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Kinetics of olefin polymerization catalysed by various zirconocene/aluminoxane systems at low Al/Zr ratios

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Abstract

Ethylene, propylene and 1-butene polymerization kinetics have been investigated in the presence of 16 zirconocene and ethylaluminoxane derivatives with various molecular masses and a molar ratio of Al/Zr = 23–26. It was found that zirconocene activity in combination with ethylaluminoxanes with molecular weight MW = 880 (an oligomer with $[-OAl(C_2H_5)]_n$ unit number equal to 10) increases in series: $Cp(Acac)_2ZrCl < (Fulv)_2Cp_2Zr_2Cl_2 < Cp_2ZrMe_2 < (Fulv)_2Cp_2Zr_2(O)Cl_2 < (Ind)_2ZrCl_2 < (t-Bu_2Cp)_2ZrCl_2 < Cp_2ZrCl_2 < (t-BuCp)_2ZrCl_2 < (MeCp)_2ZrCl_2 < (i-PrCp)_2ZrCl_2$, where Fulv – fulvalene. With methylaluminoxane (MW = 1930, $[-OAl(CH_3)]_n$ unit number 31) the following series of zirconocene activity was established: $(MeCp)_2ZrCl_2 < (EtCp)_2ZrCl_2 < (PrCp)_2ZrCl_2 < (BuCp)_2ZrCl_2 < (i-PrCp)_2ZrCl_2 < (Cyclo-HexCp)_2ZrCl_2$.

Keywords: Zirconocenes; Ethylaluminoxane; Methylaluminoxane; Ethylene; Propylene; 1-Butene; Polymerization

1. Introduction

The discovery of α -olefin polymerization using catalytic systems based on Group IV metallocenes and alkylaluminoxanes made by Kaminsky and coworkers [1,2] in 1980 attracted much attention from investigators engaged in metal complex catalysis. Great scientific and practical interest in these catalysts is seen particularly by the avalanche of patents as well as specified international conferences and monographs [3]. Particular interest in these catalysts results from the fact that they are:

- homogeneous and stable;
- give high, virtually 100%, active centers of one type and high catalyst activity;
- offer the possibility of obtaining polyolefins with narrow molecular-mass distribution of required molecular mass;
- offer the chance to produce polyolefins with either iso- and/or syndiotactic or atactic structure.

The significant influence of the ligand environment on the polymerization activity and selectivity and the necessity to keep very high molar ratio of aluminoxane to metallocene ($> 1 \times 10^4$) in the reaction zone are characteristic properties of these catalytic systems. In practice

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methylalumoxane (MAO) has been used as the alumoxane in all investigations concerning these catalysts.

The following series of activity for various zirconocenes in combination with MAO have already been described [4–10]. Studies [4–6] at $T = 70\text{--}80^\circ\text{C}$, $\text{Al/Zr} = 1.5 \times 10^4\text{--}2.4 \times 10^4$, $[\text{Zr}] = 1 \times 10^{-7}$ mol/l demonstrate the following series of activity: $(\text{MeCp})_2\text{ZrCl}_2 > (\text{EtCp})_2\text{ZrCl}_2 > (\text{NMCp})_2\text{ZrCl}_2 > \text{Cp}_2\text{ZrCl}_2 > (\text{Me}_5\text{Cp})_2\text{ZrCl}_2$, where NM – neomethyl.

Nekhaeva et al. [7] at $T = 70^\circ\text{C}$, $\text{Al/Zr} = 1.1 \times 10^4$, $[\text{Zr}] = 3 \times 10^{-6}$ mol/l have found the following series of the activity: $(\text{Me}_3\text{SiCp})_2\text{ZrCl}_2 > \text{Cp}_2\text{ZrCl}_2 > (\text{BuCp})_2\text{ZrCl}_2$.

Giannetti et al. [8] at $T = 50^\circ\text{C}$, $\text{Al/Zr} = 1.5 \times 10^4$, $[\text{Zr}] = 3 \times 10^{-7}$ mol/l have found the following series of the activity: $(\text{Ind})_2\text{ZrCl}_2 > \text{Cp}_2\text{Zr}(\text{CH}_2\text{SiMe}_3)_2 > \text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2 > \text{Cp}_2\text{ZrPh}_2 > \text{Cp}_2\text{ZrMe}_2$.

