= **CATALYSIS** =

Alkene Polymerization with Catalysts Containing Ionic Complexes [2L·M@dibenzo-18-crown-6]$^+$[TiCl$_5$·L]$^-$ (L = CH$_3$CN, M = Li$^+$, K$^+$)

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Abstract—The polymerization of ethylene and propylene and the copolymerization of ethylene with 1-octene with novel type of post-metallocene catalysts containing ionic complexes [2L·M@dibenzo-18-crown-6]$^+$ [TiCl$_5$·L]$^-$ (L = CH$_3$CN, M = Li, K) are studied. The binary activator Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ at [Al] : [Mg] ~ 3 is used as a cocatalyst. A linear crystalline polyethylene, an almost fully amorphous, atactic polypropylene, and statistical ethylene-1-octene copolymers containing from 2 to 9 mol % 1-octene are synthesized. The copolymers exhibit a broad molecular-weight distribution and a nonuniform composition distribution like copolymers synthesized over classical Ziegler−Natta catalysts and many post-metallocene systems.

INTRODUCTION

The first catalyst based on titanium compounds for the synthesis of PE at a low pressure was discovered by K. Ziegler in 1953. This catalyst, a combination of TiCl$_4$ and Al(C$_2$H$_5$)$_2$Cl, had a number of technological advantages, its components were produced commercially, were cheap, and showed solubility in aliphatic and aromatic hydrocarbons. Therefore, it was practically immediately employed for the industrial production of high-density PE [1, 2].

This paper presents the results of studying the reactions of homo- and copolymerization of alkenes with two catalysts based on ionic complexes containing anion [TiCl$_5$·L]$^-$ and cations Li$^+$ and K$^+$ coordinated with a crown ether. The crystalline complexes have composition [2L·M@dibenzo-18-crown-6]$^+$[TiCl$_5$·L]$^-$, where L = CH$_3$CN; M = Li, K. The first successful attempt to use these complexes as components of ethylene polymerization catalysts was described in [3, 4]. The purposes of this work were a detailed probing of these complexes in the reactions of ethylene and propylene polymerization and ethylene copolymerization with 1-octene, the kinetic study of alkene polymerization and copolymerization reactions, a detailed analysis of the properties of the resulting polymers, and a comparison of the the TiCl$_5$-based catalysts with the classical Ziegler catalyst.

A binary cocatalyst Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ at [Al] : [Mg] ≈ 3 was used as an activator. As was shown previously, this is a versatile activator of traditional Ziegler−Natta catalysts [5−8], compounds of type Ti(OR)$_4$ [6, 9], metallocene complexes [10], and various post-metallocene catalysts [5, 6, 11−14]. Specifically, the system TiCl$_4$−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ is a very active catalyst of ethylene polymerization, ethylene copolymerization with alkenes (synthesis of LDPE), and propylene polymerization (synthesis of atactic PP) [7, 8].

EXPERIMENTAL

Materials

The components of catalytic systems were ionic complexes containing anion [TiCl$_5$·CH$_3$CN]$^-$ and cations Li$^+$ or K$^+$ coordinated with a dibenzo-18-crown-6 molecule. The general formula of the complexes in the crystalline state is [2CH$_3$CN·M@dibenzo-18-crown-6]$^+$ [TiCl$_5$·CH$_3$CN]$^-$, where M = Li (pre-catalyst **Cr-I**) or K (pre-catalyst **Cr-II**):

Cr-I   Cr-II
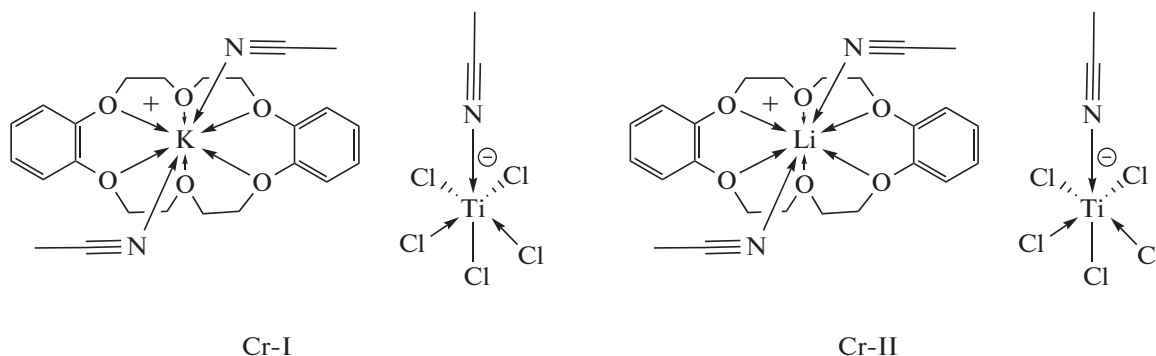
The ionic complexes were obtained by the reaction of LiCl or KCl with $TiCl_4$ in the presence of one equivalent of dibenzo-18-crown-6 in anhydrous acetonitrile, as described in [3, 4]. The composition and crystalline structure of the complexes were determined by the methods of elemental analysis, NMR and MALDI MS spectroscopy, and X-ray diffraction analysis [4].

Ethylene and propylene (both of polymerization grade, 99.9 vol %) purchased from the Moscow refinery, as well as $AlEt_2Cl$ (solution in heptane 0.8 mol/L) and $MgBu_2$ (solution in heptane 0.5 mol/L) purchased from Acros, were used as received. Toluene (special purity grade) and 1-octene were refluxed over Na and distilled in a flow of argon.

