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A Study of TI Group (IV) Synthesis Complexes Post-Metallocene for Olefin Polymerization

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Abstract – Five modern catalysts have been synthesized with various ligand structures for polymerization of aqueous polar and non-polar olefins. New complexes of titanium [TiLCl2] Catalyst [TiLCl2] LH2=2-(3,5-Di-tert-butyl-2-hydroxybenzylamino-hydroxybenzylamino)-succinic acid] [Catalyst 1]} [Catalyst 2] with N and O as a pendant donor was synthesized. {LH2=2-(((2, 4-di-tert-butyl-6-hydroxybenzyl) amino] amino) acetic acid). Oxalic [Catalyst 3] Ti (IV) complexes have been synthesized, with Oxalic (TiL2Cl 2), Oxalic, Malonic and Succinic acid (LH= Oxalic), Malonic and Succinic acid) and Succinic [Catalyst 5] acids. Many of the above synthesized catalysts were tested for polar and non-polar olefins (MMA, MA, styrene) homo- polymerization as well as at ambient temperature for their catalytic activities in aqueous emulsion polymerization. The present work describes in greater depth the synthesis and characterization of both ligands and catalysts. For studies the elementary analyzer characterizations methods 1 H NMR, 13C NMR, HRMS, IR, UV-spectroscopy and CHN have been used.

Keywords – Olefins Polymerization, Post-Metallocene, Group 4 Catalyst;

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INTRODUCTION

For the polymerization of olefins, it has long been investigated to produce and apply organo-metallic compounds as catalysts. The compound of group 4 complex metallocene is widely studied in this area. In the determination of the kinetic, stereo, regional selectivity and reactiveness of the Co-polymerization reactions, electronic atmosphere and steric factors play a crucial role. The stability factors and their effect on stereoselectivity could be assessed for the active centers and catalytic function. New post-metallocene complexes centered on transitional metals group 4-6 were discovered to resolve the stabilization of active centers and catalyst action. As the majority of catalytic systems of organic solvents operate, aqueous polymerizations have taken on significance in polymerization responses because of growing environmental issues about the use of organic solvents.

Ziegler–Natta catalysis

In 1963, Ziegler and Natta earned the Science Nobel Prize "for their findings in the area of high-polymer chemistry and technology'.' Ziegler and Natta discovered that transitional metal and trialkyl aluminum compound mixtures could lead to heterogeneous polymerization of ethylene and propanol; these systems included $TiCl_4/AlEt_3$. The majority of polyolefins produced in industry are manufactured in this way to date. These devices have been widely produced during the last 50 years and serve in several forms of olefin polymerizations as effective and selective catalysts. The major concern is the lack of definition on the active site for these catalysts. The logical catalyst design and characterization is difficult without a well-defined active site, and the polymer formed by such a method has a wide distribution of molecular weight. This is the place to learn from the analysis of homogenous catalysis. The molecules that now serve as an active site for catalysis can now be fully described and characterized with relatively easy approaches to rational catalyst design, such as NMR spectroscopy and X-ray crystallography. This brief guide, which focuses on Group 4 metals, and especially metallic and half-bulb style compounds, is not aimed at providing a thorough overview of the literature by any way. For a more complete description of the homogeneous Ziegler–Natta catalysis, the reader will write some review papers.

Metallocene catalysts

Sir Geoffrey Wilkinson was independent of the chemistry, who received the 1973 Nobel Prize along with Fischer's Ernst Otto for their pioneering work.