Van Beek et al. [9] at $T = 50^\circ\text{C}$, $\text{Al/Zr} = 2 \times 10^3$ have found the following series of the activity:

$(1\text{-EtInd})_2\text{ZrCl}_2 > \text{Et}(2\text{-Ind})_2\text{ZrCl}_2 > (2\text{-EtInd})_2\text{ZrCl}_2 > \text{Et}(1\text{-Ind})(2\text{-Ind})\text{ZrCl}_2 > \text{rac Et}(1\text{-Ind})_2\text{ZrCl}_2$.

Kaminsky [10] at $T = 30^\circ\text{C}$, $\text{Al/Zr} = 2.5 \times 10^2$, $[\text{Zr}] = 6.25 \times 10^{-6}$ mol/l have found the following series of the activity: $[\text{Me}_2\text{Si}(2,4,7\text{-Me}_3\text{Ind})_2]\text{ZrCl}_2 > [\text{Et}(2,4,7\text{-Me}_3\text{Ind})_2]\text{ZrCl}_2 > \text{Cp}_2\text{ZrCl}_2 > [\text{O}(\text{SiMe}_2\text{Cp})_2]\text{ZrCl}_2 > [\text{Et}(\text{Ind})_2]\text{ZrCl}_2 > [\text{Me}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2 > [\text{Me}_2\text{Si}(\text{IndH}_4)_2]\text{ZrCl}_2 > [\text{Et}(\text{Cp})(3\text{-}t\text{-BuCp})]\text{ZrCl}_2 > [\text{Et}(\text{IndH}_4)_2]\text{ZrCl}_2 > [\text{Ph}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2 > (\text{Me}_4\text{EtCp})_2\text{ZrCl}_2 > (\text{NMCp})_2\text{ZrCl}_2 = [\text{Bz}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2 > [\text{O}(\text{SiMe}_2(3\text{-}t\text{-BuCp}))_2]\text{ZrCl}_2 > [\text{Ph}_2\text{HSi}(2,3,5\text{-Me}_3\text{Cp})]\text{ZrCl}_3 > [\text{Ph}_2\text{C}(\text{Ind})(\text{Cp})]\text{ZrCl}_2 > [\text{Ph}_2\text{C}(\text{Fluo})(\text{Cp})]\text{ZrCl}_2 > [\text{Me}_2\text{C}(\text{Ind})(3\text{-MeCp})]\text{ZrCl}_2 > [\text{Me}_2\text{C}(\text{Fluo})(\text{Cp})]\text{ZrCl}_2 > [\text{Me}_2\text{C}(\text{Fluo})(\text{Cp})]\text{ZrCl}_2 \gg [\text{Et}(\text{Cp})(3\text{-PhCp})]\text{ZrCl}_2 <_2$, where Fluo – fluorenyl, Et – ethyl (in the original ‘En’).

There is more evidence [11,12] that not only MAO but other oxanes, e.g. ethylaluminumoxanes

(EAO) can be used as alkylaluminumoxanes. Mohring and Coville [13] made an attempt to qualitatively access ligand effects in zirconocenes in the polymerization of ethylene using the $(\text{CpR})_2\text{ZrCl}_2\text{-EAO}$ catalytic system. They found that in this case zirconocene activity decreased in a series: $(t\text{-BuCp})_2\text{ZrCl}_2 > (\text{Me}_3\text{SiCp})_2\text{ZrCl}_2 > (\text{EtCp})_2\text{ZrCl}_2 > (i\text{-PrCp})_2\text{ZrCl}_2 \gg \text{Cp}_2\text{ZrCl}_2 > (\text{Me}_2\text{Cp})_2\text{ZrCl}_2 = (\text{Me}_2\text{PhCp})_2\text{ZrCl}_2$, $T = 70^\circ\text{C}$, $\text{Al/Zr} = 4.25 \times 10^4$, $[\text{Zr}] = 1.25 \times 10^{-4}$ mol/l.

This paper is devoted to the study of ethylene, propylene and α -butylene polymerization kinetics under the effect of various zirconocenes and alkylaluminumoxanes. Particular attention was paid to EAO as it has been less investigated than MAO. It should be mentioned the EAO is produced by a simpler synthetic method [14], it is less pyrophoric, more water-resistant, and its cost is much lower than MAO. EAO's of various molecular masses were synthesized and studied. They were produced by direct hydrolysis of triethylaluminum (TEA) with water. Catalysts with lower molar ratio of Al/Zr in comparison with similar catalysts involving MAO have been studied.

