



## **Polymerization of Ethylene in the Presence of Various Ligand Organometallic Catalytic Systems**

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### **Authors' contributions**

*This work was carried out in collaboration among all authors. Authors QZ and KA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author AH managed the analyses of the study. Author KM managed the literature searches. All authors read and approved the final manuscript.*

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### **ABSTRACT**

This work presents the results on the preparation of new readily available zirconium-containing arylimine complex catalytic systems and their application together with metallocenes in ethylene polymerization. For this purpose, zirconium complexes with grafted ionic liquid type ligands were synthesized and tested in the ethylene polymerization process. On the other hand, it is known that one of the main industrial catalysts for the polymerization process of ethylene is dicyclopentadienyl titanium and zirconium dichloride. Therefore, one of the main objectives of the work is to test the using of the newly synthesized complexes with the industrial  $Cp_2TiCl_2$  catalyst. The products obtained were identified by various physicochemical methods and it was found that these catalytic systems allow one to control the structure and composition of the products obtained.

**Keywords:** *Ethylene polymerization oligomerization; (non)metallocene catalysts; titanocene and zirconocene complexes.*

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## 1. INTRODUCTION

Currently, the production of polyolefins is developing rapidly. The modern world production of polyolefins exceeds 100 million tons, which makes this group the undisputed leader in the range of synthetic polymers. The modern chemical industry produces mainly polyethylene (PE) and polypropylene (PP). In addition, in recent years, the production of specific types of polyolefins, in particular, propylene-butene and ethylene-propylene-ethylidene norbornene copolymers has been steadily grown. At the present stage, polyethylene is understood as both a homopolymer of ethylene and its copolymers containing up to 20% of other comonomers (butene-1, hexane-1, octene, etc.). Polypropylene, in turn, includes not only a homopolymer, but also propylene-ethylene copolymers with a low ethylene content.

Such a wide range of polyolefins requires the development of flexible and productive technologies for their production. Progress in this area is achieved by improving the polymerization technology and the development of highly active catalytic systems. And if for the production of homopolymers - "pure" polyethylene and polypropylene - classical heterogeneous catalysts are quite suitable for which extremely effective technologies have been developed (Spheripol, Spherylene and their analogs), the synthesis of homopolymers with desired properties and, moreover, copolymers, in many cases requires "fine" tuning of the catalyst, which is difficult to implement for heterogeneous systems. To solve such problems, "single-site" catalysts are in demand, and one of the well-known and effective classes of such catalysts is the metallocenes of group 4 elements.

The main reasons for the attractiveness of metallocene catalysts are as follows: Metallocene catalysts are initially homogeneous, which in many cases causes high activity. Metallocenes are stable under catalysis conditions. The consequence of this is the uniformity of catalytic particles (the term "single-site catalyst" reflects this fact), due to which metallocenes are able to catalyze the formation of polymers with a narrow molecular weight distribution ( $M_w/M_n \sim 2$ ). Relatively high stability, as well as wide possibilities in the design of ligands, make it possible to create unique heterogeneous catalysts based on metallocenes that combine the advantages of modern technological schemes and the "monocenter"

nature of the resulting polymers. Despite the broad positive aspects of these catalytic systems, a complex multistage synthesis of metallocene ligands (sandwich complexes and semi-sandwich compounds with a constrained geometry) is required to achieve a "polycentric" nature.

At present, other types of monocenter catalysts are being intensively developed, for which the term "post-metallocene" is fixed, however, despite half a century of intensive research, cyclopentadienyl complexes of group 4 elements are still relevant. Post-metallocene catalysts use a variety of chelating. These ligands are available in a wide variety of steric and electronic properties. Such post-metallocene catalysts have enabled the introduction of chain shuttle polymerization. It should be noted that, in order to control the molecular characteristics of (co)polyolefins, it is also necessary to carry out complex syntheses for the design of postmetallocene catalyst systems.

Despite the many developed processes, there is still a need to increase the productivity of metallocene and postmetallocene catalyst systems and their efficiency, which is necessary for carrying out polymerization processes of olefins, including ethylene. The regulation of the characteristics of metallocene and postmetallocene catalytic systems for the polymerization of ethylene and the properties of the products obtained with their help is an urgent fundamental and applied task.