Polymerization Reactions

The polymerizations of ethylene and propylene and the copolymerization of ethylene with 1-octene were carried out in a 200 mL stainless steel reactor equipped with a stirrer. Before experiments the reactor was evacuated for 1 h at polymerization temperature. In the case of ethylene polymerization and ethylene copolymerization with 1-octene, the reactor was filled with toluene or a mixture of toluene with 1-octene; the volume of the liquid phase was 100 mL. $AlEt_2Cl$ and $MgBu_2$ were then sequentially added in the reaction medium, the resulting mixture was saturated with ethylene (propylene), and an ampoule with the crystalline complex was broken inside the reactor. The pressure in the reactor during the experiment was maintained constant, and the consumption of ethylene (propylene) was compensated by recharging from a calibrated vessel.

The monomer concentration in toluene was calculated by Henry's law $C_{E(P)}^{mon} = K_H^{E(P)} P_{E(P)} = K_H^{E(P)}(P_{total} - P_{tol})$, where $K_H^{E(P)}$ is Henry's constant ($K_H^E = 9 \times 10^{-4} e^{2990/RT}$ and $K_H^P = 2.1 \times 10^{-3} e^{1340/RT}$ [15]), P_{total} is the total pressure in the reactor, and $P_{E(P)}$ and P_{tol} is the partial pressure (atm) of the monomer and toluene, respectively.

The catalyst activity was characterized by the polymer yield per h per mol of complex, Q/C_{Ti} (kg mol_{Ti}^{-1}).

The effective rate constant of polymerization was estimated as $k_{eff} = R_{pol}(C_E C_{Ti})^{-1}$ [L $(mol_{Ti}\ min)^{-1}$], where R_{pol} is the rate of polymerization, mol/(L min) and C_E and C_{Ti} are the concentrations of ethylene and complex, mol/L.

The synthesized polymers and ethylene−1-octene copolymers were treated with a mixture of ethyl alcohol and HCl (10% solution), washed many times with water and alcohol, and dried to a constant mass. PP samples were fractionated with boiling n-heptane into two fractions: a soluble amorphous fraction and an insoluble partially crystalline fraction.

Analysis of Polymers

The MW and MWD of polymers were measured at 160°C on a PL-220 instrument equipped with PL-gel Olexis columns, a refractometer, and a differential viscometer. The solvent was 1,2,4-trichlorobenzene, and the elution rate was 1 mL/min. The average molecular weight of products was calculated from the universal calibration curve plotted using PS and PE standards with the narrow MWDs and molecular weights in the range of 750−(1.3 × 10^7). Mark−Houwink parameters for PE are $K = 6.14 \times 10^{-4}$ and $\alpha = 0.67$; for PS, $K = 2.80 \times 10^{-4}$ and $\alpha = 0.64$.

The procedure for the resolution of GPC curves into curves of individual Flory components was described in [16, 17]. The Flory component is a polymer produced by one type of active centers; for each Flory component $M_w/M_n = 2$.

The viscosity-average molecular weight M_v (g/mol) of high-molecular weight PE samples was calculated by the Mark−Houwink equation $M_v = 5.37 \times 10^4 [\eta]^{1.37}$, where $[\eta]$ is the intrinsic viscosity in decalin at 135°C (dL/g); $[\eta] = (2\eta_{sp} - 2\ln\eta_r)^{1/2}/0.056$ (η_{sp} is the specific viscosity, and η_r is the relative viscosity; $\eta_r = \eta_{sp} + 1$) [18].

The ^{13}C NMR spectra of polymers (~5% solutions in o-dichlorobenzene) were recorded at 110°C on a Bruker

Table 1. Parameters of ethylene polymerization and ethylene−1-octene copolymerization with Cr-I and Cr-II (solvent toluene, temperature 50°, P_E = 5.6 atm, C_E^{mon} = 0.54 mol/L, reaction time 1 h)

C_O^{mon}, mol/L	Content of 1-octene, mol %	[Ti] × 10^6, mol	Molar ratio		Yield, kg mol_{Ti}^{-1}	C_O^{copol}, mol %
			[Al] : [Ti]	[Al] : [Mg]		
Cr-I−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$						
0*	0	7.2	326	2.9	1380	0
0	0	4.8	342	2.7	5200	0
0.32	36.2	5.4	348	2.9	1760	1.6
0.64	54.3	4.8	342	2.7	2810	2.0
1.50	74.6	4.8	342	2.7	3280	3.9
Cr-II−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$						
0	0	3.7	348	2.9	2830	0
0.32	36.2	3.8	339	2.9	2470	3.4
1.60	74.6	4.1	343	2.8	3240	9.0

* Temperature 30°.

Avance-400 spectrometer (frequency 10.613 MHz, relaxation time 15 s, and acquisition number from 500 to 2000). The assignment of signals in the ^{13}C NMR spectra of ethylene-1-octene copolymers was performed in accordance with [19]. The content of 1-octene in the copolymers was calculated from ^{13}C NMR spectra as described in [20].

The IR spectra of polymers were recorded on a Bruker Tensor 27 FTIR spectrophotometer. The ratios of optical densities of absorption bands D_{998}/D_{973} and D_{841}/D_{973} were used as the stereoregularity parameters of PP. These parameters characterize the presence of isotactic sequences with lengths of more than 11−13 and 13−15 of monomer units in a chain [21, 22].

