

Araştırma Makalesi / Research Article

Molecular Modelling of Ionic Liquid Ligands based Zirconium Complexes for Ethylene Copolymerization with Octene-1**Zeynab GANBARLI¹, Hamida AZIZBEYLI^{*1}, Matlab KHAMIYEV¹, Khayala SEIDOVA¹, Yetar BABASHOVA¹**¹The Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Polymerization catalysis laboratory, Baku

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Abstract

This paper presents the results of obtaining new easily preparing zirconium-containing complex catalytic systems for ethylene copolymerization and their theoretical studies. The synthesized arylimine metal complexes with "grafted" ionic-liquid ligands have been tested in the liquid-phase copolymerization process of ethylene in the aromatic solvents medium. It has been shown that the prepared catalytic systems can be used together with ionic liquids such as [bmim]BF₄ and [bmim]HSO₄. Using of organoaluminum compounds such as methylaluminiumoxane and (C₂H₅)₂AlCl, these catalytic systems provide the formation of mixtures of the linear PE with high density, different thermodynamic characteristics, molecular mass distribution and crystallinity. It was found that these catalytic systems allow to control the structure and composition of the products obtained. It is known that in organometallic catalysis, ligands within a metal complexes play an important role in the formation of catalytic active centers. The nature of the catalytic centers also has a great influence on preparation of (co)polymers with various structures. Therefore, the choice of ligands is a very important factor for obtaining products with desired properties. The structural parameters of the synthesized catalytic systems were investigated using HyperChem software (version 8, Hypercube Inc.). Activation energy, dipole moment, bond angle, the bond length, the HOMO and LUMO orbitals have been calculated.

KeywordsEthylene;
Polymerization; ionic
liquids; Metal complex;
Polyethylene**Etilenin Okten-1 ile Kopolimerizasyonu için İyonik Sıvı Ligandlar İçeren Zirkonyum Komplekslerin Moleküler Modellemesi****Öz**

Bu makale, etilen kopolimerizasyonu için yeni kolayca hazırlanabilen zirkonyum içeren kompleks katalitik sistemlerin elde edilmesinin sonuçlarını ve teorik çalışmalarını sunmaktadır. "Aşılınmış" iyonik sıvı ligandları ile sentezlenen arilimin metal kompleksleri, aromatik çözücüler ortamında etilenin sıvı fazlı kopolimerizasyon işleminde test edilmiştir. Hazırlanan katalitik sistemlerin [bmim]BF₄ ve [bmim]HSO₄ gibi iyonik sıvılarla birlikte kullanılabileceği gösterilmiştir. Metilalüminyumoksan ve (C₂H₅)₂AlCl gibi organoalüminyum bileşikleri kullanıldığında bu katalitik sistemler farklı termodinamik özellik, moleküler kütle dağılımı ve kristal yapıya sahip, lineer yüksek yoğunluklu PE karışımlarının oluşmasını sağlar. Bu katalitik sistemlerin, elde edilen ürünlerin yapısını ve bileşimini kontrol etmeye izin verdiği bulunmuştur. Organometalik katalizde, metal kompleksler içindeki ligandların, katalitik aktif merkezlerin oluşumunda önemli bir rol oynadığı bilinmektedir. Katalitik merkezlerin doğası da çeşitli yapılara sahip kopolimerlerin

Anahtar kelimelerEtilen; Polimerizasyon;
İyonik sıvılar; Metal
kompleks; Polietilen

hazırlanmasında büyük etkiye sahiptir. Bu nedenle istenilen özelliklere sahip ürünlerin elde edilmesinde ligand seçimi çok önemli bir faktördür. Sentezlenen katalitik sistemlerin yapısal parametreleri HyperChem yazılımı (versiyon 8, Hypercube Inc.) kullanılarak araştırıldı. Aktivasyon enerjisi, dipol momenti, bağ açısı, bağ uzunluğu, HOMO ve LUMO orbitalleri hesaplanmıştır.

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1. Introduction

The scientific direction called "Green Chemistry" appeared in the 90s of the 20th century and has found quickly supporters in the chemistry community. New approach to the chemical reactions and processes that have being developed in many laboratories around the world have been designed to drastically reduce the environmental impact of large-scale chemical production (IntRef.1) Chemical risks can be inevitably arise when aggressive environments are used in the chemical industry. Taking precautions against these risks is traditionally done by industrial workers by limiting their contact with these substances. "Green chemistry" suggests a different strategy such as thoughtfully and eco-friendly selection of initial materials and process schemes generally excluding the use of harmful substances (Azizov 2010, Greer 2020, Akhundova 2019).

