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New Cocatalyst for Alkene Polymerization Reactions with Transition Metal Catalysts

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Abstract—The effect of a cocatalyst in alkene homo- and copolymerizations with transition metal catalysts of different types was studied. The results of studies of polymerizations of ethylene, propylene, and higher linear 1-alkenes and copolymerizations of ethylene with linear 1-alkenes using catalysts of different types in combination with a binary cocatalyst $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ at $[Al] : [Mg] > 2.5$ were summarized. The traditional Ziegler–Natta catalysts ($TiCl_4$, $Ti(Oi\text{-}C_3H_7)_4$, and $TiCl_3$) and titanium postmetallocene complexes with various organic ligands were studied. The binary cocatalyst significantly increased the activity of the traditional catalysts compared with that of $Al(C_2H_5)_2Cl$ and the activity of postmetallocene complexes compared with that of polymethylaluminoxane (MAO). The active centers of these catalytic systems differ in their kinetic parameters, stereospecificity, and copolymerization ability. The efficiency of the $Al(C_3H_5)_2Cl/Mg(C_4H_9)_2$ cocatalyst can be explained by the in situ formation of finely dispersed $MgCl_2$ and immobilization of the cationic active centers on its surface.

INTRODUCTION

The combinations of AlR_2Cl and MgR_2' at a molar ratio of $[Al] : [Mg] > 2.5$ are effective cocatalysts for all types of metal complex catalysts in alkene polymerizations [1]. The present paper summarizes the results of recent studies of polymerizations of ethylene, propylene, and higher linear 1-alkenes and copolymerizations of ethylene with linear 1-alkenes in the presence of various metal complex catalysts in combination with the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ binary cocatalyst. The traditional $TiCl_4$, $Ti(Oi\text{-}C_3H_7)_4$, and $TiCl_3$ catalysts and titanium postmetallocene (PMC) complexes with various organic ligands were studied. For comparison, we used the conventional activators of metal complex catalysts $Al(C_2H_5)_2Cl$ and polymethylaluminoxane (MAO).

EXPERIMENTAL

Materials

Ethylene and propylene of polymerization degree of purity (99.9 vol %, Moscow oil refinery) were used without further purification. $TiCl_4$, $Ti(Oi\text{-}C_3H_7)_4$, and $Al(C_2H_5)_2Cl$ (0.8 M heptane solution) and $Mg(C_4H_9)_2$ (0.5 M heptane solution, Acros) were also used without further purification. Toluene (analytical grade), 1-hexene, and 1-octene were boiled over Na and distilled in an argon flow. 1-Decene was kept over molecular sieves and blown with argon.

Table 1 shows the PMC complexes used in this work. The syntheses of the ligands and complexes were described in [2–4]. Complexes II, III, and V were introduced in the reaction medium in pure form; complexes I and IV were added in the form of suspensions in toluene without isolating the $MgCl_2$ by-product.

Polymerzations

All polymerizations were performed in a 200 mL steel reactor with a stirrer. Before the experiments, the reactor was evacuated for 1 h at the temperature of experiment. Propylene was polymerized in the mode of the reactor completely filled with the liquid monomer using the procedure described in [5]. In the case of polymerization of ethylene and copolymerization of ethylene with 1-alkenes, the reactor was filled with toluene (or *n*-heptane) or a mixture of a solvent with 1-alkene; the volume of the liquid phase was 100 mL. Then, $Al(C_2H_5)_2Cl$ and $Mg(C_4H_9)_2$ were added in

Table 1. Titanium postmetallocene complexes

Complex	Formula
Dioxolane complex, **I**	[(4R,5R)-2,2-$(CH_3)_2$-α,α,α',α-tetra-(F_5-phenyl)-1,3-dioxolane-4,4-dimethanol]$TiCl_2$
Naphthalate complex, **II**	1,1'-di-2-naphthalate-bis(iso-propoxy)Ti
Phenoxyimine complex, **III**	bis-[N-(3,5-*t*-Bu_2-salicylidene)-2,3,5,6-F_4-aniline]$TiCl_2$
Saligenin complex, **IV**	{2-[α,α-$(CF_3)_2$-methanolato]-4,6-*t*-Bu_2-phenolato}$TiCl_2$
Quinoline complex, **V**	{2-[oxalate(diphenyl)methyl]-8-hydroxyquinolinate}$TiCl_2$···(HO*i*-C_3H_7)

sequence to the reaction medium. The resulting mixture was saturated with ethylene, and then an ampule with the catalyst was broken inside the reactor. The pressure in the reactor during the experiments was kept constant, compensating for ethylene consumption by feeding from a calibrated vessel. The resulting polymers and copolymers were treated with a mixture of ethanol with HCl (10% solution), then repeatedly washed with water and alcohol, and dried to constant weight.

The activity of the catalysts was evaluated from the polymer yield per mol of Ti (kg/mol Ti). The effective rate constant of polymerization was calculated as $k_{eff} = R_{pol}/(C_{mon}C_{Ti})$ (L/mol Ti min), where R_{pol} is the polymerization rate (M min), and C_{mon} and C_{Ti} are the concentrations of the monomer and Ti compound (M).

Analysis of Polymers

The molecular weight (MW) and MW distribution (MWD) of the polymers were measured by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 135°C on a Waters GPCV-2000 chromatograph with a PL-gel column. The MW was calculated from the universal calibration curve using polystyrene standards.

The procedure for separating the GPC curves into the curves of individual Flory components was described previously [6, 7]. The Flory component is a polymer product produced by one type of active site.

The ^{13}C NMR spectra of the 5% polymer solutions in *o*-dichlorobenzene at 99°C were recorded on a Bruker AVANCE III 400 instrument (frequency 100.613 MHz). The signals in the spectra of the copolymers of ethylene with 1-alkenes and polypropylene (PP) were attributed based on published data [8–12]. The contents of 1-alkene in the copolymers and of steric pentads and heptads in PP were determined from the ^{13}C NMR spectra of the samples.