The melting of PE, PP, and ethylene−1-octene copolymers was studied by the DSC method on a Netzsch DSC-209 F1 analyzer. Samples (3−5 mg) were first heated to 160°C in the case of PE and ethylene−1-octene copolymers and to 190°C in the case of PP at a rate of 5°C/min. The samples were then cooled to 30°C at a rate of 2°C/min and heated again at a rate of 5°C/min; the data obtained in the second melting of the samples were used. The resolution of the DSC melting curves of the copolymers into the melting profiles of components with different C_O^{copol} was carried out as described in [23].

The degree of crystallinity of polymers was determined from the heat of melting ΔH_m as $(\Delta H_m/\Delta H_m^\circ)$ 100, where ΔH_m° = 293 J/g for PE and 209 J/g for PP.

The mechanical properties of PE and ethylene−1-octene copolymers were studied on an Instron 3365 testing machine at 20°C in accordance with GOST (State Standard) 11262-2017. The samples of standard size 5 were obtained by hot pressing at a temperature of 180°C followed by cooling to 30°C at a rate of

9°C/min and at a pressure of 10 MPa. For each sample the following parameters were measured: the elastic modulus E at the stretching speed of 1 mm/min, the yield stress σ_y and the corresponding yield elongation ε_y, the end-of-neching stress σ_m and elongation ε_m, the breaking strength σ_b, and the relative elongation at break ε_b (all at the stretching speed of 50 mm/min). The error of E and σ_b measurements was below 10%, and the error of ε_b measurements was 20%.

RESULTS AND DISCUSSION

Polymerization of Ethylene and Copolymerization of Ethylene with 1-Octene

The combinations of Cr-I and Cr-II with Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ as an activator are very efficient catalysts of ethylene polymerization and its copolymerization with 1-octene. The yield of PE for 1 h at 50°C and P_E = 5.6 atm is 5200 and 2830 kg mol_{Ti}^{-1} and the yield of the ethylene−1-octene copolymer, depending on the composition of the monomer mixture, is ~1800−3300 and ~2500−3200 kg mol_{Ti}^{-1} for Cr-I and Cr-II, respectively (Table 1).

The introduction of 1-octene in the polymerization of ethylene was generally accompanied by some reduction in the activity of both catalysts. However, in the case of Cr-II an increase in the content of 1-octene in the reaction medium up to ~75% caused an increase in the catalyst productivity by 15−20%. This comonomer effect is typical for many Ziegler−Natta catalysts and post-metallocene catalysts [9, 17].

The ability to efficiently copolymerize ethylene with alkenes is an important characteristic of any titanium-based catalyst used for the synthesis of LDPE and HDPE. Ethylene−1-octene copolymers synthe-
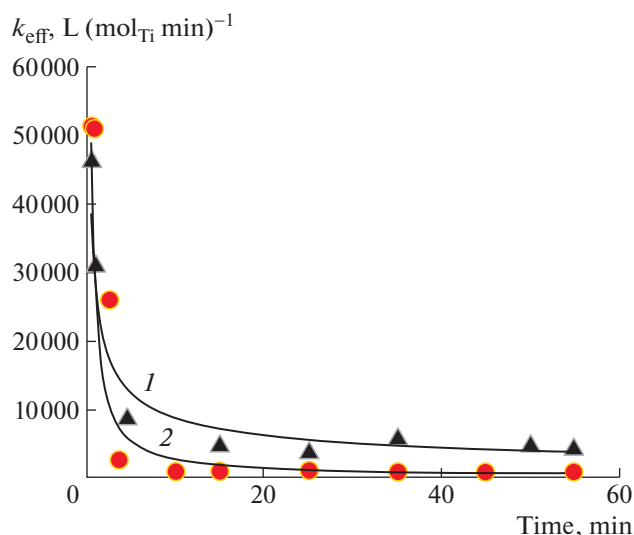
k_{eff}, L $(\text{mol}_{\text{Ti}} \text{ min})^{-1}$

Fig. 1. Kinetics of ethylene consumption in the polymerization of ethylene (*1*) and copolymerization of ethylene with 1-octene ($C_{\text{oct}}^{\text{mon}} = 74.6$ mol %) (*2*) over the system Cr-I−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$.

sized with Cr-I contain up to ~4 mol % 1-octene and 9 mol % in the case of copolymers synthesized with Cr-II. The data presented in Table 1 make it possible to roughly estimate the reactivity ratio r_1 in the copolymerization reactions by formula

$$r_1 = k_{\text{E–E}}/k_{\text{E–O}} \approx (C_{\text{E}}/C_{\text{O}})^{\text{copol}}/(C_{\text{E}}/C_{\text{O}})^{\text{mon}} \quad (1)$$

where $C_{\text{E}}^{\text{copol}} = 100 - C_{\text{O}}^{\text{copol}}$ and $C_{\text{E}}^{\text{mon}}$ and $C_{\text{O}}^{\text{mon}}$ are the molar concentrations of ethylene and 1-octene in monomer mixtures. Expression (1) for r_1 is valid only for copolymers with low $C_{\text{O}}^{\text{copol}}$ values. The value of r_1 is 35−55 for Cr-I and ~20 for Cr-II; that is, the catalyst based on Cr-II copolymerizes ethylene with 1-octene 2 to 3 times more efficiently.