2. Experimental

Polymerization kinetics were studied in vacuum circulation apparatus. The pressure in the process was kept constant by means of a contact relay. Reaction mass mixing was carried out by a magnetic agitator. Polymer was washed with boiling isopropyl alcohol and dried under vacuum at 70°C to a fixed weight. Intrinsic viscosities were measured in decalin at 135°C . Toluene was purified over Na followed by distillation under argon.

Ethylaluminumoxanes were produced by TEA direct hydrolysis with water in toluene. The synthesis was carried out on a laboratory plant in a glass reactor, provided with a reflux condenser agitator, thermometer and two funnels with back-pressure and calibration.

TEA in toluene was loaded from the back-pressure funnel into an argon pre-blown reactor in an inert gas flow, the temperature was maintained at 0°C, and then water was added to TEA solution under intensive mixing. The reaction mass was held at reaction temperature until the evolution of gas had ceased, then the temperature was smoothly raised to 20–25°C. Ethylaluminumoxane was isolated after removal of toluene by distillation in vacuum (~0.5 mm Hg). The end product was analyzed for the content of alkyl groups and organically bonded aluminum. The molecular masses of the ethylaluminumoxane samples was determined by cryoscopy.

The molecular mass of the ethylaluminumoxane obtained depends on the molar ratio of initial reagents TEA:H₂O. Ethylaluminumoxane synthesis was carried out at 2, 1.9, 1.8, 1.7 molar ratio, products with molecular masses of 370, 470, 660, 880, respectively, were obtained. Results of analysis of samples synthesized are given in Table 1.

Methylaluminumoxanes (MAO) were synthesized by two methods. MAO with molecular weight of 570 and elemental unit number of 8 was prepared by trimethylaluminum hydrolysis with water from AlCl₃·6H₂O. The synthesis and properties of this MAO were described in [15]. MAO with molecular weight of 1930 (elemental unit number 31) was prepared by TMA hydrolysis with water according to our method of simultaneous addition of water and TMA toluene [15,16].

The ethylaluminumoxanes synthesized were investigated by IR-, NMR-spectroscopy and gel-

chromatography. IR spectra were recorded, using an IR-24 spectrometer, in the range of 400–4000 cm⁻¹ with prisms of KBr and NaCl.

Ethylaluminumoxanes IR-spectra were characterized by intense absorption bands in 650 and 800 cm⁻¹ region. These bands may be respectively attributed to symmetric and asymmetric vibrations of Al–O bonds in Al–O–Al. Absorption bands in the 650 and 1050–1100 cm⁻¹ region relate to symmetric and asymmetric vibrations of Al–O and C–O in Al–O–C, respectively, in oxidation products of the ethylaluminumoxanes. In the 900–1500 cm⁻¹ region absorption bands relevant to deformation vibrations of ethyl groups are present.

Ethylaluminumoxane Et₈Al₄O₂ was characterized by ²⁷Al and ¹H NMR spectroscopy. The 360 MHz NMR ¹H spectra were recorded using a Bruker AM-360 spectrometer at 300 K, triplet at δ 1.2 ppm and quartet at δ 0.45 ppm arise from protons of methyl and methylene groups of ethylaluminumoxane, respectively, (Fig. 1a). The 93 MHz NMR ²⁷Al spectrum was measured on the same spectrometer. It contains an intense broad signal at δ 157 ppm (*W*_{1/2} = 3129 Hz) and a broad signal of low intensity at 67 ppm that may be attributed to 4- and 5- coordinated aluminum atoms (Fig. 1b) [17]. The detailed NMR characteristics of MAO were described in our previous work [15].