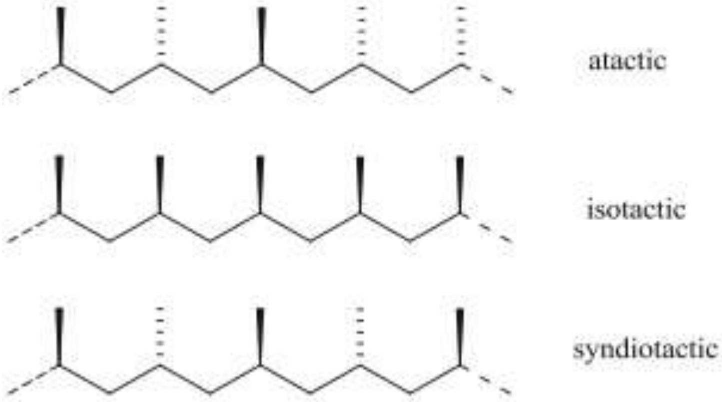


Figure 1: Main Potential Distinct Polypropene

The synthesis of Cp2TiBr2 and Cp2ZrBr2 was recorded in 1953 by organometallic compounds, named sandwich compounds.' The bent metallocene Cp2TiCl2 along with Et2AlCl or AlEt3 were reporter of both Natta and Breslow in 1957 and they could polymerize ethylene but not propylene. However, the polymerizations were sluggish, this method was not perfect. In 1980, Sinn and Kaminsky found that a limited quantity of water is greatly expanded to include polymerizations in the metallocene/alkyl aluminum systems. The result was methyl aluminum formation (MAO), which is made of trimethyl aluminum partial hydrolysis (TMA) and which can be prepared in situ before polymerization. In general MAO can be used for the enhanced ethylene or a-olefin polymerizations of a number of Group 4 metallozens.

Even polymerizations-capable propylene is metallocene systems allowed by MAO. The zirconocenic method Cp2ZrCl2/MAO is one such system. An additional factor when the existence of an extra methyl group per monomer is polymerizing propylene is tactics. The relative chiral arrangement of the adjacent pendant methyl groups is described. Examples of the main potential distinct polypropene stereochemistry can be observed in Fig. 1.

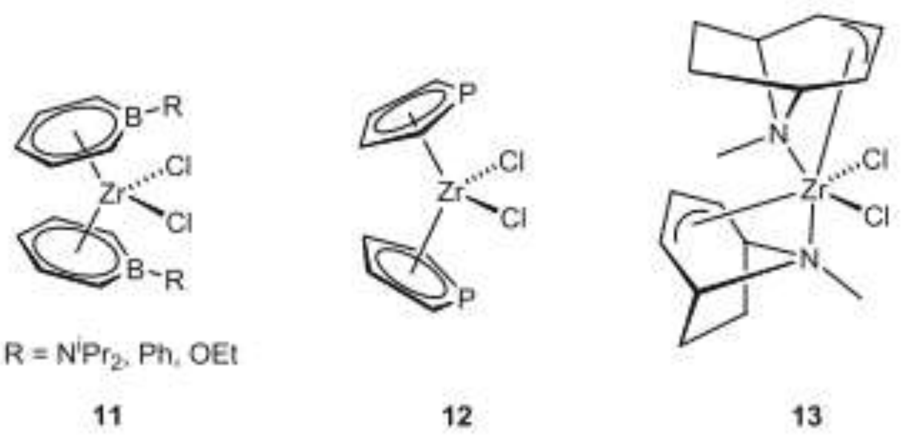
Catalysts for post-metallocene and isolobal analogy

In the 1990's and even beyond, new post-metallocene systems were of considerable scientific concern as a result of widespread patenting of more conventional metallocane Group 4 systems and CGCs. Research into different forms of catalysts has provided an opportunity to develop and monitor the resulting polymer properties and to discover new combinations of monomers. Post-metallocene structures are aimed at replacing with a separate movement one or two cyclopentadienyl ligands at the metal core. An isolobal comparison created by Hoffman for which he and Fukui won an award for their "independently developed hypotheses about the course of chemical reactions" is a strategic technique that was effectively used to create a ligand new design. The symmetry, the form and the energy of frontier orbitals are identical when two electronically determined structures are isolobal to each other. This theory can be powerful in ligand design for new catalysts in combination with the right steric properties.