In the last 20–25 years, low-melting salts (ionic liquids-IL) have attracted great attention of researchers due to the uniqueness of their properties - non-volatility, incombustibility, a wide temperature range of being in a liquid state, high thermal and electrical conductivity, low toxicity, and high thermal stability. According to these properties, IL is the main focus of Green Chemistry. A remarkable feature of ionic liquids is the ability of "fine tuning" their properties which can be tailored by judicious selection of cation, anion, and substituents. This make it possible to obtain hydrophilic and hydrophobic, acidic and basic ionic liquids. For example, tetrafluoroborate ILs miscible with water at any molar ratio whereas ionic liquids with the same cations based on the hexafluorophosphate anion show hydrophobic properties and also insoluble in saturated hydrocarbons (Meindersma 2012).

Increasing interest to studying and using of ILs in chemistry and chemical technology is not only simulated by their unusual and in many unique properties, but also the possibility of solving some of the environmental problems caused and apply their in chemical production. This is primarily related to the vapor pressure of ionic liquids, which favorably distinguishes them from traditional volatile organic solvents. Due to their ability to dissolve metal complexes and even metal salts, which are immiscible with non-polar solvents, ionic liquids make it possible to organize two-phase catalytic systems. This property of the IL makes catalyst recycle and product separation easily. Because of these qualities IL can be safely used in the processes of the two-phase catalysis by metal (Mao 2013).

Although there are many experimental data in this field, complex theoretical researches have a special value and are very important nowadays. Preliminary theoretical calculations allow to save time on while conducting experiments, predict results and set the correct tasks (Reis 2022).

This scientific work is devoted to the results on the preparation of new and easily obtaining zirconium-containing arylimine complex catalytic systems and molecular modelling of obtaining ligands and arylimine catalytic systems. Zirconium complexes with ionic liquid type ligands were synthesized and tested in the ethylene polymerization process. The ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium methyl sulfate were used as modifiers in these reactions.

2. Materials and methods

Schlenk techniques (operating in an inert atmosphere) were mainly used in experimental works. The common features of all working methods in an inert atmosphere were the

removal of air from the reaction medium by vacuum, as well as the use of inert gases such as argon or nitrogen.

Ethylene used as a monomer (with a purity of 99.9%) was obtained from the pyrolysis process EP-300 in Sumgayit, Republic of Azerbaijan and dried over aluminum oxide.

Toluene, heptane and hexane stored in Schlenk-type glass containers were used as solvents for polymerization processes (99% purity, German production "Alfa Aesar"), precleaned, dried on sodium, and then stored in Schlenk glass bottles.

Ethyl and isopropyl alcohols have been used as deactivators of catalytic systems after the polymerization of ethylene.

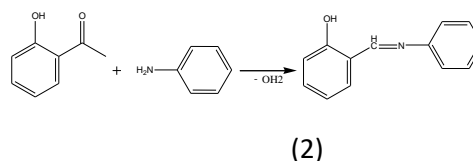
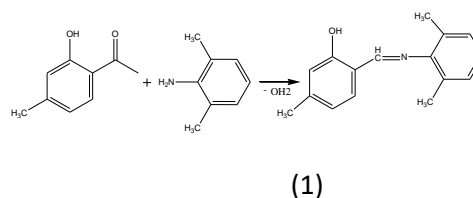
Ionic liquid - 1-butyl-3-methylimidazolium tetrafluoroborate - [bmim]BF₄ - (AlfaAesar, A Johnson Matthey Company), MM = 226.02 g/mol, d₄₂₀ = 1.21 g/cm³ nd₂₀ = 1.52.

Ionic liquid - 1-butyl-3-methylimidazolium methyl sulfate - [bmim]HSO₄ - (AlfaAesar, A Johnson Matthey Company), MM= 208.24 g/mol, d₄₂₀ = 1.367 g/cm³, nd₂₀ = 1.5316.