Both systems are unstable at 50°C; the rate of polymerization drops abruptly after 3−5 min of reaction. As an example, Fig. 1 illustrates the kinetics of ethylene consumption in the reactions of ethylene polymerization and copolymerization with 1-octene carried out using Cr-I.

Molecular Chain Structure.
IR and ^{13}C NMR Spectroscopy Data

According to the IR data, ethylene homopolymers synthesized with Cr-I- and Cr-II-based systems are linear: the absorption bands of methyl groups in branches (1378 cm^{-1}) are absent in the spectra of the samples.

Figure 2 presents the ^{13}C NMR spectrum of the ethylene−1-octene copolymer with $C_{\text{O}}^{\text{copol}} = 9.0$ mol %

synthesized with Cr-II and the assignment of signals of various sequences. In the case of the studied copolymers the most suitable spectral range for molecular structure analysis is C(H) signals in the range of 35.5−38.5 ppm: the signal of C(H) in triad ethylene−1-octene−ethylene (isolated 1-octene units in a chain) is observed at ~38.2 ppm, while the signal of C(H) in triad ethylene−1-octene−1-octene (two linked 1-octene units) is seen at ~35.9 ppm.

The ^{13}C NMR spectra copolymers with $C_{\text{O}}^{\text{copol}} <$ 5 mol % show a single signal of triads ethylene−1-octene−ethylene; that is, the majority of 1-octene units in chains are isolated. And only the spectrum of the copolymer with $C_{\text{O}}^{\text{copol}} \sim$ 9 mol % 1-octene contains both signals (Fig. 2).

The ability of active centers to alternate monomer units can be assessed from the product of reactivity ratios $r_1 r_2$, where $r_1 = k_{\text{E–E}}/k_{\text{E–O}}$ and $r_2 = k_{\text{O–O}}/k_{\text{O–E}}$ [20]. ^{13}C NMR spectra are the most sensitive tool for determining $r_1 r_2$. This value can be assessed using the statistical equation to calculate the content of triads in ethylene−1-alkene copolymers as a function of copolymer composition $C_{\text{O}}^{\text{copol}}$ and $r_1 r_2$ [24]

$$[\text{O–O–E} + \text{E–O–O}] / [\text{E–O–E}]$$
$$= 4 r_1 r_2/\{(f - 1) + [(f - 1)^2 + 4 r_1 r_2 f]^{0.5}\}, \quad (2)$$

where $f = (C_{\text{E}}/C_{\text{O}})^{\text{copol}} = (1 - C_{\text{O}}^{\text{copol}})/C_{\text{O}}^{\text{copol}}$.

In the case of the ethylene−1-octene copolymer containing 9.0 mol % 1-octene-($f = 10.1$), the ratio of areas [O–O–E + E–O–O]/[E–O–E] is ~ 0.22 (Fig. 2). Estimation via Eq. (2) gives the average value of $r_1 r_2 \sim 1.1$. This implies than the relative probability of finding a given monomer unit in a chain depends only on its content in the copolymer and is independent of the nature of the preceding monomer unit (statistical copolymers); in this case monomer units in copolymer chains are distributed almost randomly. For ideally statistical copolymers $r_1 r_2 = 1.0$.

Molecular Weights and Molecular-Weight Distributions
of PE and Ethylene−1-Octene Copolymers

PE samples have a very high molecular weight ($M_\eta = 65 \times 10^4 - 70 \times 10^4$), which makes it difficult to study them by GPC. The molecular weight of ethylene−1-octene copolymers is much smaller, ~20 × $10^4 - \sim 30 \times 10^4$ (Table 2).

A broad MWD of ethylene−1-octene copolymers indicates that the catalysts contain various types of active centers differing in the kinetic parameters of polymerization reactions. The resolution of the GPC curves of ethylene−1-octene copolymers into Flory components shows that these polymer products are a mixture of six components with M_{w} from ~6000−7000 to ~2 × 10^6 (Tables 3, 4). Figure 3a presents the GPC
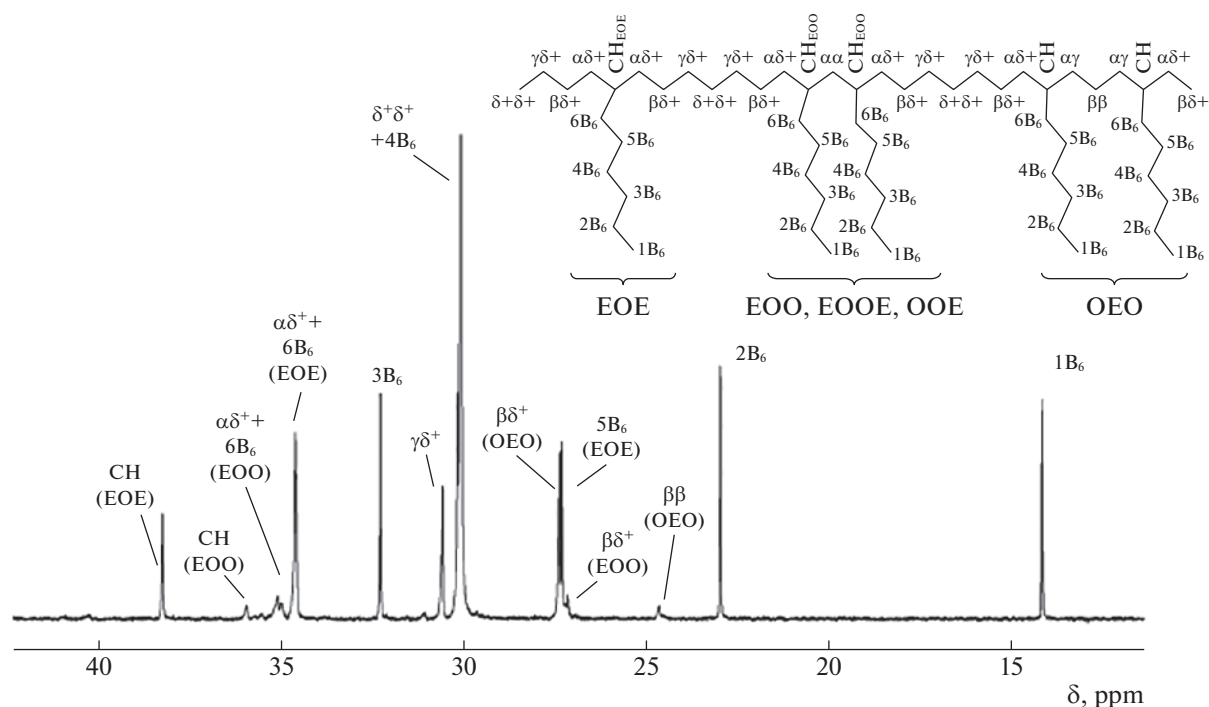
Fig. 2. Fragmented ^{13}C NMR spectrum of the ethylene−1-octene copolymer with C_O^{copol} = 9.0 mol % and the assignment of signals.