This paper presents the results of the creation of new readily available zirconium-containing complex catalytic systems with arylimine and their use together with metallocenes in the processes of controlled polymerization of ethylene, in particular, for the preparation of polymers with specified molecular characteristics.

## 2. EXPERIMENTAL DETAILS AND METHODOLOGY

In the practical works, Schlenk methods were mainly used to work with substances sensitive to the air, including organometallic compounds.

Ethylene (obtained from the EP-300 installation, Sumgayit city) was subjected to additional purification and drying in the presence of freshly calcined aluminum.

Arylimine compounds were selected as ligands for the components of the catalytic systems: 2 - {[2,6-dimethylphenyl] imino} methyl} 4-methylphenol – L<sub>1</sub>; 2 - [(phenylimino) methyl] phenol – L<sub>2</sub>.

The above mentioned compounds used as ligands (L) were synthesized according to the relevant Schiff base formation reaction. L<sub>1</sub> and L<sub>2</sub> ligands were obtained by interaction of 4-methyl salicylic aldehyde with 2,6-dimethylaniline and salicylic aldehyde with aniline respectively. Metal complexes (AIC<sub>1</sub> and AIC<sub>2</sub>, respectively) based on them were obtained according to the procedure [1] of the interaction of these imino-phenolic compounds (as ligands) with ZrCl<sub>4</sub>.

Dicyclopentadienyl zirconium dichloride (Cp<sub>2</sub>ZrCl<sub>2</sub>) - (manufactured by Kasei, Kogyo Co. L.t., Tokyo, Japan) was chosen as the metallocene component of the catalytic systems.

As a co-catalyst of the catalyst system was used methylaluminoxane (MAO) of Aldrich Chemical Company. It was consumed as a 10% toluene solution.

As solvents of the polymerization processes were used solvents (manufactured by Germany - Alfa Aesar): toluene, xylene and nonane, which had previously been purified, dried, distilled over metallic sodium.

Ethylene was polymerized in an autoclave made of stainless steel. The temperature in the reaction zone was maintained with an ultra-thermostat and measured with the use of a thermocouple with a recording device.

The thermodynamic parameters of the polymers were determined by DSC on a Q-20 differential scanning calorimeter Thermoelectron Corporation (USA) with a heating rate of 10 deg / min in an atmosphere of air or nitrogen.

The values of Mw, Mn, and MMP were determined by GPC on a chromatograph (GPC Waters 150-C) at 135°C in trichlorobenzene, as well as by a viscometric method.

The structure and composition of the obtained products were identified using IR spectroscopy on a Spectrum One spectrophotometer (Perkin Elmer, USA) in the region of 50-4000 cm<sup>-1</sup>.

On a scanning atomic force microscope (AFM), as well as on an optical microscope with special attachments, the reliefs of the obtained products were studied.

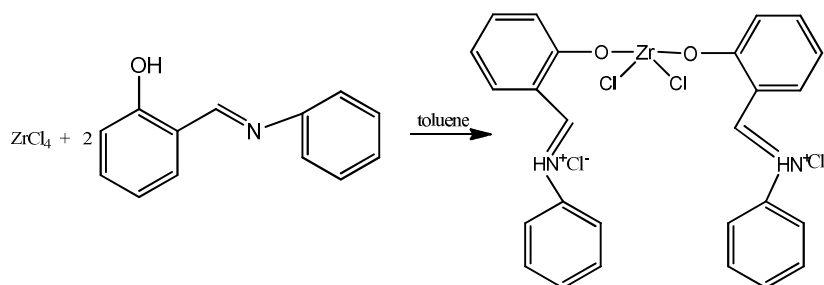
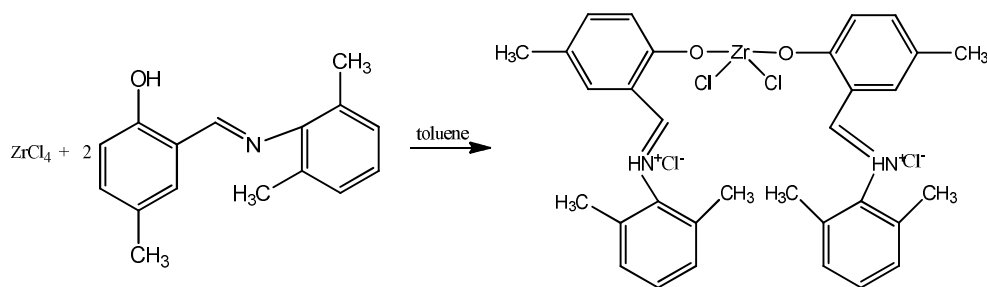
X-ray diffraction RFA of the samples was carried out on a PANalytical Empyren diffractometer manufactured in the Netherlands