The anionic heteroatom links to the metal center in the J1 modes are important for this project, as they fulfill the conditions proposed by the isolobal analogy. Taking the cyclopentadienide ligand into account and comparing its electronic characteristics with the common form of anionic donor j1-bound, for instance an imido ligand, an isolobal comparison can be seen in action. A single r-donor and two p-donor orbits interacting with the metal center, form the frontière orbits of each ligand.

Other Group 4 post-metallocene catalysts

Many catalysts that are not a cyclopentadienyl supporting ligand have also been formed for post-metallocene. They also in some cases also provided ligands to mimic CP, such as the catalysts 11 and 12 supported by boratobenzene and phosphacyclopentadienyl.



11 **12** **13**

Figure 2: Oxalic, malonic and succinic acid TI(IV) dynamic syntheses:

The reaction of acids (Oxalic, Malonic and Succinic) and TiCl4 was synthesized by three related titanium (IV) complexes at a ratio of 2:1 respectively. The catalysts have been synthesized using the same method as for the catalyst synthesis mentioned earlier. Figure 3 showed the graphical description of the titanium complexes.

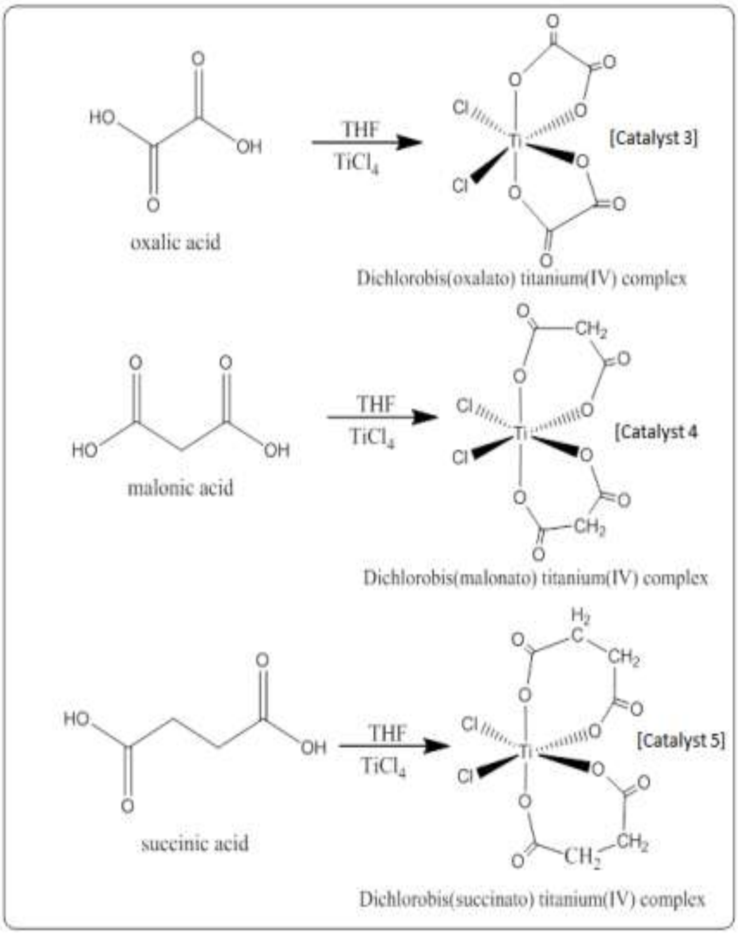


Figure 3: Syntheses of Ti(IV) complexes of Oxalic, Malonic and Succinic acid

^{1}H NMR spectrum of Dichlorobis (malonato)Ti (IV) complex

Complex dichlorobic (oxalato) titanium (IV) has no protons, therefore the NMR range for the complex has not been recorded. The 1H NMR range (500 MHz, 71 CDCl3) Seven peaks are presented in Figure 4 of the Dichlorobis (malonate) titanium (IV). One peak for the carbon protons in the same atmosphere is β 1.8 ppm and for the carbon protons in the same environment − 3.4 ppm (THF). For two protons of -CH2, the peaks at μ 3.6 ppm and ć 3.8 ppm. The sharp point is referred to at · 0 ppm (TMS).