The IR spectra of the polymers were recorded on a Perkin-Elmer Fourier spectrometer. The content of 1-alkenes in the copolymers C_M^{copol} (mol %) was determined from the ratio of the absorbance of the 1380, 1368, and 722 cm^{-1} bands (D_{1380}/D_{1368} and D_{1380}/D_{722}) using the calibration curves [13]. The absorbance ratios of the 998, 841, and 973 cm^{-1} bands (D_{998}/D_{973} and D_{841}/D_{973}), which characterize the presence of isotactic sequences of propylene units longer than 11−13, 13−15, and 3−5 monomer units in the polymer chain, respectively, were used as the stereoregularity parameters of PP [14, 15].

The polymer melting curves were recorded on a Netzsch DSC-209 F1 DSC analyzer (3−5 mg samples) at a heating rate of 10°C/min. For detailed analysis of the composition and structural inhomogeneities of the polymers, we used the data obtained during the second melting of the samples (heating rate 2°C/min) after slow crystallization. The crystallinity χ of polyethylene (PE), PP, and ethylene copolymers was calculated from the heat of fusion ΔH_f as $(\Delta H_m/\Delta H_f^\circ) \times 100\%$, where ΔH_m° for PE and PP is 293 and 167 J/g, respectively.

The XRD patterns of the polymers were recorded on a DRON-2 diffractometer (Cu(K_α) radiation, Ni filter, scan rate 1°(2θ)/min). The crystallinity of the samples was found from the ratio of the integrated intensity of the crystalline component and the total intensity.

RESULTS AND DISCUSSION

Catalytic Systems Based on TiCl₄, Ti(Oi-C₃H₇)₄, and TiCl₃

Homopolymerization of ethylene and copolymerization of ethylene with 1-hexene. Table 2 presents the main results of the polymerization of ethylene and copolymerization of ethylene with 1-hexene (E/H). $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ were used as cocatalysts. The use of $Al(C_2H_5)_2Cl$ in combination with $Mg(C_4H_9)_2$ led to an abrupt activation of these catalysts in all instances. When the Ziegler catalyst $TiCl_4–Al(C_2H_5)_2Cl$ (without $Mg(C_4H_9)_2$) was used, the yield of PE was 223 kg/mol Ti; in the case of $Ti(Oi-C_3H_7)_4$, only traces of the polymer were obtained under these conditions. However, the addition of $Mg(C_4H_9)_2$ at a molar ratio of [Al] : [Mg] ~ 3 led to a sharp increase in the yield of PE to ~1.4−1.5 t/mol Ti.

The kinetics of ethylene polymerization is markedly non-steady-state in both cases: at 50°C, the polymer product mostly forms already within the first 10 min of the reaction. Figure 1 shows the kinetic

Table 2. Copolymerization of ethylene with 1-hexene[a]

System	C_M^{mon}, M	$[Ti] \times 10^5$, mol	[Al] : [Ti], mol/mol	[Al] : [Mg], mol/mol	Yield, kg/mol Ti	C_H^{copol}, mol %[b]
TiCl$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$	0	3.20	400	–	223	0
	0	0.90	330	3.0	1380	0
	0.15	0.95	330	3.2	2280	2.1
	0.36	0.84	380	3.2	2130	6.0
	1.52	0.85	350	3.0	2310	21
Ti(Oi-C$_3$H$_7$)$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$	0	2.36	335	–	–	0
	0	0.62	370	3.0	1480	0
	0.60	0.84	320	3.2	840	1.3
	0.90	0.84	320	3.2	2430	8.4
	1.5	0.79	290	3.0	3010	15.8

[a] 50°C, toluene, reaction time 60 min; P_E and C_E are 4.1 atm and 0.41 M, respectively, for Ti(Oi-C$_3$H$_7$)$_4$ and 3.6 atm and 0.35 M for TiCl$_4$.
[b] ^{13}C NMR data.

curves of ethylene polymerization in the presence of Ti(Oi-C$_3$H$_7$)$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ and TiCl$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$.

The yield of copolymers was ~2 t/mol Ti h when the TiCl$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ system was used at 50°C and from 0.8 to ~3 t/mol Ti h in the case of the Ti(Oiso-C$_3$H$_7$)$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$) system depending on the composition of the monomer mixture. The content of 1-hexene in the copolymers varied from ~1 to ~15−20 mol %. At high 1-hexene concentrations in the presence of these systems, a comonomer effect was observed, namely, an increase in catalyst activity in ethylene polymerizations with 1-alkene additions. This effect is well known for both heterogeneous Ziegler−Natta catalysts and metallocene and PMC catalysts [16−18].

The ability to efficiently copolymerize 1-alkenes with ethylene is an important characteristic of any Ti-based catalyst used for the synthesis of medium- and low-density PE. A comparison of the compositions of the monomer mixture and copolymer made it possible to approximately evaluate the copolymerization constants r_1 in the case of reactions with low 1-hexene contents:

$$r_1 = k_{E\text{-}E}/k_{E\text{-}H} \cong \left(C_E/C_H\right)^{copol}/\left(C_E/C_H\right)^{mon}, \quad (1)$$

where $k_{E\text{-}E}$ and $k_{E\text{-}H}$ are the rate constants of ethylnene and 1-hexene addition to the growing polymer chain with a terminal ethylene unit >Ti−CH$_2$−CH$_2$−polymer.

Ethylene has the highest reactivity in chain propagation reactions compared to all 1-alkenes, and r_1 is always higher than 1. For the reactions catalyzed by TiCl$_4$ and Ti(Oi-C$_3$H$_7$)$_4$, r_1 is 16−20 and ~60, respectively.