### 3. RESULTS AND DISCUSSION

In the literature [2-7], can be found many examples of catalysts mixed with nonmetallocene systems based on transition metal complexes containing diimine ligands (with Ni, Pd and Cu), phenoxy-imine ligands (with Ni, V, Cr, Ti, Zr and Hf), diimine-pyridine ligands (with Fe and Co), diamide ligands (with Ti and Zr), diamide-ether ligands (with Ti, Zr and Hf), diamide-amine ligands (with Ti, Zr and Hf), phosphine -imide ligands (with Ti), bis (phenoxy-amine) ligands (with Ti, Zr and Hf), bis (phenoxy) -thioether ligands (with Ti, V), Tris (pyrazolyl) borate ligands (with Ti), pyrrolide -imine ligands (with Ti, Zr and Hf), indolide imine ligands (with Ti) [8-15], phenoxyimide ligands (with V), phenoxy-cyclopentadienyl ligands (with Ti), amidine cyclopentadienyl ligands (with Zr), quinoline-cyclopentadienyl ligands (with Cr), anilide-tropone ligands (with Ni) and amide-pyridine ligands (with Ti, Zr). Many of these catalysts show activity not less than metallocene catalysts [16–21].

Some of the catalysts have extraordinary capabilities for the synthesis of polymers with various microstructures (for example, hyperbranched polymers, copolymers of polar monomers, polyolefin block copolymers), which previously could not be obtained with the use of other polymerization methods. However, despite the advantages of these catalyst systems, they have some drawbacks. One of them is that they are synthesized in a multistage manner.

In our studies according to a previously developed, acceptable and simple method, were synthesized zirconium-containing arylimine complexes (AIC) that were used with Cp<sub>2</sub>ZrCl<sub>2</sub> for ethylene polymerization. The goal is the preparation of catalytic systems by the low-stage method and the production of PE with various parameters with their participation. The reaction of obtaining AIC can be represented in the following scheme:



The synthesized aryline complexes – AIC can be represented in various forms:

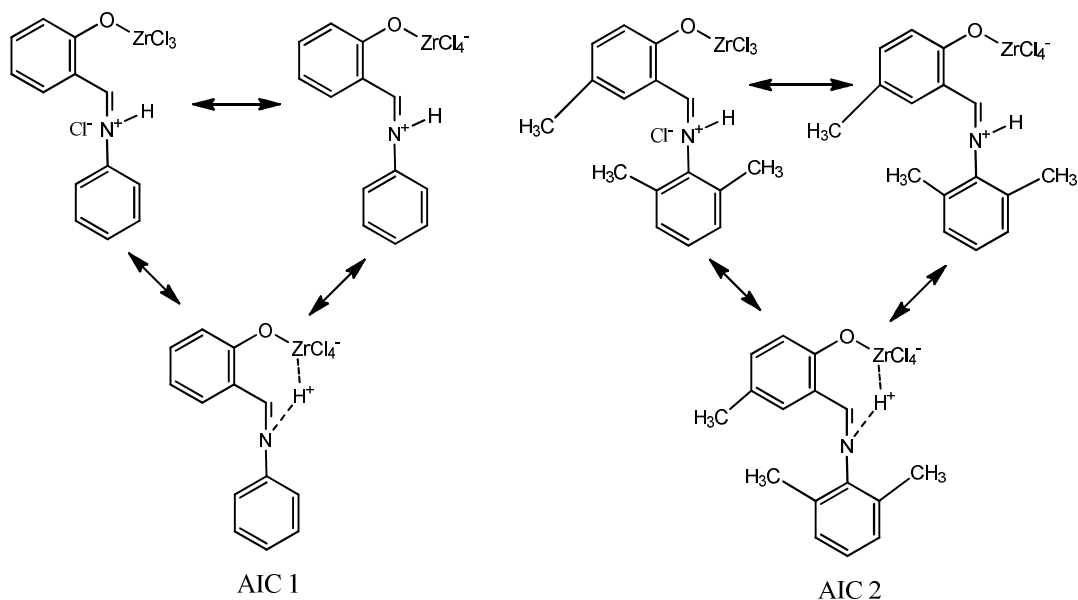


Fig. 1. Synthesized aryline complexes (AIC)