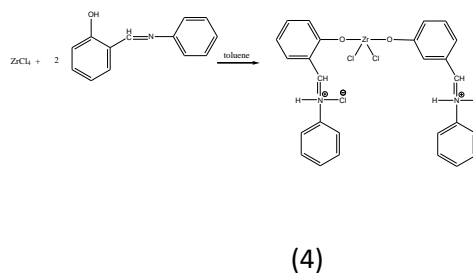
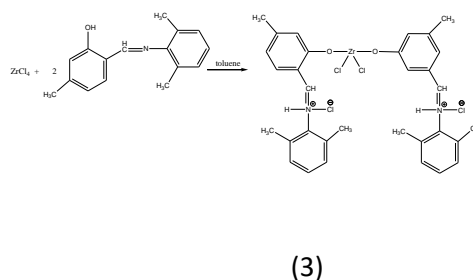
As a co-catalyst of the catalytic system was used 10% solution in toluene of methylaluminoxane (MAO) was purchased from Aldrich Chemical Company (d=0,875 g/sm³, Tb.p =111oC).

2.1. Synthesis of metal complexes with ionic-liquid type ligands

The above mentioned compounds used as ligands (L) were synthesized according to the relevant Schiff base formation reaction. 2,6-dimethylaniline and aniline were used as aromatic amine donors to form Schiff's base. L₁ ligand were obtained by the condensation of 4-methyl salicylic aldehyde with 2,6-dimethylaniline (1). L₂ ligand were obtained by the condensation of salicylic aldehyde with aniline (2). These ligands also are lewis bases because they donate electron pairs to the central atom.



Since the nitrogen atom in the imine bond, also known as azomethine nitrogen, contains unpaired electrons, they can form complexes. On the other hand, by means of its π -orbitals the azomethine system can be a coordination site for ions. So, MC1 (3) and MC2 (4) metal complexes were obtained by adding Schiff based L1 and L2 ligands to ZrCl₄ solution in toluene under stirring in a nitrogen, respectively.



In a short period of time the reaction solution turned to yellow. The released HCl binds to the ligand by forming an ionic bond with the π -orbital of azomethine group and form strong metal complex. The obtained complexes are conventionally called "ionic-liquid ligand based complexes" due to forming quaternary ammonium salt-type structures (Qanbarli 2020, Ganbarli 2022).

2.2. Polymerization of ethylene

Ethylene polymerization was carried out in an autoclave made of stainless steel and designed for high pressure. The temperature in the reaction zone was maintained by an ultrathermostat and measured by a thermocouple of the recording device. The autoclave was equipped with a mixer, a jacket for cooling or heating, and nozzles for the entry of components, solvent, and aluminum-organic compound. The pressure in the reactor and ethylene stored cylinder was monitored by a manometer. Prior to the process, the reactor was connected to a vacuum system, cleaned of oxygen and moisture under vacuum at a temperature of 65-70°C during 1-2 hours. Then the reactor was fed with dry argon or nitrogen. The polymerization of ethylene was mainly carried out in an aromatic solvent medium. Preparation the solutions of the catalyst components and delivery to the reactor were carried out under argon or nitrogen. The components of the reaction mixture were introduced into the reactor as follows: solution of metal complex, ionic liquid, aluminum organic compounds (MAO or $(C_2H_5)_2AlCl$) and the residual amount of solvent. After mixing the component of the catalytic systems during 15-20 minute at room temperature (20-22 °C) ethylene was introduced to the reactor. At the end of the reaction, the active catalyst was decontaminated with a 10% of alcohol solution of HCl acid. The polymer is filtered and washed well with acidified ethanol and then with distilled water. After washing and filtration, the polymer is heated to 60-70 °C and dried in vacuum for obtaining constant weight.

2.3. Physicochemical methods of analysis

The thermodynamic parameters of polymers were determined by the DSC method using a Q-20 differential-scanning calorimeter (manufactured by Thermoelectron Corporation (USA)) at 10 °C/min in an air or nitrogen atmosphere.

The structure and composition of the obtained products were determined by Spectrum One spectrophotometer (manufactured by Perkin

Elmer (USA)) and infrared spectroscopy in the spectral range of 400-4000 cm^{-1} .

The density of the polymer samples was measured by pycnometric method.

X-ray diffraction of the samples were carried out on a PANalytical Empyren diffractometer manufactured in the Netherlands.