The ^{13}C NMR spectra of PE and E/H copolymers were analyzed; the signals were attributed according to the data of [9]. It follows from the analysis of the ^{13}C NMR spectrum of PE that this is a linear polymer: its spectrum contains an intense signal of the −CH$_2$−groups at 29.8 ppm and weak signals of the saturated linear terminal groups. The E/H copolymers with C_H^{copol} = 1.3, 2.1, and 6.0 mol % mainly consist of long sequences of ethylene monomer units ~EEEEEEE~ (the signal of δ,δ-CH$_2$ at 29.8 ppm) and isolated 1-hexene units ~EEEHEEE~ (the signals of CH(EHE) at 38.1 mppm and 3B$_4$ of CH$_2$(EHE) at 29.5 ppm).
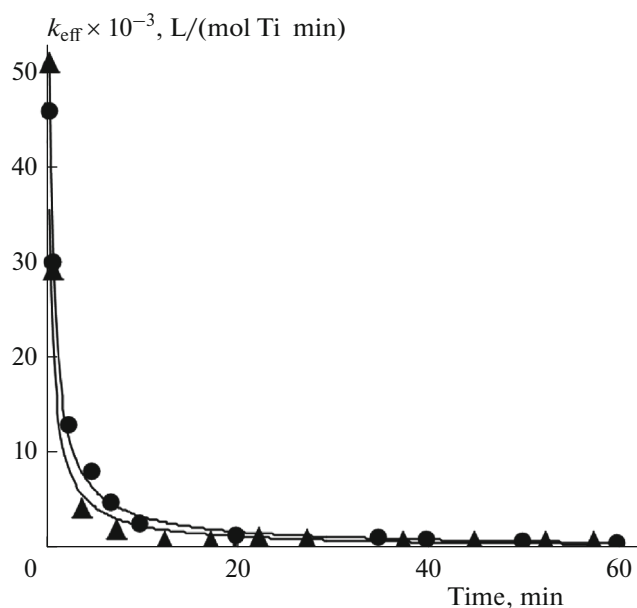
Fig. 1. Kinetic curves of ethylene polymerization for the (▲) Ti(Oi-C$_3$H$_7$)$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ and (●) TiCl$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ systems.
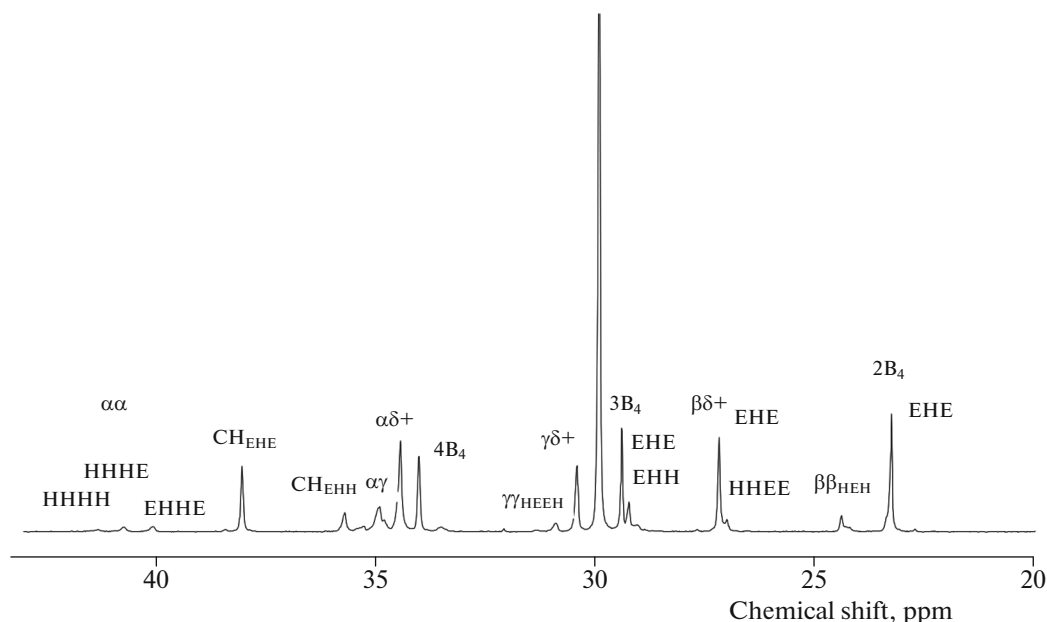
Fig. 2. ^{13}C NMR spectrum of the E/H copolymer with $C_H^{copol} \sim 21$ mol %. The TiCl$_4$−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ system. The position of the CH$_2$ groups relative to CH is indicated by Greek letters; the position of the CH$_2$ groups in butyl (B) side groups relative to CH$_3$ is indicated by numbers.

Only the spectrum of the copolymer with $C_H^{copol} \sim 21$ mol % (Fig. 2) contains weak signals of the ~EEHHE~ sequences (the signal of (CH(EHH) at 35.8 ppm, 3B$_4$ of CH$_2$(EHH) at 29.1 ppm, and of α,α-CH$_2$(EHHE) at 40.2 ppm). The intensity ratio of these signals allows us to roughly determine the product of the copolymerization constants $r_1 r_2$ [19]. For example, the [HHE] : [EHE] and [EHHE] : [EHE] signal ratios for the copolymer with $C_H^{copol} \sim 21$ mol %, obtained in the presence of the TiCl$_4$−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ system in n-heptane, are 0.52 and 0.14, respectively; for the copolymer of the same composition obtained in toluene, these ratios are 0.45 and 0.15. Using the statistical equations for the contents of various triads and tetrads in the copolymers of ethylene with 1-alkenes as functions of C_M^{copol} and $r_1 r_2$ [19], it was determined that $r_1 r_2$ is in the range 0.8−1.0. This means that the distribution of monomer units in the chains of the E/H copolymers is mainly statistical.

An increase in the 1-hexene content in the E/P copolymers leads to a decrease in their molecular mass and effective melting temperature T_m and also to an abrupt decrease in the heat of melting ΔH_m and crystallinity χ, as typically occurs for copolymerization of ethylene and 1-alkenes in general (Table 3) [18, 19]. According to the GPC data, both PE and E/H copolymers have a wide MWD, which reflects the presence of different types of active centers in the catalysts, which differ in kinetic parameters (Fig. 3a). All these

polymer products are mixtures of components with different MWs. The decomposition of the GPC curves into the Flory components allows us to evaluate the number of types of active centers and the relative amount of the polymer produced by each type of centers. Figure 3b and Table 4 give the examples of separation of the GPC curves of the PE and E/H copolymers into the Flory components obtained in the presence of the Ti(Oi-C$_3$H$_7$)$_4$−Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ system. According to these data, the introduction of 1-hexene into the polymerization medium leads to two effects: a certain decrease in the M_w value of each Flory component and a relative increase in the fraction of active centers producing macromolecules with low MWs (components III and IV).