It can be seen from the scheme that in each case, the HCl released during the reaction is bonded with the nitrogen atom and contained in the ligand. The obtained complexes forming quaternary ammonium salts like structures were conditionally named as "ligand-charged" complexes. It is known that for deprotonation of the ligand, the step of using an additional organometallic compound, in particular butyl

lithium, is used. This stage is not applicable in our synthesis. Various analysis methods including IRS and DSC were applied for identification the structure of the synthesized complexes.

As mentioned above the aim of our work is to obtain mixed systems based on metallocene and postmetallocene catalysis and to carry out the

polymerization of ethylene in their presence. For this purpose, the above mentioned  $\text{Cp}_2\text{ZrCl}_2$ , AIC1 and AIC2 metal complexes were used, while methylaluminoxane (MAO) and diethylaluminium chloride were chosen as cocatalysts. The obtained results were presented in Table. 1. As can be seen from the table, in any case, the activity is 89,6-135,4 kg PE / g Zr /  $\text{h}^{-1}$  when using MAO as a cocatalyst, the concentration of Zr / Al = 1/5000. The use of  $\text{Et}_2\text{AlCl}$  can significantly reduce the molar ratio of Zr/Al (Zr/Al = 1/600). The concentration of the catalysts used for the polymerization of ethylene depends on many factors. It is appropriate for the concentration to be approximately in the range of 0.01-100  $\mu\text{mol} / \text{l}$ .

The efficiency of the polymerization depends on the concentration and composition of the catalyst used in the process and other factors. Polymerization lasts from a few seconds to several hours. The most important is the regulation of  $M_w$  and molecular weight distribution (MWD) characteristics of obtained PE. The flexibility of the polymerization process on new catalytic systems allows to synthesize polymers with different molecular characteristics, as a result of which the polymerization products differ markedly in operational properties.

Under the selected conditions, the highest activity belongs to the  $\text{Cp}_2\text{ZrCl}_2 + \text{MAO}$  and  $\text{Cp}_2\text{TiCl}_2 + \text{MAO} + \text{Et}_2\text{AlCl}$  and  $\text{Cp}_2\text{ZrCl}_2 + \text{AIC}_2 + \text{MAO} + \text{Et}_2\text{AlCl}$  catalyst system. The use of additional cocatalyst  $\text{Et}_2\text{AlCl}$  has a positive effect on the activity of the system. Activity in the AIC<sub>1</sub> + MAO and AIC<sub>2</sub> + MAO systems is relatively low. This indicator increases with the addition of a second cocatalyst. In general, the activity of AIC systems in comparison with the known non-metallocene systems is comparable. The design of these systems allows to control the polymerization

processes of ethylene and with their participation it becomes possible to obtain polyethylene with desired properties.

As noted above, the most important for polymerization processes is the regulation of the  $M_w$  and MWD characteristics of obtained PE. The flexibility of the polymerization process on new catalytic systems makes it possible to synthesize polymers with different molecular characteristics, as a result of which the polymerization products differ markedly in their operational properties. The molecular weight indicators and the molecular weight distribution of the obtained polyethylene samples were determined (Table 1). The study of these indicators is a great importance, since the difference between them affects the physical and mechanical properties, including the materials, especially nanomaterial will be obtained based on their in the future. Synthesized each polymer sample contains macromolecules with different size and weight. During the determination of the molecular weight by various methods, an average value is also calculated. Typically used indicators are number average ( $M_n$ ) and weight average molecular weight ( $M_w$ ). Generally, the number average and weight average molecular weights of polymers do not coincide, and always should be noted that  $M_w$  is higher than. The  $M_w/M_n$  ratio characterizes the degree of polydispersity or MWD. The obtained PE samples have different values of MW and MWD. Polyethylene sample (PE1) obtained in the presence of  $\text{Cp}_2\text{ZrCl}_2 + \text{MAO}$  has a narrow molecular weight distribution (MWD=3). Polyethylene (PE5) obtained in the presence of  $\text{Cp}_2\text{ZrCl}_2 + \text{AIC}_1 + \text{MAO} + \text{Et}_2\text{AlCl}$  has a wide molecular weight distribution (MWD= 40.8). Also, polyethylene sample (PE<sub>9</sub>) obtained in the presence of AIC1 + MAO +  $\text{Et}_2\text{AlCl}$  has a wide MWD value.