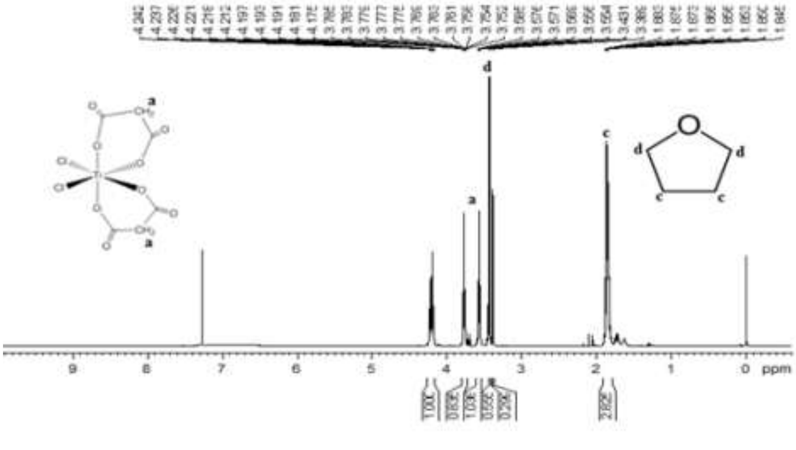


Figure 4: ^{1}H NMR spectrum of the Dichlorobis(malonato)titanium (IV) complex

^{1}H NMR spectrum of Dichlorobis(succinato)titanium (iv) complex

Figures 5 display the 1H NMR distribution of the complex titanium (IV) of dichlorobes (succinato). The high peak of 2,6 ppm in the complex is for protons of -CH2. The maximum for carbon protons is 1.8 ppm and the maximum for oxygen-assembled carbon protons is 3.5 ppm (THF). At β 0,03 ppm the sharp peak is a guide (TMS).

^{13}C NMR spectrum of Dichlorobis(oxalate)titanium(iv) complex

Figure 6 of the complex of 13C NMR (CDCl3) Figure 6 reveals the highest at 162,108 ppm attributed to the complex of carboxylate carbon 1. For the carbon fitted to Oxygen, THF is the highest at 26,108 ppm and 26,694 dpm attributed to two carbon atoms in the same atmosphere and the highest at 66,113 and 66,643 ppm. The strong peak of the solvent CDCl3 is 77,278 ppm

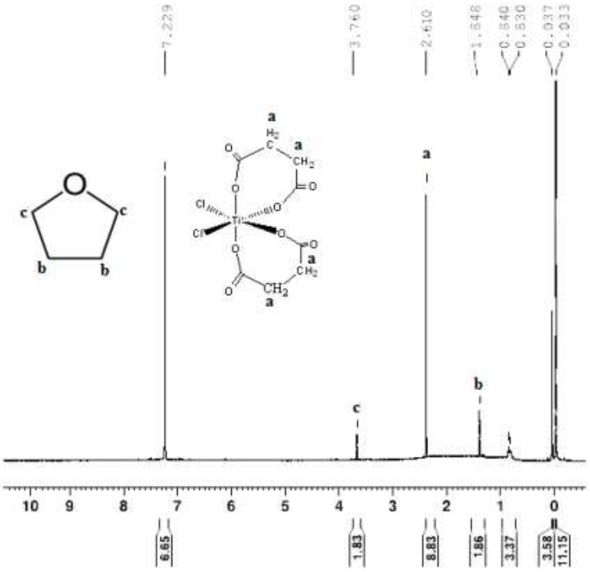


Figure 5: Dichlorobis (succinato)titanium (IV) 1H NMR range

Dichlorobis (malonate)titanium(iv) complex 13C NMR range Spectrum with 13C NMR (500 MHz, CDCl3) The eight summits in Figure 7 of the complex. Due to the carbon bound to THF oxygen, the peaks at 25,857 and 28,974 ppm are two carbon atoms in the same climate and the peaks at 66,013 and 67,918 ppm. Carbon of –CH2 is at peaks of 41.512 and 44.273 ppm. For carboxylate carbon atoms, the peaks at 166,357 ppm up to 169,497 ppm are. The solvent CDCl3 has a sharp peak at 77,003 ppm.