The presence of various types of active centers suggests that macromolecules can differ not only in the MW characteristics, but also in composition [19]. To verify this assumption, the DSC method was used. It was shown [20] that the position of the maximum on the DSC melting curve and the shape of the melting curve of ethylene−1-alkene copolymers depend on the composition of the copolymers and the degree of their compositional inhomogeneity. The compositionally homogeneous copolymers obtained on single-site metallocene catalysts have relatively narrow melting curves, and their T_m values decrease rapidly with the increasing 1-alkene content in the copolymer. In contrast, the inhomogeneous copolymers synthesized in the presence of multicenter heterogeneous catalysts have wide melting curves (sometimes they consist of

Table 3. Molecular weight and structural characteristics of PE and E/H copolymers

| C_H^{copol}, mol %	$M_w \times 10^{-3}$	M_w/M_n	T_m, °C[a]	ΔH_f, J/g[a]	χ, %[b]
TiCl₄–Al(C₂H₅)₂Cl/Mg(C₄H₉)₂					
0			134	142.6	60
2.1	222.5	8.1	124	99.5	42
6.0	161.2	7.6	124	57.7	24
21	154.6	7.5	123	19.0	~8
Ti(Oi-C₃H₇)₄–Al(C₂H₅)₂Cl/Mg(C₄H₉)₂					
0	446	24	133	190	65
1.3	400	19	127	125	43
8.4	354	11	123	44	15
15.8	142	20	–	16	~6

[a] The heating rate was 2°C/min, the second melting.
[b] DSC data.

Table 4. Separation of the GPC curves of PE and E/H copolymers[a]

Flory component	$M_w \times 10^{-3}$	Content, %	$M_w \times 10^{-3}$	Content, %	$M_w \times 10^{-3}$	Content, %
	$C_H^{copol} = 0$		$C_H^{copol} = 1.3$ mol %		$C_H^{copol} = 8.4$ mol %	
I	1.8	2.1	1.8	2.0	1.6	0.4
II	7.6	4.3	7.2	5.6	6.7	4.3
III	28	10.8	27	10.4	26	15.6
IV	86	19.1	81	19.1	77	25.0
V	254	29.0	225	29.9	222	25.3
VI	660	20.4	600	20.0	550	16.4
VII	1700	14.3	1600	13.0	1600	13.0
Average values[b]	$M_w^{av} = 470\,000$ $M_w/M_n = 24$		$M_w^{av} = 418\,000$ $M_w/M_n = 22$		$M_w^{av} = 363\,000$ $M_w/M_n = 14.5$	

[a] Conditions of polymerization are given in Table 2.
[b] Calculated from M_w of the Flory components and their contents.

several components), and their T_m are relatively weakly dependent on the copolymer composition. This approach allows us to separate any copolymer synthesized in the presence of a multicenter catalyst into two main components: the partially crystalline component with a low 1-alkene content (it can be obtained on one or several types of active centers) and the amorphous component. Figure 4 shows the melting curve of the E/H copolymer with $C_H^{copol} = 6.0$ mol %, obtained in the presence of the TiCl₄–Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ system, and this curve separated into five components. The parameters of these components are given in Table 5. The crystalline part of this copolymer ($C_H^{copol} \sim 3.1$ mol %) is ~50% of the total polymer product, the rest being a completely amorphous copolymer not detectable by DSC.

Polymerizations of propylene. Table 6 gives the main results of propylene polymerization in the presence of TiCl₄, Ti(Oi-C₃H₇)₄, and δ-TiCl₃ catalysts using Al(C₂H₅)₂Cl and the Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ combination as cocatalysts. As in the cases of ethylene homo- and copolymerization, the use of a binary cocatalyst leads to abrupt activation of these catalysts. The Ti(Oi-C₃H₇)₄–Al(C₂H₅)₂Cl system did not show any activity at all. When the classical Ziegler catalyst TiCl₄–Al(C₂H₅)₂Cl was used, the yield of PP was only ~8 kg/mol Ti. When the Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ combination was used, it increased to ~10 t/mol Ti in both cases. When the binary cocatalyst was used, the yield of PP in the presence of δ-TiCl₃ also increased ~25 times.

(a)

(b)
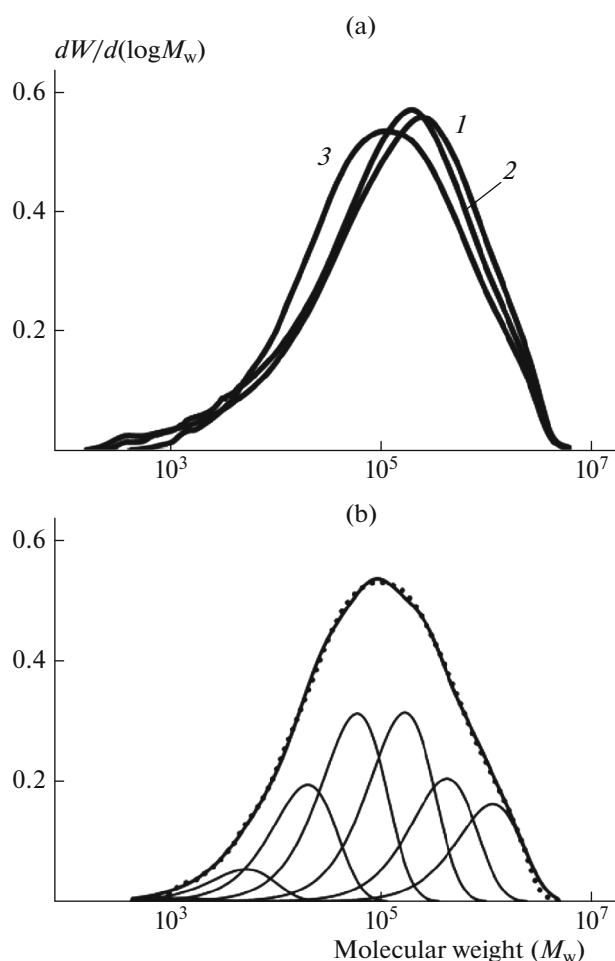
Fig. 3. (a) GPC curves of (*1*) PE and E/H copolymers with C_H^{copol} = (*2*) 1.3 and (*3*) 8.4 mol %; (b) separation of the GPC curve of the copolymer with C_H^{copol} = 8.4 mol % into the Flory components; dots: experimental data, lines: calculated data.

