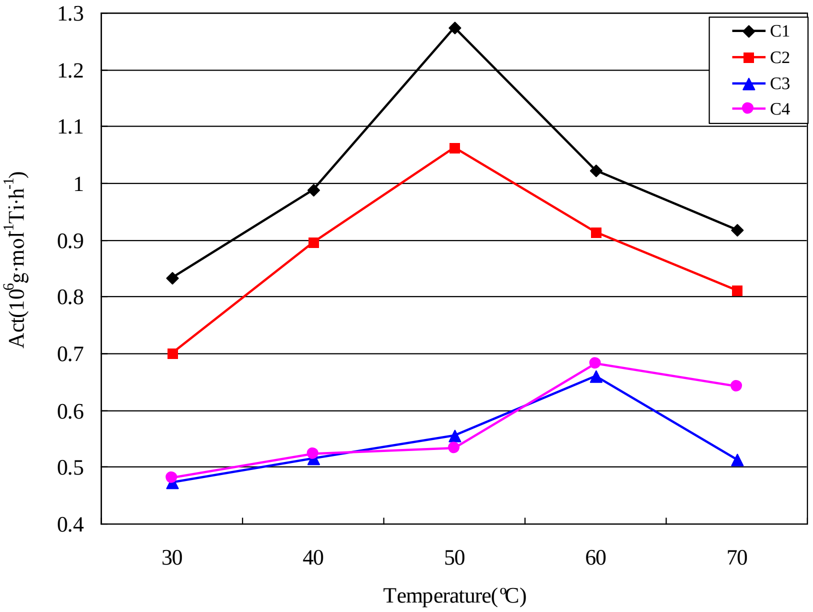
In this paper, ^{13}C NMR spectra of polymers is classified by Seger and Gary (2004) and Liu *et al*. (2017) method, the copolymer of ethylene/1-ocetene with **C1** are chosen to characterization, the ^{13}C NMR characterization of copolymer is shown in Fig. 1.

From Fig. 1, it is found that, compared to the metallocene, the more "open" spatial structure of **C1** provide the necessary space for 1-octene randomly insertion, even allowed 1-octene alternately inserting to form a small amount alternating copolymerization fragments EOEO, actually, the OO fragment is also found.

There are no triads of [OOO] fragment and the [OOE] is too little to confirm the long sequence of 1-octene exists, which imply that the distribution of 1-octene is irregular, which is beneficial to homogenization of the performance of the whole copolymer.

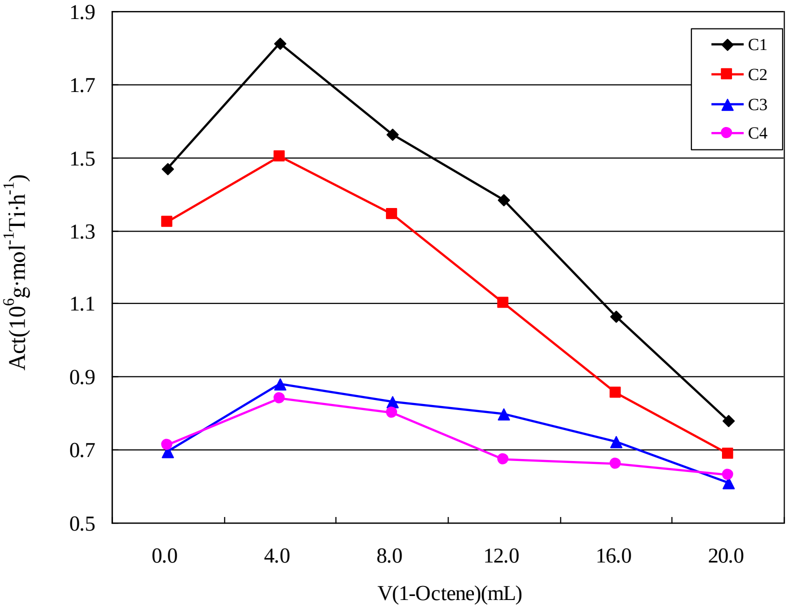
The effect of polymerization temperature, time, content of comonomer and the ratio of Al/Ti on polymerization reaction was also investigated. The influence of polymerization temperature on copolymnerization reaction was carried out and the result was shown in Fig. 2.