**Table 1. Polymerization of ethylene in the presence of various catalytic systems [conditions: Ethylene = 30 atm, T = 25°C, time = 15 min]**

No	Catalytic system	Activity, kg PE/ gr.Zr/ $\text{h}^{-1}$	$M_w$
PE <sub>1</sub>	$\text{Cp}_2\text{ZrCl}_2 + \text{MAO}$	129,2	320000
PE <sub>2</sub>	$\text{Cp}_2\text{ZrCl}_2 + \text{MAO} + \text{Et}_2\text{AlCl}$	135,4	250213
PE <sub>3</sub>	$\text{Cp}_2\text{ZrCl}_2 + \text{AIC}_1 + \text{MAO}$	118,6	382300
PE <sub>4</sub>	$\text{Cp}_2\text{ZrCl}_2 + \text{AIC}_2 + \text{MAO}$	122,3	234500
PE <sub>5</sub>	$\text{Cp}_2\text{ZrCl}_2 + \text{AIC}_1 + \text{MAO} + \text{Et}_2\text{AlCl}$	128,7	227800
PE <sub>6</sub>	$\text{Cp}_2\text{ZrCl}_2 + \text{AIC}_2 + \text{MAO} + \text{Et}_2\text{AlCl}$	132,3	343230
PE <sub>7</sub>	AIC <sub>1</sub> + MAO	89,6	143000
PE <sub>8</sub>	AIC <sub>2</sub> + MAO	93,2	276300
PE <sub>9</sub>	AIC <sub>1</sub> + MAO + $\text{Et}_2\text{AlCl}$	114,9	147970
PE <sub>10</sub>	AIC <sub>2</sub> + MAO + $\text{Et}_2\text{AlCl}$	111,8	231500

The synthesized polymers were analyzed using IR spectroscopy. With this method, the degree of branching was determined (according to the formula  $-\text{CH}_3 / 1000\text{CH}_2 = 188 \times D_{1380} / D_{730}$ ) [22], unsaturation (by the line intensity  $-\text{D}_{1640}$  and by the ratios  $-\text{CH} = \text{CH}_2 / 1000\text{CH}_2 = 18 \times D_{910} / D_{720}$ ;  $-\text{CH} = \text{CH} / 1000\text{CH}_2 = 19 \times D_{969} / D_{720}$ ), the ratio and characteristic of asymmetric and symmetric methylene groups ( $D_{2919} / D_{2851}$ ). In all IR spectrums of the obtained PEs, there are intense absorption bands of methylene groups: in the region of  $720 \text{ cm}^{-1}$  (deformation vibrations of  $-\text{CH}_2$ -methylene groups),  $1464 \text{ cm}^{-1}$  (doublet of heme-dimethyl groups),  $2847 \text{ cm}^{-1}$  (symmetric vibrations of methylene groups),  $2914 \text{ cm}^{-1}$  (asymmetric vibrations of methylene groups). The signals of symmetric deformation vibrations  $-\text{CH}_3$  of methyl groups -  $1380 \text{ cm}^{-1}$  and unsaturated bonds -  $1650 \text{ cm}^{-1}$  are very weak. It was found that the obtained PE samples of mainly linear structure contain very insignificant amounts of double bonds, the proportion of asymmetric and symmetric vibrations is approximately equal.