2.4. Theoretical methods of analysis

The chemical structure of the desired ligands and their complexes was built using HyperChem software (version 8, Hypercube Inc.) (IntRef. 2). Conformational analysis of the compounds was performed through the semiempirical molecular orbital calculation method. Semiempirical methods introduce parameters based on molecular data. The most commonly used semiempirical methods included in Hyperchem software are AM1 and PM3 methods. They are suitable for predicting heats of formation, ground state geometries and ionization potentials. There is also ZINDO method which is suitable for predicting the visible-UV band of the molecules containing hydrogen atoms and first or second period elements.

Geometry optimization of ligands and their metal complexes was performed through the calculations for activation energy, dipol moment, bond angles and bond length.

Frontier orbitals and chemical reactivity of the ligands and their metal complexes was described through the HOMO and LUMO orbital calculations. The HOMO and LUMO orbitals are commonly known as Frontier Orbitals and were found extremely useful in explaining chemical reactivity.

Total energy gradient was calculated as a root mean square (RMS) value. The gradient (G) is the rate of change of total energy (E) with respect to displacement of each atom in the x, y, and z directions for atoms from 1 to n.

3. Theory/calculation/discussion

For comparison, we have carried out both experimental and theoretical studies.

3.1. Polymerization of ethylene in the presence of MC

The zirconium-containing aryylimine complexes were synthesized according to the previously reported simple method by us (Azizov2008). The HCl released during the reaction is bonded with the nitrogen atom and contained in the ionic liquid type ligand. The obtained complexes forming quaternary ammonium salts like structures were conditionally named as “ligand-charged” complexes. It is known that the step of using an additional organometallic compound, in particular butyl lithium is used for deprotonation of the ligand.

Our previous studies have shown that these catalytic systems are highly effective in the oligomerization (Azizov 2015, Khamiyev 2017, Khamiyev 2016) of ethylene and the polymerization of ethylene in tandem systems with metallocene catalytic systems (Qanbarli 2020).

The results obtained are shown in table 1. As can be seen from the table, the productivity of the catalytic system is 72-134 kg PE / g Zr h⁻¹. Comparative experiments were carried out under the same conditions using TiCl₄ as a precursor of the catalytic system. In this case, the catalyst activity is 110 kg PE / g Zr h⁻¹.

Table 1. Polymerization of ethylene (reaction conditions: P_{et}= 20-30 atm, T = 30-35°C, time = 30 minutes).

MC	IL	Aluminium organic compound	Zr /Al, molar ratio	Catalytic Activity, kg PE/g rZr h-1
MC1	-	MAO	1/5000	79
MC1	[bmim]BF ₄	MAO	1/5000	83
MC1	[bmim]HSO ₄	MAO	1/5000	89
MC1	-	MAO+(C ₂ H ₅) ₂ AlCl	1/1000/300	115
MC1	[bmim]BF ₄	MAO+(C ₂ H ₅) ₂ AlCl	1/1000/300	121
MC1	[bmim]HSO ₄	MAO+(C ₂ H ₅) ₂ AlCl	1/1000/300	132
MC2	-	MAO	1/5000	85