From Fig. 2, it is find that, with the increase of temperature, the catalytic activity of copolymerization augmented first and then decreased, and the activity of **C1** and **C2** are higher than that of **C3** and **C4**, the reason is that the density of the electron of the central metal in mononuclear compound is higher than that of the binuclear compound, which resulting in a significant difference in its catalytic activity. It is well known that the reaction rate constant



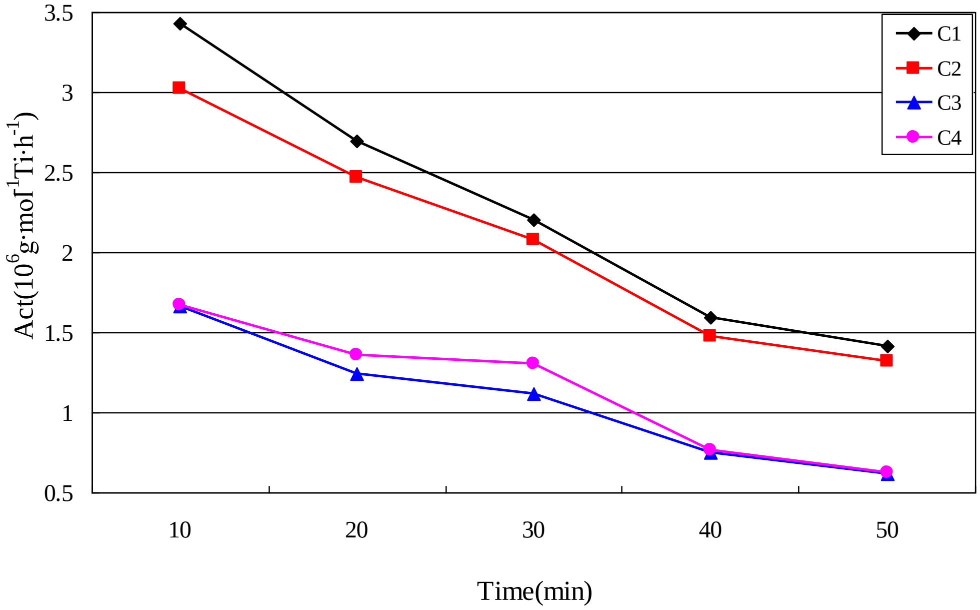
Condition: 1-octene = 10 mL；MAO：6.25 mL；[Cat] = 2.0×10^{-4} mol/L,
Al/Ti =1000；Time = 0.5 h；Pressure of ethylene = 0.5 MPa；Soluvent = toluene, V = 100 mL

Fig. 2 Influence of temperature on activity of copolymerization of ethylene/1-octene



Condition: T = 50℃, MAO = 6.25 mL, Al/Ti =1000；[Cat] = 2.0×10^{-4} mol/L
Time = 0.5 h；Pressure of ethylene = 1.0 MPa；Soluvent = toluene, V = 100 mL

Fig. 3 Influence of 1-octene's volume on activity of copolymerization of ethylene/1-octene



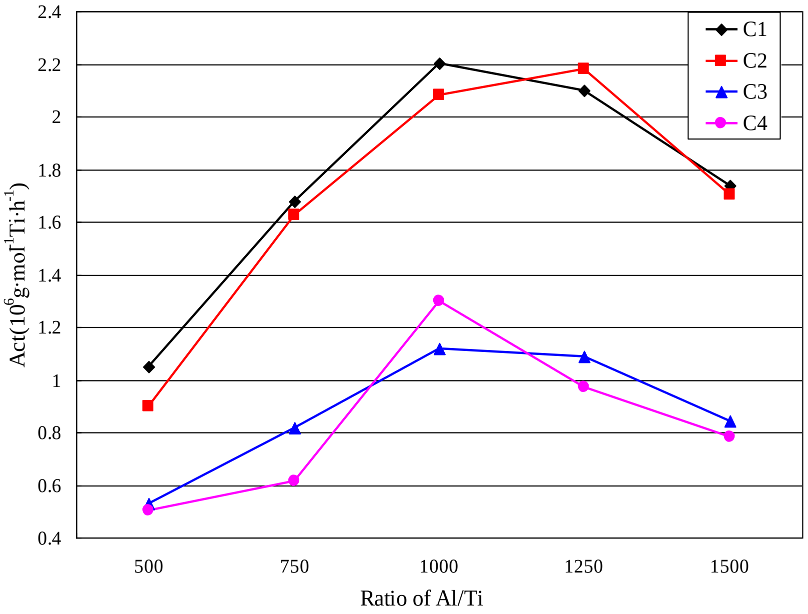
Condition: T = 50℃, MAO = 6.25 mL, Al/Ti =1000；[Cat] = 2.0×10^{-4} mol/L
Pressure of ethylene = 1.0 MPa；Soluvent = toluene, V = 100 mL, 1-octene = 16 mL