The thermophysical properties of the obtained polyethylene were studied using DSC. The beginning of melting ( $T_{b.m.}$ ), the end of melting ( $T_{e.m.}$ ), the melting temperature ( $T_m$ ), the enthalpy of melting ( $\Delta H_m$ ), the entropy of melting ( $\Delta S_m$ ) and the degree of crystallinity ( $\chi$ ) were determined. It is known that DSC is a method very similar to DTA; it fixes the dependence of the heat flux  $dH/dT$  required to maintain the temperatures of sample and standard the same from the temperature-

It is clear from Fig. 2 that  $\text{PE}_1$  obtained in the presence of catalytic system based on  $\text{Cp}_2\text{TiCl}_2$  is characterized by  $T_m = 137.47^\circ\text{C}$  with  $\Delta H = 189.3 \text{ J/g}$ . For this peak is appropriate the  $T_{b.m.} = 129.08^\circ\text{C}$ , and the end of melting is fixed at  $T_{e.m.} = 147.48^\circ\text{C}$ . From Fig. 2 it can be seen that for  $\text{PE}_2$ , at  $T_m = 142.46^\circ\text{C}$ ,  $T_{b.m.} = 128.51^\circ\text{C}$  and  $T_{e.m.} = 154.23^\circ\text{C}$ , the enthalpy is:  $\Delta H = 101.5 \text{ J / g}$ . The following  $\text{PE}_3$  sample (Fig. 2.c) is described as followings:

$T_m = 135.68^\circ\text{C}$ , with  $\Delta H = 159 \text{ J / g}$ .  $T_{b.m.} = 123.33^\circ\text{C}$  and  $T_{e.m.} = 149.74^\circ\text{C}$  are also characteristic for the abovementioned.

The thermodynamic parameters of the obtained polymer samples were determined by DSC. As can be seen (Fig. 2, straight line)  $\text{PE}_3$  sample, which was obtained in the presence of a catalytic system based on  $\text{Cp}_2\text{ZrCl}_2$ , is characterized with

$T_m = 135^\circ\text{C}$  and  $\Delta H = 190.4 \text{ J / g}$ . From Fig. 2 (dotted line), it can be seen that for  $\text{PE}_4$  sample, the melting point the enthalpy are  $145^\circ\text{C}$  and  $120.5 \text{ J/g}$  respectively. The next sample  $\text{PE}_5$  is characterized with  $T_m = 148.7^\circ\text{C}$  and  $\Delta H = 142 \text{ J/g}$ .

Thus, the PE obtained by us in the presence of various catalytic systems are characterized by various thermodynamic parameters, which indicates the reciprocity of macromolecules of various structures. The design of these catalytic systems allows the production of polyethylene with the variety of indicators, which is important for the regulation of polymerization processes.

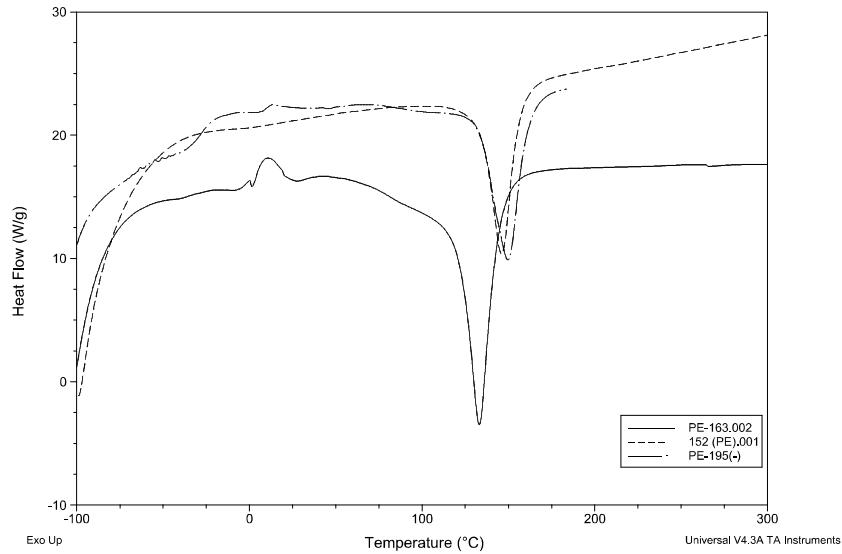
X-ray phase analysis is a method for determining the phase composition of solid crystalline and some amorphous substances. Each crystalline substance has a strictly individual crystal lattice geometry, which is characterized by a set of interplanar spacings [23]. The resulting PEs were analyzed by XRD (Fig. 3). Peaks corresponding to paraffins ( $d = 4.09 \text{ \AA}$  and  $3.70 \text{ \AA}$ ) were found in the diffraction patterns of XRD. A high peak intensity indicates a high degree of crystallinity of PE. It is known that the process of crystallization of polymers is associated with a partial ordering of their molecular chains. These chains add up together and form the "lamella" regions, then these regions create the largest spherical structure called spherulite. Crystallization of polymers affects the optical, mechanical, thermal and chemical properties.