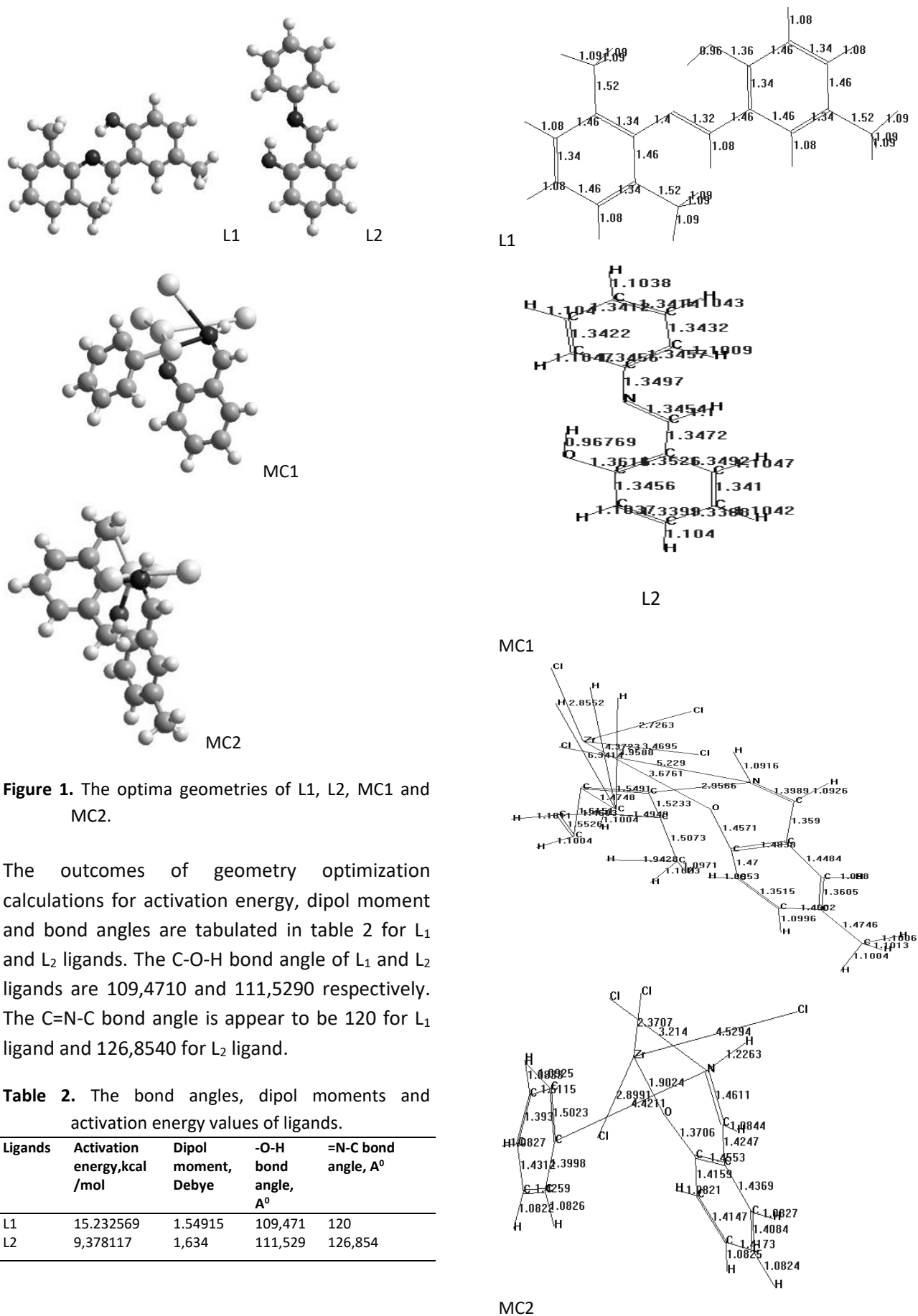
MC2	[bmim]BF ₄	MAO	1/5000	72
MC2	[bmim]HSO ₄	MAO	1/5000	82
MC2	-	MAO+(C ₂ H ₅) ₂ AlCl	1/1000/300	120
MC2	[bmim]BF ₄	MAO+(C ₂ H ₅) ₂ AlCl	1/1000/300	126
MC2	[bmim]HSO ₄	MAO+(C ₂ H ₅) ₂ AlCl	1/1000/300	134

As can be seen from the table 1, MAO and (C₂H₅)₂AlCl were used as cocatalyst in the polymerization process of ethylene. Additional using of (C₂H₅)₂AlCl leads to an increase the activity of the catalytic systems. In this case, it is possible to reduce the amount of MAO. Also, IL are used as solvent of metal complexes. Application of IL as solvent lead to an increase the activity of the catalytic systems. Various analysis methods including infrared spectroscopy, DSC and X-ray diffraction were applied for identification the structure of the synthesized PE (Qanbarli 2020).

The prepared catalytic systems provide for the formation of mixtures of linear PEs having a high molecular weight (150000-350000), high density (0,96-0,97), mono/multimodality and narrow or wide MWD (3-76), various crystal parameters (56-78) and melting temperature (130-141°C) (Ganbarli 2022). The advantage of these catalytic systems is that they can be prepared directly in the polymerization reactor using a one-pot reaction with catalyst components and ionic liquids. This process can be carried out before the introduction of the aluminum organic compound or separately prepared precursor of the catalytic system into the polymerization reactor in a medium ethylene, inert gas or vacuum.