All the products are highly molecular, partially crystalline polymers with T_m = 151−153°C (Table 7). Fractionation in boiling heptane makes it possible to separate PP into two fractions: a soluble fraction (amorphous polymer) and insoluble fraction partially

Table 5. Parameters of the crystalline components in the E/H copolymer with C_H^{copol} = 6 mol %

Component	T_m, °C	Content, %	χ, %
DSC-I	123.1	19	50
DSC-II	108.7	32	38
DSC-III	98.2	15	30
DSC-IV	86.3	19	22
DSC-V	75.5	15	16
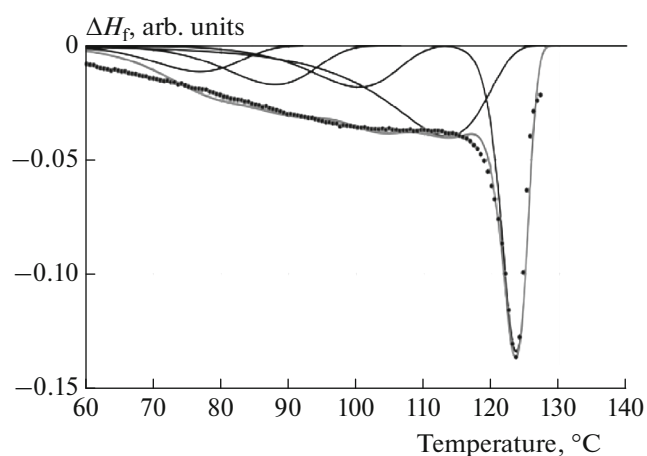
Fig. 4. Melting curve of the E/H copolymer with C_H^{copol} = 6 mol % obtained for the TiCl$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ system (dots) and its separation into components.

consisting of a crystalline isotactic polymer. The presence of two fractions suggests that the active centers of the catalysts differ in stereospecificity.

The wide MMD of propylene polymers and their fractions reflects the inhomogeneity of the active centers in the kinetic parameters. Figure 5 shows an example of the GPC curve of the polymer synthesized in the presence of the Ti(Oi-C$_3$H$_7$)$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ system at 50°C and the curves of its soluble and insoluble fractions. The separation of the GPC curves of the PP fractions into the Flory components showed that each fraction is a mixture of six components with different MMs that correspond to active centers of six types. The average MMs of insoluble fractions are always higher than the MMs of soluble fractions.

Propylene polymers obtained in the presence of TiCl$_4$ and Ti(Oi-C$_3$H$_7$)$_4$ with Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ as a cocatalyst are almost completely amorphous and atactic materials; their fractions insoluble in heptane account for only 10−15%.

Figure 6 shows the ^{13}C NMR spectra of the fractions of PP synthesized in the presence of the TiCl$_4$–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$ system at 50°C. The spectrum of the soluble fraction is typical for the spectra of atactic PP [8−10]. A comparison of the spectra of the two fractions in Figs. 6a and 6b shows that the insoluble fraction contains the same signals of stereoirregular sequences in the range 22.1−19.2 ppm and in the same proportions as the soluble fraction. This suggests that the insoluble fraction is a mixture of two sterically different polymers: amorphous atactic and crystalline isotactic polymers. This atactic component has the same structure as the soluble fraction, but higher MM, which explains its low solubility. The spectrum of the crystalline component was isolated by subtracting the spectrum of the soluble fraction from the spectrum of the insoluble one. After this procedure (Fig. 6c), only

Table 6. Propylene polymerization[a]

Catalyst	Cocatalyst	[Ti] × 10^5, mol	[Al] : [Ti], mol/mol	[Al] : [Mg], mol/mol	Yield, kg/mol Ti
$TiCl_4$ [b]	$Al(C_2H_5)_2Cl$	1.20	340	–	~8
$TiCl_4$	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	0.54	440	2.5	10740
$Ti(Oi\text{-}C_3H_7)_4$	$Al(C_2H_5)_2Cl$	1.25	326	–	–
$Ti(Oi\text{-}C_3H_7)_4$	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	0.62	353	3.48	9680
$\delta\text{-}TiCl_3$	$Al(C_2H_5)_2Cl$	5.11	49	–	49
$\delta\text{-}TiCl_3$	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	4.72	60	2.96	1207

[a] 50°C, liquid monomer, reaction time 60 min.
[b] 40°C.

Table 7. Properties of PP and its fractions

Sample	Content, %	M_w	M_w/M_n	[*mmmm*], %[a]	A_{998}/A_{973}[b]	A_{841}/A_{973}[b]	T_m, °C	ΔH_f, J/g	χ, %[c]
$TiCl_4–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$									
Total polymer		54700	4.8		0.40	0.33	154	12	6
Insoluble fraction	11	93400	3.6	66	0.80	0.609	153	53.5	32
$Ti(Oi\text{-}C_3H_7)_4–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$									
Total polymer		98400	8.1	34	0.37	0.20			
Insoluble fraction	14	217400	7.5	41	0.80	0.59	158	81.5	49
Soluble fraction	86	80400	7.8	21	0.30	0.14			

[a] ^{13}C NMR;
[b] IR;
[c] DSC data.

three signals of stereoirregular sequences remained in the spectrum: *mmmr*, *mmrr*, and *mrrm* in a ratio of ~2 : 2 : 1 at 21.03, 20.52, and 19.28 ppm. Pentads of this type and in this ratio are characteristic of the chains of predominantly isotactic PP with isolated stereoerrors, i.e., for sequences of the ···*mmmmrrmmm*··· type. These stereoerrors are typical for PP obtained on heterogeneous Ziegler–Natta catalysts and on *rac*-bis(indenyl)zirconium bridged complexes. We can conclude from these data that the mechanism of stereocontrol of chain growth on the given catalytic systems is enantiomorphic, when each random steric error is corrected in the next act of polymer chain propagation, for example, ···DDDDLDDDD···.