The degree of crystallinity is estimated by various analytical methods and is usually considered within 10-80%. Chains interact with each other due to van der Waals interactions. The strength of these interactions depends on the distance between the parallel chains. It mainly determines the mechanical and thermal properties of polymers. The polyethylenes synthesized by us have a high degree of crystallinity (65-70%). This indicates the receipt of linear and least branched chains.

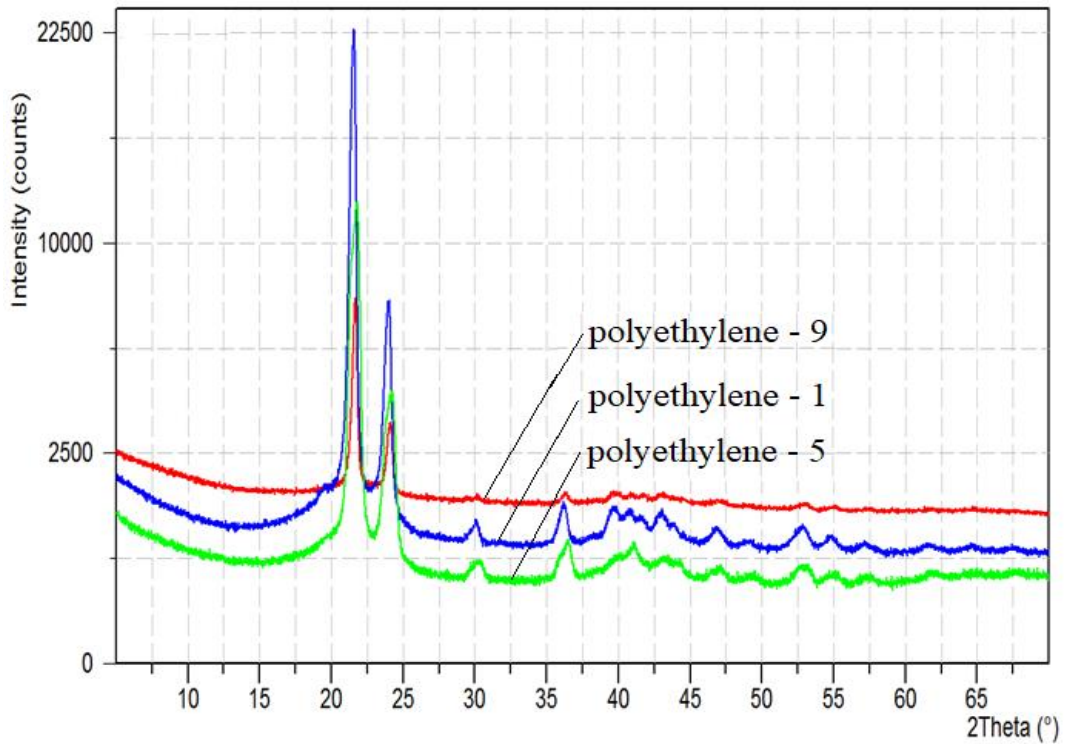
All modern concepts of the structure of amorphous and crystalline polymers are mainly associated with the success of the development of electron microscopy. The variety of structural ordering forms in amorphous and crystalline polymer systems has been convincingly shown at present, ranging from the simplest aggregates

of chains such as bundles and fibrils to very complex structures like spherulites and monocrystals. Microphotographs of the synthesized PEs were obtained using SEM (Fig. 4).