curves obtained for ethylene−1-octene copolymers with C_O^{copol} = 3.4 and 9.0 mol % which were synthesized using Cr-II. At first glance, the introduction of large amounts of 1-octene in the copolymerization reaction causes a considerable shift in the maximum of the MWD curve toward low MW values: the maxima of peaks on the GPC curves decrease from ~110 × 10^3 to ~55 × 10^3 and M_w^{av} decreases from ~320 × 10^3 to 245 × 10^3.

However, a more detailed analysis of MWDs provides another explanation for this phenomenon. The resolution of the GPC curves of the copolymers into Flory components suggests that these components have almost the same M_w values but their proportions are different (Fig. 3b, Table 3). The copolymer with C_O^{copol} = 3.4 mol % contains a somewhat larger fraction of components IV and V with a high M_w, whereas the copolymer with C_O^{copol} = 9.0 mol % contains more low molecular weight components II and III. The values of M_w for all main Flory components gradually decrease with an increase in C_O^{copol}.

The GPC curves obtained for all three ethylene−1-octene copolymers with a similar content of 1-octene, which were synthesized using Cr-I, are very similar (Fig. 4). Taking into account the limited accuracy of the GPC method it can be stated that all the three copolymers have similar M_w values. Table 4 presents the results of resolution of the GPC curves of the three copolymers into Flory components. All six components in these copolymers have somewhat lower M_w values and a broader MWD compared with the copolymers synthesized using Cr-II; ratio M_w/M_n for them is in the range of 11−18.

Table 2. Molecular-weight characteristics of PE and ethylene−1-octene copolymers

C_O^{copol}, mol %	$M_w \times 10^{-3}$	M_w/M_n
Cr-I−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$
0	690*	
1.6	284.3	10.6
2.0	214.1	15.2
3.9	284.4	18.0
Cr-II−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$
0	650^a	
3.4	318.5	7.2
9.0	245.1	10.6

* Viscosity-average MW.

Table 3. MWD of ethylene−1-octene copolymers synthesized with Cr-II

Flory component, no.	C_O^{copol} = 3.4 mol %		C_O^{copol} = 9.0 mol %	
	$M_w \times 10^{-3}$	Content, %	$M_w \times 10^{-3}$	Content, %
I	−	−	5.7	2.6
II	24	12.6	19	17.2
III	70.6	29.1	54	33.5
IV	210	33.9	160	26.2
V	640	20.0	520	15.9
VI	2200	4.3	2100	4.7
Average values	$M_w^{av} = 318.5 \times 10^3$ M_w/M_n = 7.2		$M_w^{av} = 245.1 \times 10^3$ M_w/M_n = 10.6	

Compositional Heterogeneity of Ethylene−1-Octene Copolymers. DSC Data

DSC is a suitable technique for studying the compositional heterogeneity of ethylene−1-alkene copolymers prepared with catalysts based on transition-metal compounds. The copolymers of ethylene with 1-alkenes synthesized using single-center metallocene catalysts have the uniform composition distribution; that is, all their macromolecules have almost the same composition regardless of MW. The melting peaks of these copolymers are fairly narrow. Note that the melting temperature T_m and the degree of crystallinity of the copolymer rapidly decrease with increasing content of 1-alkene [23]. In contrast, ethylene−1-alkene copolymers synthesized with Ziegler−Natta catalysts and many post-metallocene catalysts are, in fact, complex mixtures of fractions of copolymers of completely different compositions. During melting and subsequent slow crystallization these mixtures separate into components with different degree of crystallinity and T_m [23].