The content of the crystalline component created by the isospecific sites does not exceed 5–7%. The bulk of the polymer product is atactic PP (over 85% in the soluble fraction and ~50% in the insoluble fraction).

Atactic PP is an important commercial product used for the production of construction adhesives, sealing and caulking compounds, road coatings, and adhesive films. The possibility of selective synthesis of atactic PP using systems based on commonly available

titanium compounds ($TiCl_4$ or $Ti(Oi\text{-}C_3H_7)_4$) and $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ binary cocatalyst is of interest from practical viewpoint. The advantages of this system are high activity, low cost, and ease of synthesis. All the components of this system are cheap commercial products soluble in aromatic and aliphatic hydrocarbons.
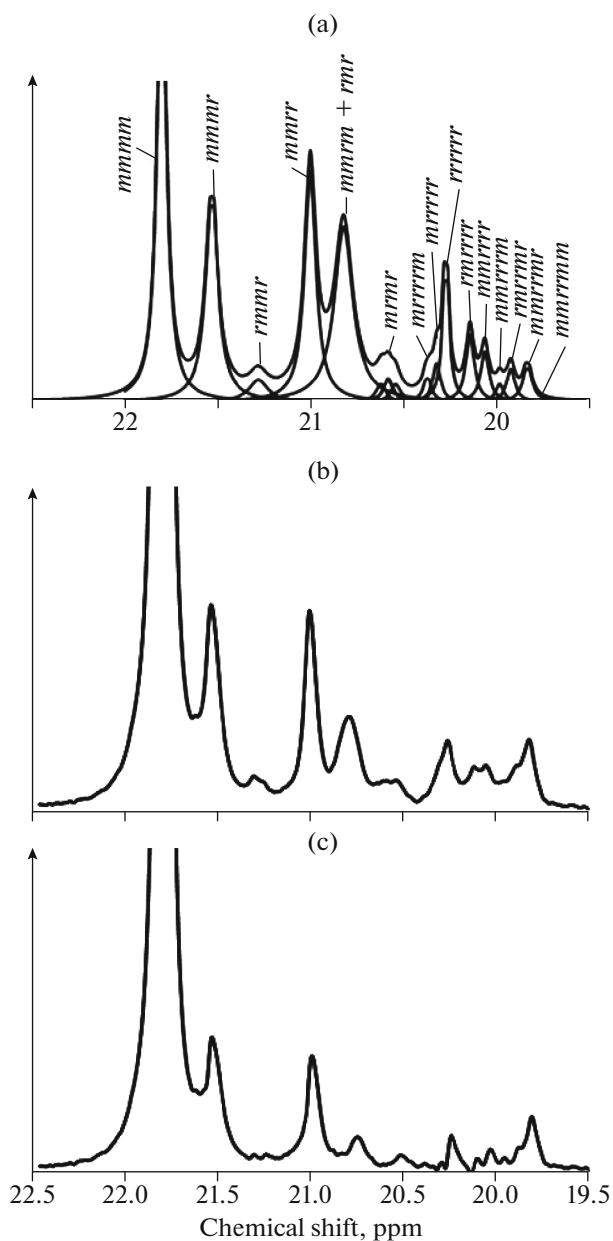
Catalytic Systems Based on Ti Postmetallocene Complexes

Homo- and copolymerizations of ethylene with 1-alkenes. Table 8 shows the main results of copolymerization of ethylene with 1-alkenes on Ti PMC complexes using the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ and MAO cocatalysts. The systems with the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ binary cocatalyst were more active and had higher copolymerization ability than the systems with MAO. Thus, the yield of E/H copolymers was 1.7–4.3 t/mol of Ti for the system IV–$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ containing from 3.5 to ~22 mol % 1-hexene; while the use of MAO in the presence of complex IV gave copolymers with $C_H^{copol} = 0.3$ and ~8–9 mol % in yields of 670–850 kg/mol of Ti.
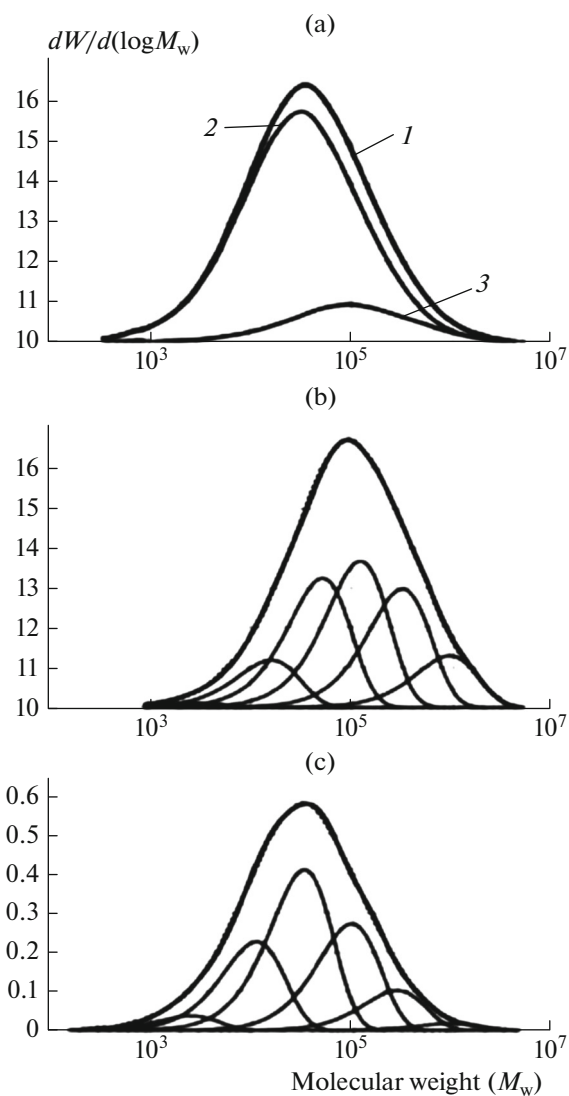
Fig. 5. GPC curves of PP: (a) (*1*) total polymer, (*2*) soluble fraction, and (*3*) insoluble fraction; (b) and (c) separation of the GPC curves of the insoluble and soluble fractions into the Flory components.