Molecular-mass distribution of ethylaluminumoxanes was studied by gel permeation chromatography that was previously used with success in investigations on a variety of organometallic compounds [18]. On fractionat-

Table 1
Effect of initial reagents ratio on ethylaluminumoxane composition and molecular mass

N	Chemical formula	Molar ratio of initial reagents	Molecular weight	Ethylaluminumoxanes composition (mass %)			
				R–Et		Al	
				theory	actual	theory	actual
1	Et ₈ Al ₄ O ₂	2.0	370	62.4	62.7	29.0	29.2
2	Et ₈ Al ₆ O ₅	1.9	470	49.0	49.4	34.2	34.5
3	Et ₁₁ Al ₉ O ₈	1.8	660	46.9	46.3	35.7	35.8
4	Et ₁₄ Al ₁₂ O ₁₁	1.7	880	45.3	45.1	36.2	35.9

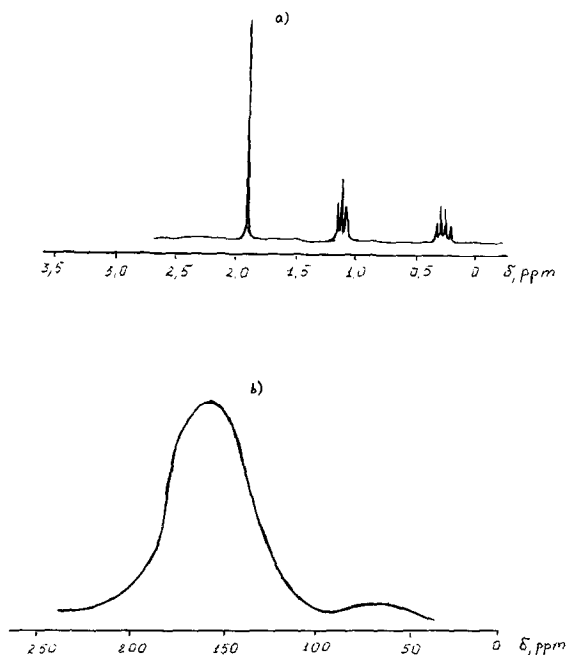


Fig. 1. ^1H and ^{27}Al NMR spectra of ethylaluminumoxane, MW = 880. (a) ^1H NMR; (b) ^{27}Al NMR, $W_{1/2} = 3100$ Hz.

ing the initial formed alkylaluminum particularly TEA and oligomeric and polymeric EAO it was found that TEA was monodisperse; however, the products of its hydrolysis were of multimodal molecular-mass distribution. Increasing nonuniformity of hydrolysis products based on molecular mass was observed as the

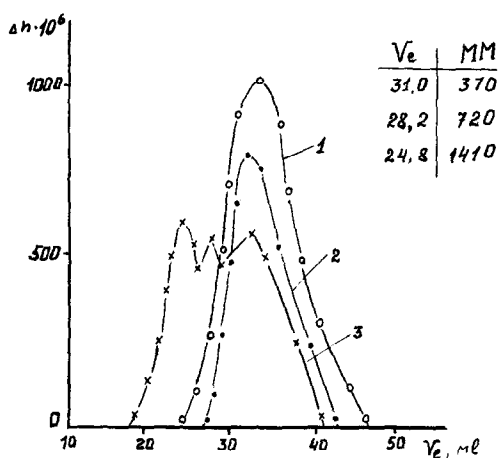


Fig. 2. GPC curves for aluminum ethyl derivatives. 1 – TEA; 2 – EAO, MW = 370; 3 – EAO, MW = 880; V_e – elution volume in ml.

molecular mass of the EAO increased, as seen in Fig. 2.

Zirconocenes were synthesized by well-known methods [19].

3. Results and discussion

Data on the effect of the nature of the aluminoxane on catalyst activity have already been published. Particularly it was noted [20] that replacement of the methyl groups in MAO by ethyl- or iso-butyl groups leads to an activity loss of nearly 1000 times and this may be even higher with increasing extent of oligomerization in the aluminoxane.

It was shown by Nekhaeva and coworkers [12] that the activity in ethylene polymerization of catalytic systems based on EAO (oligomerization degree of $n = 2$) and Cp_2ZrCl_2 is at the level of 30 kg PE/mol Zr h and when using EAO (oligomerization degree of $n = 10\text{--}30$) more than 1000 kg PE/mol Zr h. is achieved.

The effects of polymerization degree of iso-butylaluminumoxane on activity and structure of forming polyacetylene were observed by us [21] for iso-butylaluminumoxane – $\text{Ti}(\text{O}i\text{Bu})_4$ with oligomerization degree of $n = 6$.