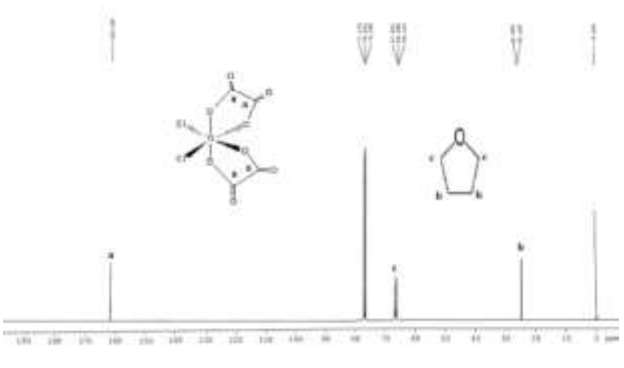


Figure 6: Dichlorobis(oxalate)titule (IV) complex 13C NMR spectrum complex

13C Dichlorobis(succinato)titanium(iv) complex NMR spectrum complex Figure 8 shows the 13C NMR complex for titanium (IV) dichlorobis(succinate). The maximum volumes for carbon of –CH2 are 30.278 ppm and 30.960 ppm. Due to the carboxylate carbon atoms the peaks are 177,108 ppm to 177,198 ppm. The solvent CDCl3 has a sharp peak of 77,278 ppm.

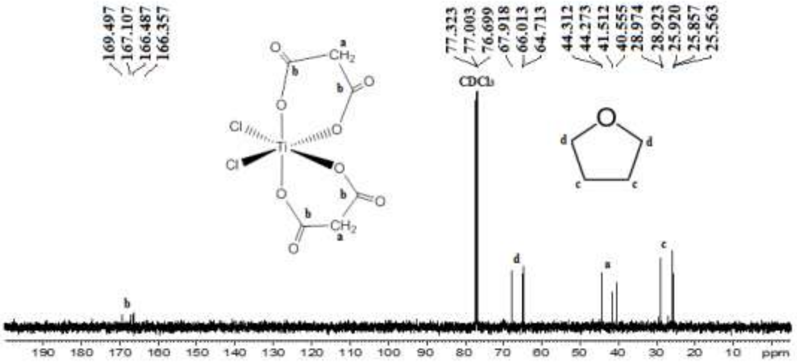


Figure 7: 13C NMR spectrum of Dichlorobis(malonato)titanium(IV) complex

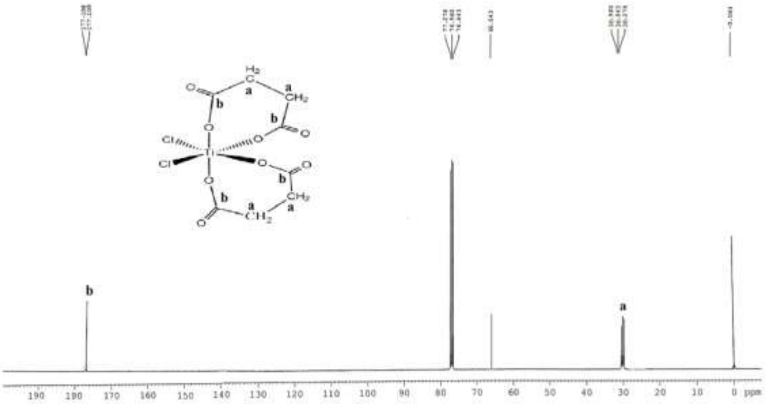


Figure 8: 13C NMR spectrum of Dichlorobis(succinato)titanium (IV) complex

HRMS of Dichlorobis(oxalato)titanium(iv) complex

Figure 9 shows the high-resolution mass spectrum for the complex of Dichlorobis(oxalato)titanium (IV). Due to C4Cl2O8Ti+1, this compound has a high HRMS spectrum of 293.8324 m/z. The diverse structure often fits isotope patterns.