Ethylene−1-octene copolymers synthesized in the presence of complexes Cr-I and Cr-II belong to the second type of copolymers. Figure 5a shows curves characterizing the melting process of PE and the ethylene−1-octene copolymer with C_O^{copol} = 3.9 mol %

Table 4. MWD of ethylene−1-octene copolymers synthesized with Cr-I

Flory component, no.	$M_w \times 10^{-3}$	Content, %
I	5.5−6	5−9
II	18	13−17
III	51.5−53	25−30
IV	145−165	24−28
V	460−520	17−18
VI	~1800	5−7

prepared using Cr-I. The thermophysical characteristics of PE and ethylene−1-octene copolymers synthesized with both pre-catalysts are listed in Table 5.

The melting of the polymers has some specific features.

1. The maximum of the melting peak for the copolymer is observed at a much lower temperature (127−123°C) than that for PE (~136°C). Its position slowly shifts to lower temperatures with increasing content of 1-octene in the copolymer.

2. The crystallization of copolymers from the melt also occurs at a lower temperature (110−114°C) than the crystallization of PE (~120°C).

3. The area under the melting curve (proportional to the melting enthalpy ΔH_m) for the copolymer is much smaller than that for PE.

4. The melting temperature range of the copolymer is much wider (Fig. 5a).

The mentioned features are inherent for the melting of statistical ethylene−1-alkene copolymers with the nonuniform composition distribution, such as copolymers prepared with Ziegler−Natta catalysts and many post-metallocene catalysts.

Figure 5b presents the results of resolution of the melting curve into individual components for the ethylene−1-octene copolymer with C_O^{copol} = 9.0 mol % synthesized with Cr-II. The resolution procedure was described in detail in [23]. This product, like all other copolymers synthesized in the presence of complexes Cr-I and Cr-II, is composed of three crystalline components the ratio between which varies depending on the composition of the copolymer. As an example, Table 6 shows rough estimates of the composition, degree of crystallinity, and melting temperature of components for the two copolymers.

In both examples, the calculated average degree of crystallinity in the copolymers equal to 41 and 36%, respectively, is much higher than the measured average values 26 and 16% (Table 5). This discrepancy implies that both materials, in addition to three par-
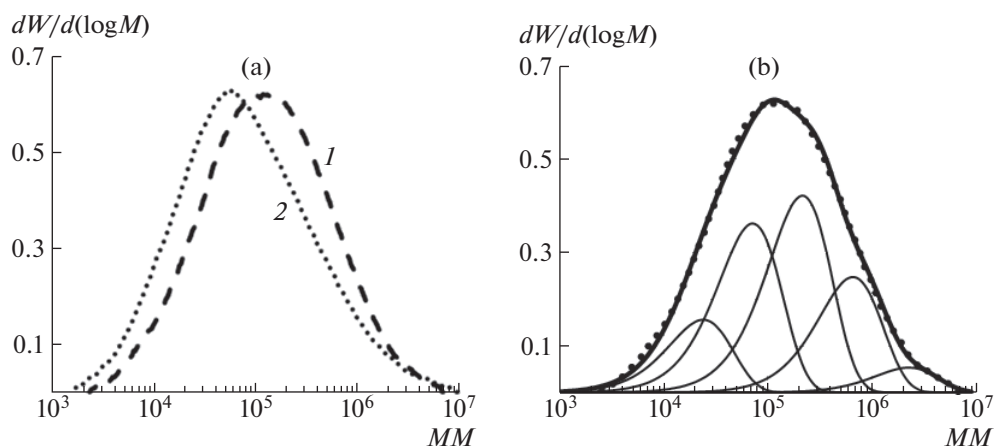
Fig. 3. (a) GPC curves of ethylene−1-octene copolymers with $C_O^{copol} = 3.4$ (*1*) and 9.0 mol % (*2*) synthesized with Cr-II; (b) resolution of the GPC curve into Flory components for the copolymer with $C_O^{copol} = 3.4$ mol %. Dots are the experimental data, thin lines are the Flory components, and the bold line is the calculated GPC curve.

tially crystalline components, contain a large, fully amorphous fraction not registered by DSC. On the other hand, a similar estimate for the copolymer containing a much smaller amount of 1-octene (1.9 mol %), which was synthesized with Cr-I, gives close degrees of crystallinity, 48 and 42%; that is, this copolymer contains a small amount of the amorphous material.

Mechanical Properties of PE and Ethylene−1-Octene Copolymers

Figure 6 displays in σ−ε coordinates the deformation curves of PE and two ethylene−1-octene copolymers synthesized with Cr-I, and Table 7 lists their mechanical characteristics. The deformation curve of PE is typical for similar materials with a large degree of crystallinity and a high MW. The polymer has a high elastic modulus, a pronounced yield stress at ε ~ 9%, a large tensile strength, and a short neck region, <200%. It lacks the distinct stage of strain hardening (the elastic tension of a fully oriented material), as is inherent for most PEs of this type.

The mechanical behavior of the ethylene−1-octene copolymers depends on their composition.

The copolymer with $C_O^{copol} = 2.0$ mol % is a partially crystalline material (the degree of crystallinity ~40%) and behaves as a typical linear LDPE. Its deformation curve exhibits a well-defined yield stress at ε_y ~ 13% and an extended neck region, $\sigma_y - \sigma_m = 1-2$ MPa compared with ~5 MPa for PE. The values of σ_y and σ_m for this copolymer are ~2 times lower than those for PE.