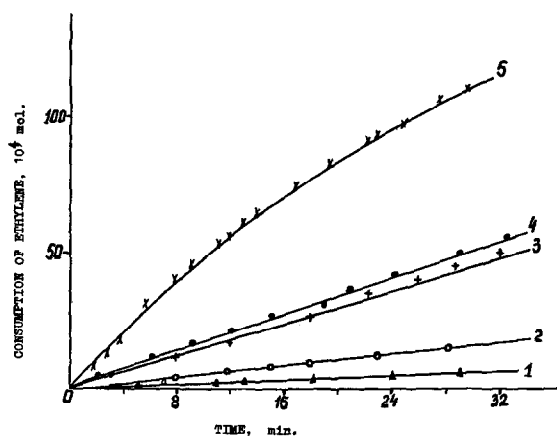


Fig. 3. Ethylene consumption kinetics for different zirconocenes $T = 30^\circ\text{C}$, pressure of $\text{C}_2\text{H}_4 = 370$ mm Hg, ethylaluminumoxane (MW = 880)/ $\text{R}_2\text{Cp}_2\text{ZrCl}_2 = 23$ mol. Curve 1 – $[\text{Zr}] = 1 \times 10^{-3}$ mol/l; Curve 2+5 – $[\text{Zr}] = 1.35 \times 10^{-3}$ mol/l; $(\text{CpR})_2\text{ZrCl}_2$, where R for 1 – $(t\text{-Bu}_2\text{Cp})_2\text{ZrCl}_2$; 2 – H; 3 – $t\text{-Bu}$; 4 – Me; 5 – $i\text{-Pr}$.

In the present work we used EAO with MW = 370, 470, 660 and 880 and the activity of the Cp_2ZrCl_2 -EAO catalytic system increased from 1.53 up to 40.09 kg PE/mol Zr h atm (see Table 2). Further, all experiments were carried out with EAO of MW = 880 since in this case the highest polymer yield was obtained. In Table 2 principal data on all catalysts investigated are presented.

Fig. 3 shows kinetic curves for ethylene polymerization in the presence of some Cp-derivatives of zirconium dichloride. On the base of data given in Fig. 3 and Table 2 it may be concluded that replacement of hydrogen atoms in the cyclopentadienyl ring by Me, *i*-Pr, *t*-Bu groups has a marked effect on the specific activity of these catalysts in ethylene polymerization. Maximum activity is observed in the case of hydrogen atom replacement by *i*-Pr group [6]. The same effect was noted in earlier work [22]. On the introduction of the more bulky *t*-Bu substituent the activity of the system is drastically decreased. Steric factors in this case, as well as in the case of acetyl-acetonate, fulvalene and indenyl substituents probably has

a dominant role in the low catalytic activity of the zirconocene.

Propylene polymerization proceeds at a rate 100 times slower than ethylene polymerization (entries 7 and 14, Table 2) when the active center formation took place in the presence of propylene. However, if after ethylene polymerization the ethylene is removed from the reaction zone and propylene is introduced, the specific rate is no more than 5 times slower than the rate of ethylene polymerization (Table 2, curves 1 and 2 in Fig. 4).

It should be emphasized that such rate decreases in propylene polymerization do not take place in the case of the $(t\text{-Bu}_2\text{Cp})_2\text{ZrCl}_2$ -EAO catalytic system. As may be seen from the Fig. 2 (3rd curve) after ethylene removal and propylene supply the steady-state rate remains unchanged. Polymerization kinetics of 1-butene (Fig. 4, 4th curve) have a pronounced non-steady-state character probably caused by the higher temperature (60°C) resulting in greater degradation of active centers.

Polymerization kinetics of ethylene in the presence of various zirconocenes appear in Fig.

Table 2
Polymerization activities (*A*) of the zirconocene/ethylalumoxane (MW = 880) catalyst applied to ethylene and propylene