Fig. 6. ^{13}C NMR spectra (region of the signals of the CH_3 group) of the fractions of PP obtained in the presence of the $TiCl_4–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ system at 40°C: (a) the fraction soluble in boiling heptane; (b) insoluble fraction; and (c) isotactic component.

The catalytic systems based on the PMC complexes of Ti are kinetically unstable. Their instability is especially pronounced when the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ binary cocatalyst is used. The effective flow rate constant of ethylene k_{eff} in the presence of system IV–$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ decreased approximately tenfold, from ~38000 to ~3900 L/(mol Ti min) within the first 10 min of the reaction (Fig. 7).

For copolymers of ethylene and 1-alkenes synthesized in the presence of complexes IV with the binary cocatalyst, the copolymerization constants r_1 were evaluated by Eq. (1):

Monomer pair	ethylene/1-hexene	ethylene/1-octene	ethylene/1-decene
r_1	16–32	41–46	46–53

Table 8. Copolymerization of ethylene with 1-alkenes on the PMC complexes of Ti with MAO and $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ cocatalysts [a]

System	C_M^{mon}, M	C^{mon}, mol %	$[Ti] \times 10^5$, mol	[Al] : [Ti], mol/mol	[Al] : [Mg], mol/mol	Yield, kg/mol Ti	C_M^{copol}, mol %[b]
1-Hexene							
$IV–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	–	–	0.66	340	3.0	1720	0
	0.24	39	0.66	340	3.0	1666	4.0
	1.6	81	1.02	320	3.4	2843	12.0
	4.4	92	0.75	360	3.2	4266	21.0
$IV–MAO$	–	–	1.79	410	–	735	0
	0.24	39	2.02	440	–	850	0.3
	1.6	81	2.27	460	–	696	9.0
1-Octene							
$IV– Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	0.26	41	0.62	360	3.2	1774	1.7
	1.7	82	0.77	350	3.2	3545	10.0
$V–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	–	–	1.17	390	3.0	1090	0
	0.32	44.5	1.55	360	3.2	1875	2.6
	0.64	61.5	1.49	380	3.2	1865	5.1
	1.28	76.1	1.47	380	3.2	2040	10.4
1-Decene							
$IV–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	0.26	41	0.75	360	3.2	1400	1.3
	1.7	82	0.77	350	3.2	3992	9.0
$IV–MAO$	0.26	41	0.75	360	–	902	0.4
	1.7	82	0.82	330	–	1223	0.7

[a] 50°C, toluene, 60 min; P_E and C_E are 3.8 atm and 0.37 M, respectively, for the system $IV–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ and 4 atm and 0.44 M for the system $V–Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$;
[b] ^{13}C NMR data.

The r_1 value gradually increases with the length of the linear alkyl group in 1-alkene; i.e., the reactivity of 1-alkenes decreases in the series 1-hexene > 1-octene > 1-decene. A similar effect is also known for copolymerization of ethylene with 1-alkenes in the presence of heterogeneous Ziegler–Natta catalysts [21].

All the polymers obtained with PMC complexes of Ti have a wide MMD: the PE and copolymer samples consist of five or six Flory components with different MMs [22]. The content of the most high-molecular components ($M_w \sim (2.0–2.2) \times 10^6$) in PE obtained using MAO is significantly higher (~22%) than in the sample synthesized with $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ (~9%). As a result, for the first polymer (~950000), M_w is significantly higher than for the second (~530000). The introduction of 1-alkenes in the PE chain always leads to a decrease in its molecular weight (Table 9). The content of various Flory components in copolymers of similar compositions is independent of the type of 1-alkene.

An analysis of the ^{13}C NMR spectra shows that the active centers of the catalytic systems based on the PMC complexes of Ti and binary cocatalyst have a pronounced tendency toward the creation of alternative copolymers: $r_1r_2 < 1$. The 1-alkene molecules in the copolymers are mainly represented by isolated units in the ~EEEMEEE~ sequences. Unlike the statistical copolymers of the same composition, the copolymers have no MMM triads, and the number of MM diads in them is very small.

Propylene polymerizations. According to Table 10, the replacement of MAO (the standard activator for PMC complexes) by the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ binary cocatalyst led to a significant increase in the activity of these catalysts. In the case of complexes I and IV, the reactor was completely filled with the polymer already in ~10 min after the start of the reaction. The activity of complex III also increased approximately fourfold. Only traces of oligomers were obtained on complex II in the presence of MAO, while
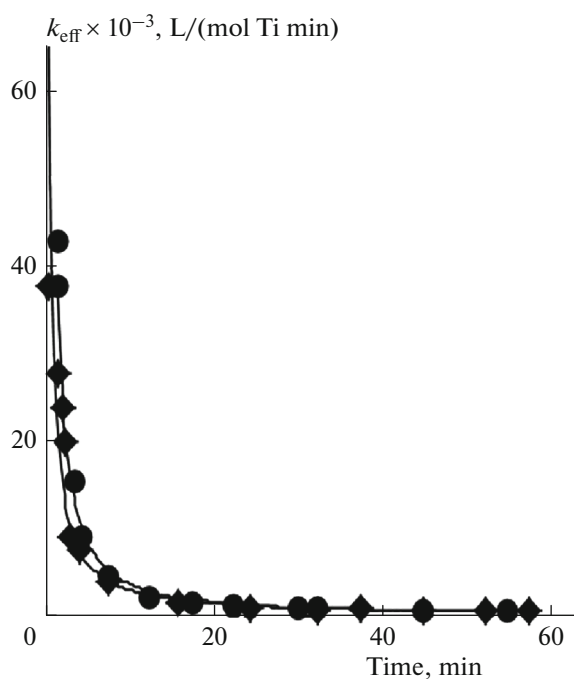
$k_{\text{eff}} \times 10^{-3}$, L/(mol Ti min)

Fig. 7. Kinetic curves of ethylene flow rate for the IV–Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ system in (◆) homopolymerization and (●) copolymerization with 1-decene ($C_D^{\text{mon}} \sim 1.7$ M).

the use of the Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ combination led to the formation of a solid high-molecular product.