The ethylene−1-octene copolymer with $C_O^{copol} = 3.9$ mol % has a much lower degree of crystallinity (~25%), a very low elastic modulus E (~150 MPa)

compared with the elastic modulus of PE (>1200 MPa), and ~3 times smaller yield stress σ_y. In general, the behavior of this copolymer is characteristic of ethylene elastomers (copolymers of ethylene with 1-alkenes).

Propylene Polymerization

System Cr-II−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ is inactive in propylene polymerization. At the same time, system Cr-I−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ produces, albeit with a small efficiency, an almost amorphous product (Table 8), in which the content of the fraction soluble in boiling heptane is ~90%. All IR and DSC charac-
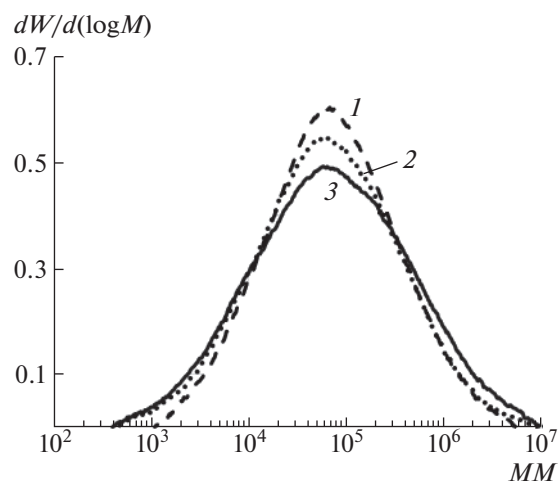

Fig. 4. GPC curves of ethylene−1-octene copolymers synthesized with Cr-I. $C_O^{copol} = 1.6$ (*1*), 2.0 (*2*), and 3.9 mol % (*3*).
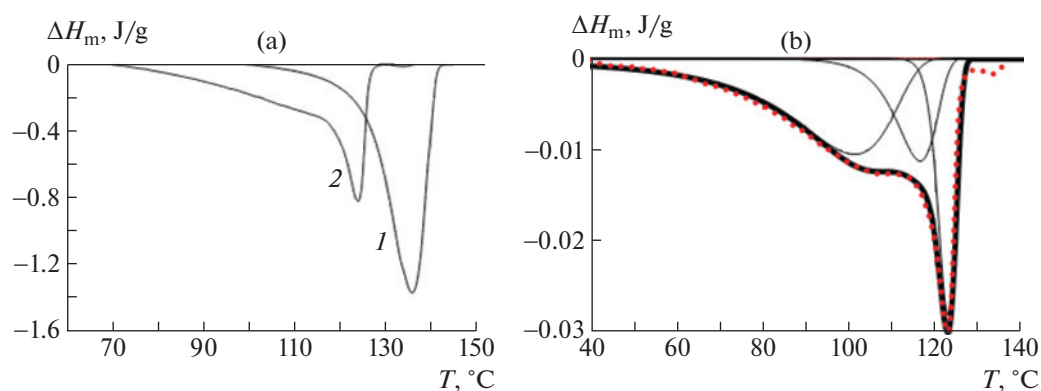
Fig. 5. (a) Melting curve of PE (*1*) and ethylene−1-octene copolymer with C_O^{copol} = 3.9 mol % (*2*) synthesized with Cr-I; (b) resolution of the melting curve into components for the ethylene−1-octene copolymer with C_O^{copol} = 9.0 mol % synthesized with Cr-II. Dots are the experimental data, and lines are the results of calculations.

teristics of the insoluble fraction are typical for a polymer with a low degree of isotacticity: the degree of crystallization 34%, T_m = 154°C, D_{998}/D_{973} = 0.83, and D_{841}/D_{973} = 0.85 [21, 23].

CONCLUSIONS

Although seven decades have passed since the discovery of first alkene polymerization catalysts based on $TiCl_4$, the nature of products arising in the reactions of $TiCl_4$ with various organoaluminum compounds remains largely unknown [25−28].

This study covers two alkene polymerization catalytic systems containing as pre-catalysts ionic complexes: anion $[TiCl_5 \cdot CH_3CN]^-$ and cation $[2CH_3CN \cdot Mt@dibenzo-18-crown-6]^+$, where Mt = Li or K. The mixture $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ at [Al] : [Mg] ~ 3 is used as an activator.

In our opinion, the efficiency of the catalysts under consideration is associated with the formation of a highly dispersed crystalline $MgCl_2$, the surface of which exhibits the Lewis acidity [5, 29].

$$Mg(C_4H_9)_2 + 2Al(C_2H_5)_2Cl \quad (3)$$
$$\rightarrow [MgCl_2] + 2Al(C_2H_5)_2(C_4H_9).$$
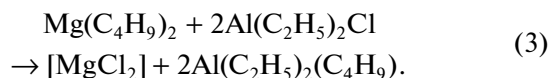
The combination of $Al(C_2H_5)_2Cl$ with $Mg(C_4H_9)_2$ was used at [Al] : [Mg] ~ 3. Thus, the $[TiCl_5 \cdot CH_3CN]^-$ anion in pre-catalysts, which were added to the combination $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ at the final stage of catalyst preparation, could interact with both the unreacted excess of $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)_2(C_4H_9)$. It can be assumed that after the loss of a coordinated acrylonitrile molecule anion $[TiCl_5 \cdot CH_3CN]^-$ is adsorbed on the surface of $MgCl_2$ in the form of anionic centers $(TiCl_5^-)_{ads}/[MgCl_2]$ associated with $[dibenzo-18-crown-6@Mt]^+$ cations. These centers can be involved in the alkylation reactions with organoaluminum compounds leading to formation of the active centers of polymerization.