3.2. The structure of metal complexes. Theoretical calculations

Theoretically probable structures of metal complexes with ligand have been estimated to find the most possible model building stable structure. The shapes appearing in figure 1 indicate the calculation optima geometries for the above mentioned ligands L₁, L₂ and their complexes MC₁, MC₂. Bond length of these ligands and metal complexes can be clarify in figure 2.



The N-H bond length of MC1 and MC2 metal complexes are 1,22634 Å and 1,0916 Å respectively. The outcomes of PM3 and AM1 method of semi-empirical calculations are tabulated in table 3 for MC1 and in table 4 for MC2 complexes.

Table 3. Semi-empirical calculations results for MC1 metal complex.

Parametres	AM1 method	PM3 method
Total energy, kkal/mol	-81299,06872	-81311,40107
Binding energy, kkal/mol	-3292, 376657	-3304,709006
Heat of formation, kkal/mol	-63,66565687	-75,99800622
Electronic energy, kkal/mol	-522667,4945	-522679,8268
Nuclear energy, kkal/mol	441368,4258	441368,4258
Free energy, kkal/mol	-	-81190,3
Dipole moment, debye	14,33	14,6
Zero-ptVib energy, kkal/mol	122,3758953	122,3758953
Heat capacity (25 OK), kkal/mol/deg	-	0,0108622
Entropy (25 OK), kkal/mol/deg	-	0,06002

The calculated rotational partition function of MC₁ complex is 127171 and vibrational partition function is 1,26479 at 25 °C temperature.

Table 4. Semi-empirical calculations results for MC2 metal complex.

Parametres	ZINDO1 method	PM3 method
Total energy, kkal/mol	-129576,6742	-91471,09877
Binding energy, kkal/mol	-11905,44606	-3960,322898
Heat of formation, kkal/mol	-7851,453063	93,67010207
Electronic energy, kkal/mol	-821316,1352	-677013,8689
Nuclear energy, kkal/mol	691739,461	585542,7701
Free energy, kkal/mol	-129577	-91471,1
Dipole moment, debye	18,91	10,71
RMS gradient, kkal/(Å mol)	0,09846	0,1003
Zero-ptVib energy, kkal/mol	177,4285333	177,4285333

The value of dipole moment helps in distinguishing between polar and non-polar molecules. Greater the dipole moment, greater is the polarity in a molecule. The dipole moment of MC1 and MC2 metal complexes, using semi-empirical PM3 calculations, are 14,6 and 10,71

Debye respectively. It is found that the dipole moment increases with the size and the MC1 metal complex is more polar than MC2 complex.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of MC1 and MC2 complexes are presented in figure 3 and figure 4 respectively. The HOMO and LUMO orbitals were found to be extremely useful in explaining chemical reactivity. Electrophilic attacks were shown to correlate very well with atomic sites having high density of the HOMO orbital, whereas nucleophilic attacks correlated very well with atomic sites having high density of the LUMO orbital (Kunichi Fukui was developed this concept and awarded the Nobel prize in chemistry in 1981).

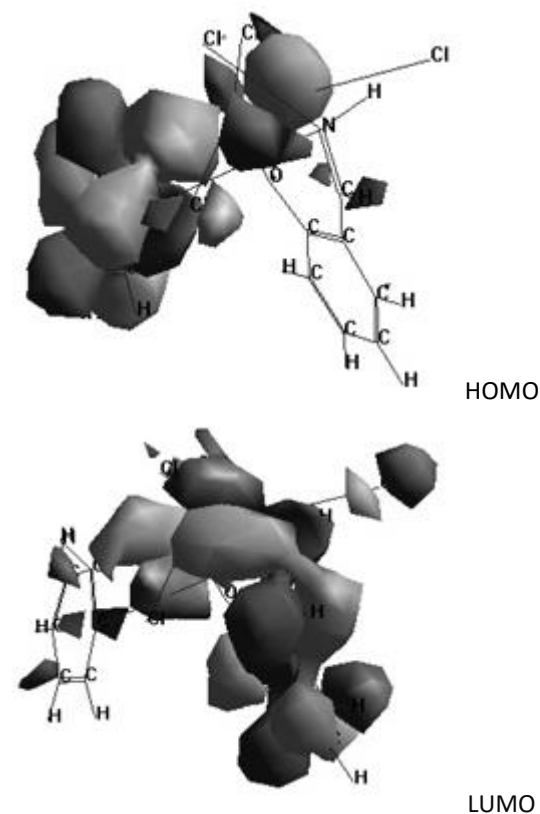


Figure 3. The HOMO and LUMO orbitals of MC1 metal complex.