<i>N</i>	Zirconocene	Zr(10 ³ mol/l)	Al/Zr (mol/mol)	Monomer	<i>T</i> (°C)	<i>A</i> (g molZr ⁻¹ h ⁻¹ bar ⁻¹)	[η]dl/g
1	CpZr(Acac) ₂ Cl	1.3	23.0	C ₂ H ₄	30	2140	
2	(Fulv) ₂ Zr ₂ Cl ₂ Cp ₂	1.1	30.9	C ₂ H ₄	30	3470	
3	Cp ₂ ZrMe ₂	1.3	23.0	C ₂ H ₄	30	4220	0.4
4	(Fulv) ₂ Cp ₂ Zr ₂ (O)Cl ₂	1.1	30.9	C ₂ H ₄	30	7640	
5	(Ind) ₂ ZrCl ₂	0.7	48.5	C ₂ H ₄	30	12 290	
6	(Bu ₂ Cp) ₂ ZrCl ₂	1.0	23.0	C ₂ H ₄	30	25 600	
7	Cp ₂ ZrCl ₂	1.4	23.0	C ₂ H ₄	30	40 090	
8	(BuCp) ₂ ZrCl ₂	1.4	23.0	C ₂ H ₄	30	124 130	0.3
9	(MeCp) ₂ ZrCl ₂	1.4	21.2	C ₂ H ₄	30	120 680	0.8
10	(<i>i</i> -PrCp) ₂ ZrCl ₂	1.4	23.0	C ₂ H ₄	30	384 020	1.2
11	CpZrH(Acac) ₂	1.7	40.0	C ₂ H ₄	70	2810	2.6
12	Cp ₂ ZrCl ₂	1.7	17.6 ^a	C ₂ H ₄	30	1530	0.3
13	Cp ₂ ZrCl ₂	1.7	23.0 ^b	C ₂ H ₄	30	7890	
14	Cp ₂ ZrCl ₂	1.7	18.3	C ₃ H ₆	30	390	
15	(<i>t</i> -BuCp) ₂ ZrCl ₂	1.1	29.0	C ₃ H ₆	60	2950	
16	(<i>t</i> -Bu ₂ Cp) ₂ ZrCl ₂	1.0	23.0	C ₃ H ₆ ^c	30	25 780	2.6

^a Used tetraethylalumoxane.

^b Used EAO (MW = 470).

^c Propylene has been used after ethylene.

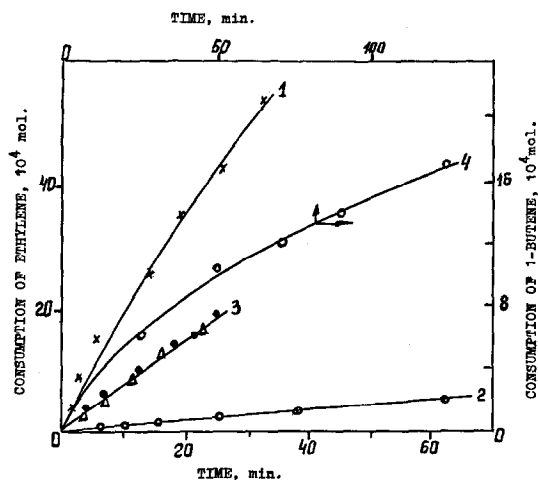


Fig. 4. Olefin consumption kinetics for catalytic system $(t\text{-BuCp})_2\text{ZrCl}_2\text{-EAO}$ (MW = 880). For curves 1–3 $[\text{Zr}] = 1 \times 10^{-3}$ mol/l, $\text{Al/Zr} = 34$, pressure of $\text{C}_2\text{H}_4 = 405$ mm Hg. Curve 1: $T = 30^\circ\text{C}$; curve 2: polymerization of C_3H_6 after C_2H_4 , pressure $\text{C}_2\text{H}_6 = 200$ mm Hg. Curve 3: $(t\text{-BuCp})_2\text{ZrCl}_2$; \circ – polymerization of ethylene; Δ – polymerization of propylene after C_2H_4 . Curve 4: $T = 60^\circ\text{C}$, pressure $\alpha\text{-C}_4\text{H}_8 = 450$ mm Hg, $\text{Al/Zr} = 26$, $[\text{Zr}] = 1.35 \times 10^{-3}$ mol/l.