Table 5. Thermophysical characteristics of PE and ethylene−1-octene copolymers synthesized over systems with Cr-I and Cr-II

C_O^{copol}, mol %	T_m^{max}, °C	ΔH_m, J/g	Degree of crystallinity, %	Crystallization temperature (max), °C
Cr-I−Al(C₂H₅)₂Cl/Mg(C₄H₉)₂				
0	135.9	199.4	68	120.0
1.6	126.6	123.8	42	114.0
2.0	124.2	113.7	39	112.2
3.9	123.7	75.3	26	110.9
Cr-II−Al(C₂H₅)₂Cl/Mg(C₄H₉)₂				
0	136.6	157.6	55	120.0
3.4	125.7	90.2	31	112.6
9.0	123.0	47.0	16	109.6

Table 6. Composition and characteristics of three crystalline components in ethylene−1-octene copolymers synthesized with Cr-I and Cr-II

Pre-catalyst	C_O^{copol}, mol %	Component	T_m, °C	The degree of crystallinity, %	Content, %	Average degree of crystallinity, %	Amorphous phase, %
Cr-I	3.9	I	~124	52	26	41	36
	3.9	II	~117	46	23		
	3.9	III	~104	32	51		
Cr-II	9.0	I	~123	52	15	36	57
	9.0	II	~116	46	16		
	9.0	III	~102	30	69		

Table 7. Mechanical characteristics of PE and ethylene−1-octene copolymers synthesized with the system Cr-I−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$

C_O^{copol}, mol %	Degree of crystallinity, %	E, MPa	σ_y, MPa	σ_m, MPa	σ_b, MPa	ε_b, %
0	68	1230	27	22	21	225
2.0	39	340	13	12	18	610
3.9	26	150	~9	8	18	670

These catalytic systems can be formally compared with the system TiCl$_4$−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ [7, 8]:

1. Systems based on Cr-I and Cr-II are very active catalysts in the polymerization of ethylene. The yield of PE for 1 h at 50°C reduced to the same monomer concentration is as high as ~10 t mol_{Ti}^{-1} C_E^{-1} for Cr-I and >5 t mol_{Ti}^{-1} C_E^{-1} for Cr-II. The productivity of the TiCl$_4$−based system under the same conditions is ~4 t mol_{Ti}^{-1} C_E^{-1}.

2. In general, the copolymerization ability of the Cr-II-based catalyst (r_1 ~20 for the ethylene−1-octene pair) is similar to that of the TiCl$_4$-based catalyst (r_1 ~ 16 for the ethylene−1-hexene pair), whereas the copolymerization ability of the catalyst based on Cr-I is lower (r_1 ~ 40−60) [7].

3. As follows from the MWDs of the copolymers, the catalysts of both types have different distributions of active centers. Even though the values of M_w^{av} for the copolymers of ethylene and 1-alkenes synthesized over both types of catalysts under similar conditions differ slightly (22 × 10^4 vs. 32 × 10^4 for copolymers with C_{alkene}^{copol} ~ 3 mol % and 16 × 10^4 vs. 24 × 10^4 for copolymers with C_{alkene}^{copol} = 6−9 mol %), the type of their MWDs is different. The catalyst based on TiCl$_4$ has one or two dominant types of active centers producing a larger part of the product [7], whereas the

distribution of active centers in the catalysts with Cr-I and Cr-II is more uniform (Tables 2, 3; Figs. 2, 3).

4. Systems with Cr-I and Cr-II are rather poor catalysts of propylene polymerization (Table 8), whereas the TiCl$_4$−based catalyst efficiently polymerizes propylene [8]. Possibly, therein lies the principal difference in the catalytic properties of systems formed by molecular and anionic pre-catalysts.
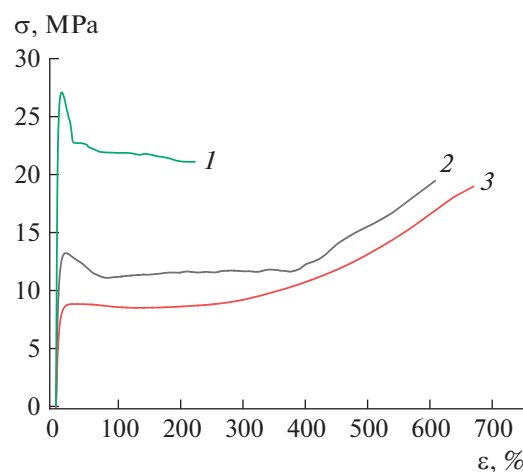

Fig. 6. Deformation curves of PE (*1*) and ethylene−1-octene copolymers with C_O^{copol} = 2.0 (*2*) and 3.9 mol % (*3*) synthesized with Cr-I.

Table 8. Parameters of propylene polymerization with complexes Cr-I and Cr-II (solvent toluene, $T = 50°C$, $P = 4$ atm, $C_{Pr} = 1.4$ mol/L, time 1 h)

Complex	$[Ti] \times 10^6$, mol	Molar ratio		Yield, $kg\ mol_{Ti}^{-1}$
		[Al] : [Ti]	[Al] : [Mg]	
Cr-I	6.7	350	2.8	119
Cr-II	6.8	345	2.8	−

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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