The HOMO orbitals energy of MC1 complex is calculated -1,519887 eV and symmetry is 54 A. The LUMO orbitals energy is calculated 0,7507896 eV and symmetry is 55 A. The energy difference (ΔE) in HOMO-LUMO is 0,769.

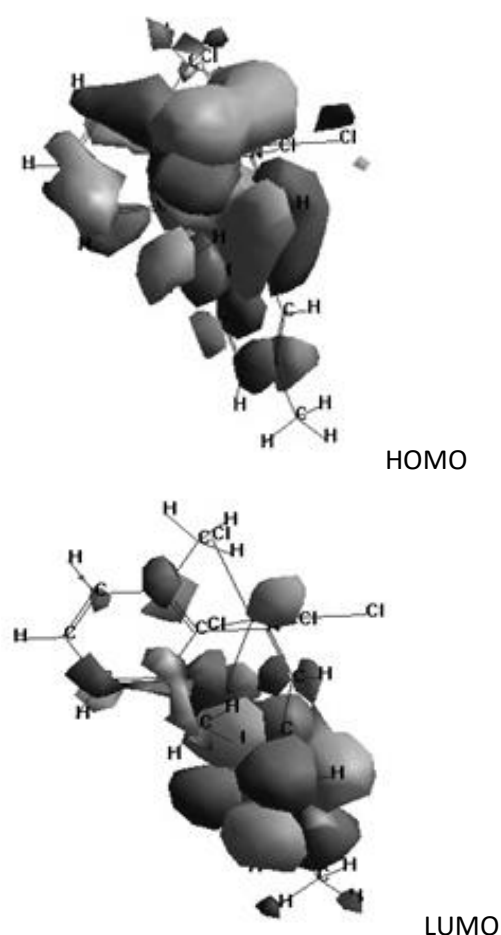


Figure 4. The HOMO and LUMO orbitals of MC2 metal complex.

The HOMO orbitals energy for MC2 metal complex is calculated $-7,427243$ eV and symmetry is 62 A. The LUMO orbitals energy is calculated $-0,4746813$ eV and symmetry is 66 A. The energy difference (ΔE) in HOMO-LUMO is 6.95.

The HOMO-LUMO energy differences (ΔE) of MC1 (0,769) and MC2 (6,95) reflects that MC2 metal complex is more stable than MC1.

4. Results

Thus, it can be concluded that based on the conducted research effective catalytic systems via simple methods have been developed and high-density polyethylene has been obtained in their presence. The structural parameters of the synthesized catalytic systems were investigated using HyperChem software (version 8, Hypercube Inc.). It was found that the metal complex (MC1) was prepared based on L1 ligand having more

steric hindrance which synthesized by the interaction of 4-methyl salicylic aldehyde with 2,6-dimethylaniline has a higher polarity and is less stable. Metal complex (MC2) based on salicylic aldehyde with aniline has a relatively simple steric hindrance is less polar and stable. The solubility of these complexes in ionic liquids during the polymerization of ethylene leads to obtain similar activity under the same conditions and production of high-density polyethylene in the presence of both catalytic systems. However, the molecular mass distribution in the presence of these catalytic systems are different. The molecular mass distribution is narrower in the presence of MC1 whereas broader molecule weight values are obtained in the presence of MC2.

5. Conclusions

It is known that the synthesis of polymeric materials with the required structure is one of the important conditions. It is important to regulate the parameters, especially the molecular characteristics of the polymers obtained both in the gas and liquid phase polymerization processes. There are many scientific directions for this purpose. One of the main conditions is easily synthesis of the ligands and metal complexes based on their and design of these compounds. In this regard, the catalytic systems we have synthesized for the polymerization of ethylene in the liquid phase in the field of metal complex catalysis and calculated various thermodynamic parameters are unique. These calculations and easily synthesis of the metal complexes will be useful in the future for the synthesis of various polymeric materials and planning of experiments in advance.

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