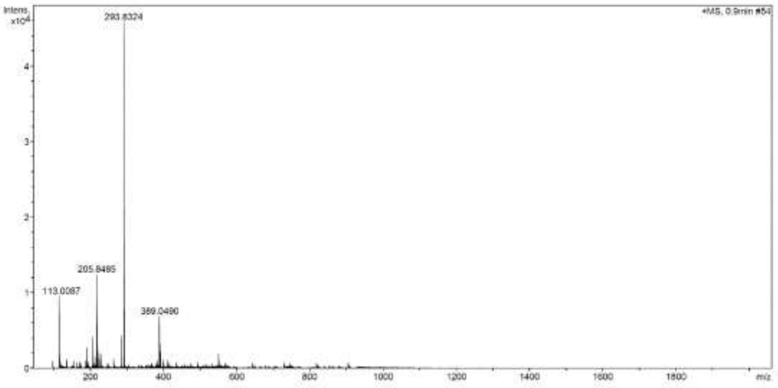


Figure 9: Dichlorobis(oxalate)titanium(IV) complex HRMS complex

Dichlorobis(malonate)titanium(iv) complex HRMS complex

Figure 10 shows the high-resolution mass distribution for titanium (IV) Dichlorobis (malonato) complex. Thanks to the complex C6H4Cl2O8Ti+1, the HRMS spectrum is peak at 321.8849 m/z. The diverse structure often fits isotope patterns.

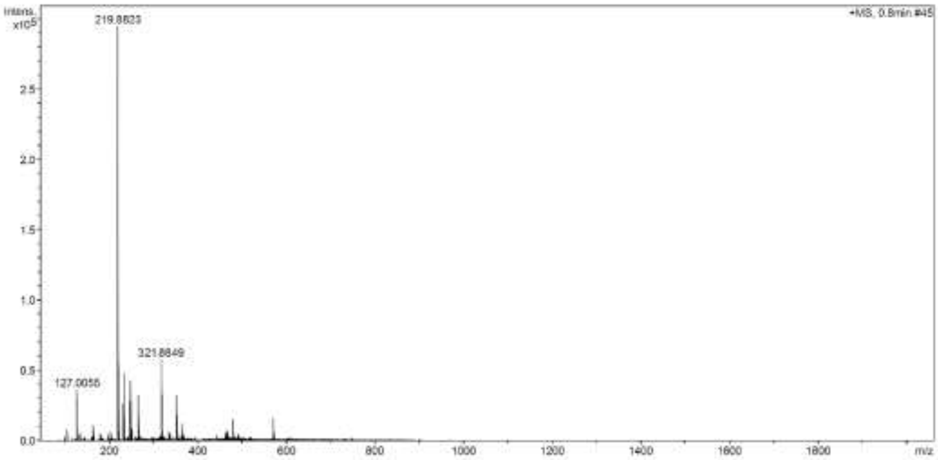


Figure 10: HRMS of Dichlorobis (malonato) titanium (IV) complex

HRMS of Dichlorobis (succinato) titanium (iv) complex

The high-resolution mass spectrum for Dichlorobis (succinato) titanium (IV)complex is shown in Figure 11. The HRMS spectrum of the complex, shows peak at m/z 349.9581 due to the C8H8cl2O8Ti+1. The composition of the complex also matches with isotopic pattern.