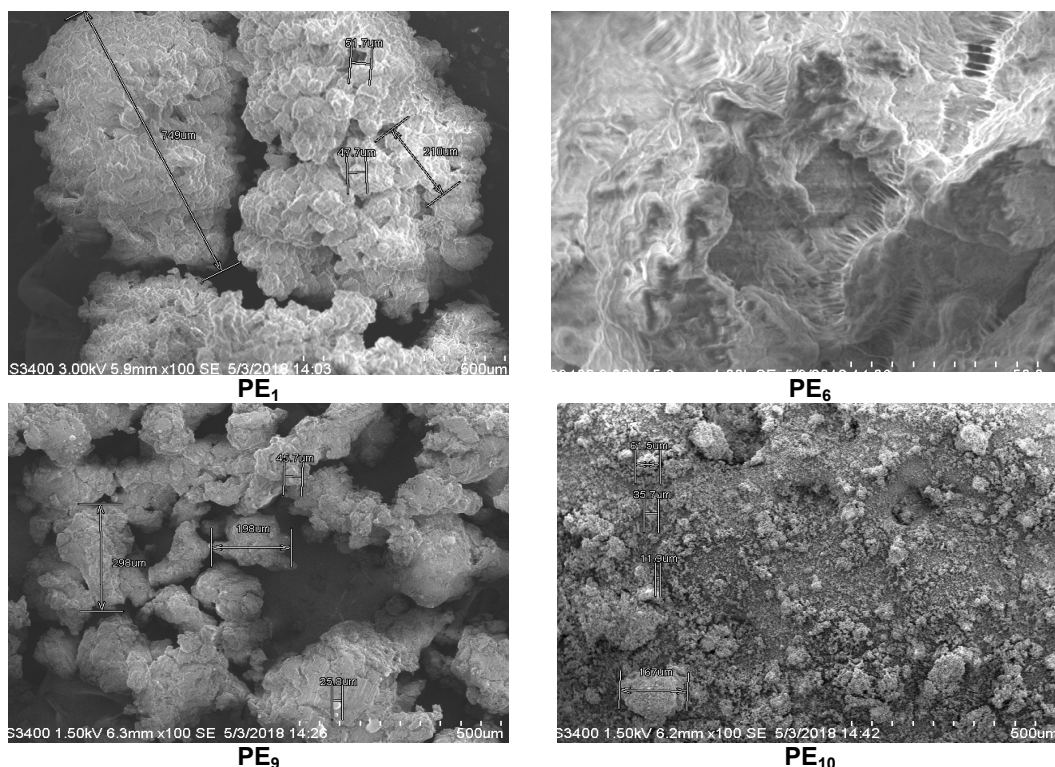
As can be seen, the obtained polymers have mainly spherulite-globular forms. It was found that in the obtained PEs there are no impurities and the elemental composition corresponds to the hydrocarbon distribution.



**Fig. 2. DSC curves of the obtained PE samples**



**Fig. 3. The diffraction patterns of the polyethylene samples obtained in the presence of various catalytic systems**



**Fig. 4. SEM images of the obtained polyethylenes**

#### 4. CONCLUSION

New zirconium-containing arylimine complexes were obtained and they are used for the polymerization of ethylene under mild conditions. In addition, under identical conditions, the  $Cp_2ZrCl_2$  metallocene complex was also used for ethylene polymerization. The possibility of combined use of  $Cp_2ZrCl_2$  with AlC under the indicated conditions for obtaining various PE is shown. The activity of catalytic systems is: 97.6-140.1 kg PE / g Zr / hour. By IR spectroscopy it was found that the obtained PEs are mainly of linear structure and practically do not contain unsaturated bonds in the composition. According to DSC and DTA, it was found that the obtained PE samples are characterized by a melting point of 130-146°C, destruction in them begins at 220-380°C. Samples are intensively oxidized at 400-500°C. The synthesized PEs are characterized by the following molecular characteristics:  $M_w = 143000-382300$ ;  $MWD=3-40.8$ . The selection of the catalytic system makes it possible to regulate these indicators and obtain PE with the specified indicators. The XRD method revealed that the polyethylenes synthesized by us have a high degree of crystallinity (65-70%). Using SEM, it

was found that the obtained polymers have mainly spherulite-globular forms.

#### DISCLAIMER

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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