5. In this case the system, containing $i\text{-C}_3\text{H}_7$ group in the Cp-ring as a substituent, offers the same high catalytic activity. The zirconocene

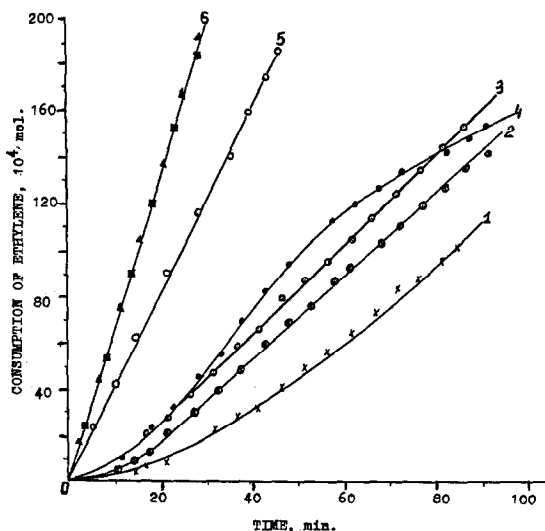


Fig. 5. Ethylene consumption kinetics for different zirconocenes: $T = 70^\circ\text{C}$, pressure of $\text{C}_2\text{H}_4 = 405$ mm Hg, $[\text{Zr}] = 1.86 \times 10^{-4}$ mol/l. Methylalumoxane (MW = 1930)/ $\text{R}_2(\text{RCp})_2\text{ZrCl}_2 = 29$. For curves 5 and 6: $\text{Al/Zr} = 100$. $(\text{RCp})_2\text{ZrCl}_2$, where R for 1 – Me; 2 – Et; 3 – n-Pr; 4 – n-Bu; 5 – i-Pr; 6 – cyclo-Hex.

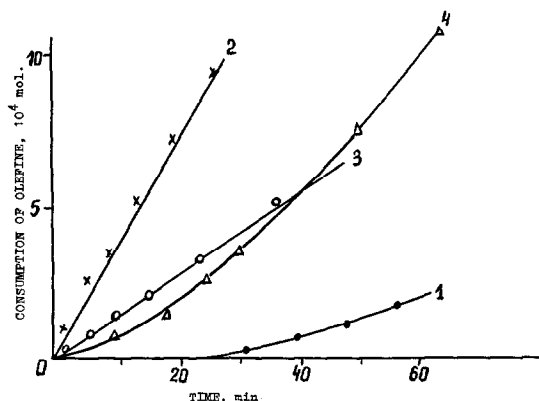


Fig. 6. The kinetics of polymerization of olefin 'vitality' of the catalytic system $\text{Cp}_2\text{ZrCl}_2\text{-MAO}$ (MM = 570), $T = 30^\circ\text{C}$, pressure of olefin = 400 mm Hg, $[\text{Zr}] = 1.35 \times 10^{-3}$ mol/l, $\text{Al/Zr} = 230$. MAO contained 7.5% (wt) of chlorine. Curve 1 – polymerization of C_2H_4 on the 1st day, curve 2 – polymerization of C_2H_4 on the 2nd day, curve 3 – polymerization of C_2H_4 on the 3rd day, curve 4 – polymerization of C_2H_4 on the 4th day.

containing a cyclohexyl substituent in the Cp-ring shows even higher activity.

It was found generally that catalysts involving zirconocene and aluminoxane demonstrate a comparatively prolonged life time. Referring to Fig. 6, the catalytic activity would be retained for some days. In this case ethylene replacement by propylene leads to only a moderate decrease in catalyst activity.

4. Conclusion

Polymerization kinetics of ethylene on the catalytic system zirconocene-EAO have been investigated. It was established that catalytic activity increases with the increase of the EAO molecular mass in the range from 370 to 880. The polymerization occurs at a relatively low molar ration Al/Zr (23–26).

The effect of alkyl substituent in cyclopentadienyl ring of zirconocene onto catalytic activity of ethylene polymerization was investigated and the best catalyst is a zirconocene with an $i\text{-Pr}$ substituent.

When using zirconocene-MAO catalytic sys-

tem zirconocene with cyclohexyl substituent shows the best activity.

The kinetics of ethylene and 1-butene polymerization on the zirconocene-EAO catalytic system have been investigated. It was found that the propylene polymerization rate was 100 times slower than ethylene but only 5 times slower if propylene was introduced into the reaction zone after ethylene polymerization. The polymerization of 1-butene ($Al/Zr = 26$) has a non-stationary character.

The important result of our investigations is the ability of the zirconocene–alkylaluminumoxane catalytic system to work for a long time with conservation of initial activity. The literature [23] and our experimental data on ethylene polymerization show us that the catalytic activity depends on experimental conditions (temperature, molar ratio of Al/Zr and zirconocene concentration).

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