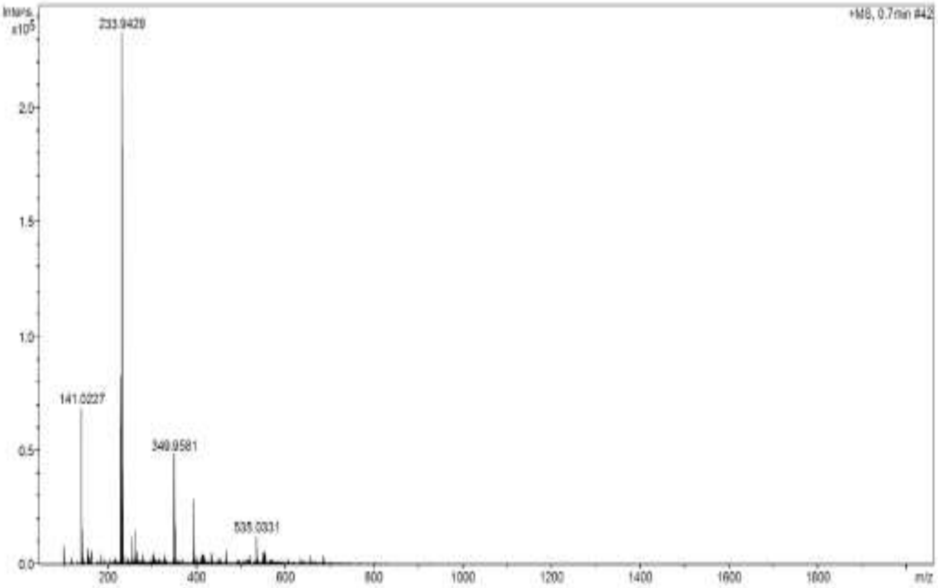
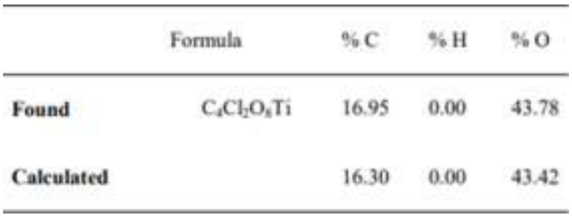


Figure 11: HRMS of Dichlorobis(succinato) titanium (IV) complex

Elemental analyses

The composition of the complex was experimentally evaluated with the CHNO analyser and measured values were compared. Table 1, Table 2 and Table 3, respectively, indicate carbon, hydrogen and nitrogen (N) levels in the complex.

Table 1: Analytical data of Dichlorobis (oxalato) titanium(IV) complex

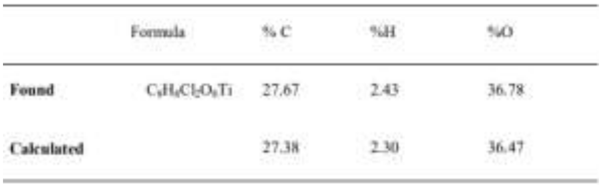


	Formula	% C	% H	% O
Found	$C_4Cl_2O_8Ti$	16.95	0.00	43.78
Calculated		16.30	0.00	43.42

Table 2: Analytical data of Dichlorobis (malonato) titanium(IV) complex

	Formula	% C	%H	%O
Found	$C_6H_4Cl_2O_8Ti$	22.45	1.37	39.87
Calculated		22.32	1.25	39.64

Table 3: Analytical data of Dichlorobis (succinato) titanium(IV) complex



	Formula	% C	%H	%O
Found	$C_8H_8Cl_2O_8Ti$	27.67	2.43	36.78
Calculated		27.38	2.30	36.47

CONCLUSION

There is a synthesis for the homo-polymerization reaction of the polar (methyl methacrylate), non-polar (styrene) monomer on room temperature, in an aqueous emulsion, in five novel single-site titanium-metallic posthallocene complexes with added-on atoms. Unlike the Ziegler Natta catalyst, these are easy, environmental benign and do not have dangerous organic and alkyl aluminum co-catalysts. These complexes are stable in aqueous media. Moreover, the power of metal complexes as catalysts can also be increased by complexes with an additional donor group. This research thus utilizes recently synthesized titanium complexes to polymerize polar and non-polar monomers.

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