Fig. 4 Influence of polymerization time on activity of copolymerization of ethylene/1-octene increases with the increasing of temperature, which responsible for the augment of catalytic activity; On the otherhand, the higher temperature could lead to decomposing of catalyst and the decreases of solubility of ethylene, and so there must exist optimal polymerization reaction temperature (OPT). However, the OPT for **C1** and **C2** is 50℃, which is lower than that of **C3** and **C4** (OPT = 60℃). It is necessary to point that the activity decrease amout of **C4** is far smaller than that of others complexes at 70℃, which implies that the tert butyl group in **C4** contributes extra stability, and resulting in higher temperature resistance of **C4** than the other compounds. The effect of conent of comonomer on polymerization reaction was studied and the results were shown in Fig. 3.

The polymerization results show that the catalytic system present higher catalytic activity for the copolymerization of ethylene with α-olefin, it is also found that, when α-olefin keep lower concentration, the catalytic activity increase first and then continually depress, the result is similar to the literature (Nomura *et al*. 2000), we attribute to the effect of comonomer. However, on the other hand, when the α-olefin concentration continully increase, the ethylene solubility in solution correspondingly decreases, which lead the activity decrease.

The influence of polymerization time on reaction is shown in Fig. 4.

From the result it is found the acticaty of **C1** and **C2** are higher than that of **C3** and **C4** under the same condition. It is also found that the activaty decrease as the polymerization time extend, however, as the reaction proceeds, the polymerization center is arrounded by more and more polymers, which hinder ethylene molecule approaching to active center and cause the decreasing of polymerization rate; on the other hand, the comonomer concentration decline as reaction time extend, that is, the "comonomer effect" will be reduced (Nomura *et al*. 2000), moreover, the stability of the catalyst decreases with the time extends, all these factors result the polymerization



Condition: T = 50℃, MAO = 6.25 mL, Al/Ti =1000；[Cat] = 2.0×10^{-4} mol/L
Pressure of ethylene = 1.0 MPa；Soluvent = toluene, V = 100 mL, 1-octene = 16 mL

Fig. 5 The influence of co-catalyst on the copolymerization of ethylene/1-octene activity decreased.

The influence of ratio of Al/Ti on polymerization reaction was also carried out and the result was shown in Fig. 5.

From Fig. 5, it is found that the activity of **C1** and **C2** is higher than that of **C3** and **C4**. It is also found the ratio of Al/Ti has greatly affected the activity. However, as the ratio of Al/Ti increase, the catalytic activity increase first and then depress. Except C2, when the ratio of Al/Ti increases from 500 to 1000, the catalytic activity increases continually because of the number of polymerization centers increasing. However, when the ratio of Al/Ti more than 1000 times, that is, the excess MAO hinder the molecular diffusion of monomer and polymer. We think that the 4-Me on phenyl ring expanding the space of the activated center, which maintain high activity in the presence of a higher ratio of cocatalyst.

4. Conclusions

In this article, four $TiCl_3(OAr)$ complexes and two $TiCl_2(OAr)_2$ complexes were synthesized and characterized. It is found that the composition of the product is greatly affected by temperature and the mono substituted $TiCl_3(OAr)$ can be separated and purified at lower temperature. The synthetic method has the advantages of simple, cheap and high yield. $TiCl_3(OAr)$ complexes are used to catalyze ethylene polymerization and copolymerization with 1-ocetene. The result indicates that $TiCl_3(OAr)$ /MAO systems complexes are effective catalyst for steric hindered α-olefin inserting propagation PE chain, and the α-olefin incorporation in polymer reaches up to 8.29 mol% (1-octene).

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