As in the case of simple titanium catalysts (TiCl₄ and Ti(O*i*-C₃H₇)₄), PP synthesized in the presence of PMC complexes of Ti was a complex mixture of a completely amorphous atactic polymer and a partially crystalline isotactic polymer. However, the content of the fraction insoluble in boiling heptane and the crys-

tallinity in the samples obtained in the presence of PMC complexes were much higher.

According to the data of Table 11, the MW of PP synthesized using the MAO cocatalyst is significantly higher than in the case of the Al(C₂H₅)₂Cl/MgBu₂ combination. Thus, M_w of the polymers obtained for the I–MAO and I–Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ systems are 319 000 and 150 000, respectively.

The results of the separation of the GPC curves of the soluble and insoluble PP fractions show that the MWs of the Flory components of each fraction synthesized in the presence of MAO are higher than the MWs of the components of the Flory fractions obtained using the Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ combination (Table 12). The content of high molecular components in each fraction is also higher in the case of the use of MAO. As a result, the average MWs of each fraction and the MW of the total polymer are significantly different:

I–MAO: M_w (insol.) = 676 500, M_w (sol.) = 298 200, M_w^{av} = 319 000;

I–Al(C₂H₅)₂Cl/Mg(C₄H₉)₂: M_w (insol.) = 272 100, M_w (sol.) = 92 500, M_w^{av} = 150 000.

This tendency is characteristic of propylene polymers obtained for all PMC complexes of Ti. In the presence of the Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ combination, the stereoregularity of the polymers also changes significantly. Thus, when complex I is used, both the IR parameters of PP stereoregularity and the content of the heptane-insoluble fraction in it increase. The stereoregulating effect of Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ is especially significant when complex III is used. In combination with MAO, an amorphous polymer completely soluble in boiling heptane is obtained on this catalyst. When the Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ com-

Table 9. Molecular weight and structural characteristics of copolymers of ethylene and 1-alkenes obtained for complex IV with MAO and Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ cocatalysts

1-Alkene	C_M^{copol}, mol %	$M_w \times 10^{-3}$	M_w/M_n	T_m, °C	ΔH_f, J/g	χ, % (XRD/DSC)
MAO cocatalyst						
–	0	951	6.2	136.0	172.7	56/59
1-Hexene	9.0	311	8.5	118.6	53.45	21/18
1-Octene	0.2	670	9.2	130.1	142.8	51/49
1-Decene	0.7	660	6.2	128.3	135.2	45/46
Al(C₂H₅)₂Cl/Mg(C₄H₉)₂ cocatalyst						
–	0	531	7.6	131.7	197.0	61/67
1-Hexene	13.0	64	8.4	118.0	36.9	21/13
1-Hexene	~21	74	9.6	118.5	7.4	Amorphous
1-Octene	10.0	70	9.7	118.8	30.1	10/10
1-Decene	8.0	85	10.4	118.6	39.9	25/14

Table 10. Polymerization of propylene on the PMC complexes of Ti with MAO and $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ cocatalysts

Complex	Cocatalyst	Ti × 10⁵, mol	[Al] : [Ti], mol/mol	[Al] : [Mg], mol/mol	Yield, kg/mol Ti
I	MAO	3.5	130	–	1160
I	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	4.3	56	2.5	2000[a]
II	MAO	22.9	59	–	–
II	$Al(C_2H_5)_2Cl$	22.9	42	–	–
II	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	13.0	26	2.8	254
III	MAO	1.3	1170	–	620
III	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	0.8	880	3.2	2370
IV	MAO	1.84	219	–	309
IV	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	2.07	154	3.7	3500[a]
V	$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$	1.49	185	3.6	2285

[a] Reaction time 10 min.

bination is used, the partially crystalline isotactic PP with $T_m = 151°C$ containing 34% insoluble fraction is obtained. Thus, the properties of the polymer can be substantially varied by using the cocatalyst.

Polymerizations of higher linear 1-alkenes. Table 13 lists the main results of polymerization of three linear 1-alkenes. The experiments were performed in the monomer medium at 2°C. Under these conditions, complex IV was activated not only by $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ and MAO, but also by $Al(C_2H_5)_2Cl$ alone. However, the IV–$Al(C_2H_5)_2Cl$ system had the lowest activity in all instances. The binary cocatalyst was most effective in the polymerization of 1-decene; in the polymerizations of 1-octene and 1-hexene, the efficiency of the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ combination and MAO was approximately the same. Like PP obtained on the PMC complexes of Ti, all the polymers of higher 1-alkenes have a medium level of isotacticity and a wide MWD.

Discussion. Chemical Aspects of Alkene Polymerization

Any titanium compound of the TiX_4 type actively reacts with organoaluminum compounds AlR_3 and AlR_2Cl, forming many products that are soluble solid materials [23]. An analysis of the reaction products of $TiCl_4$ and $Al(C_2H_5)_2Cl$ showed that the chemical composition of the precipitate gradually changes from the initial $[TiCl_3C_2H_5]$ to $[TiAl_2Cl_5]$ [24–30]. The valence state of Ti (a mixture of Ti^{IV}, Ti^{III}, and Ti^{II}) and the efficiency of the $TiCl_4$–$Al(C_2H_5)_2Cl$ catalyst also change depending on the duration of the contact. The reactions between $Ti(OR)_4$ and organoaluminum compounds also give many various products with a very complex chemical composition [31–33].

The interaction in the TiX_4–AlR_3 and TiX_4–AlR_2Cl systems can generally be described by the following reactions:

1. Alkylation of TiX_4:

$$TiX_4 + AlR_3 \ (or \ AlR_2Cl)$$
$$\rightarrow X_3Ti–\mathbf{R} + AlR_2X \ (or \ AlRXCl). \qquad (2)$$
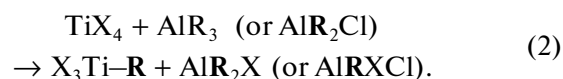
Reactions (2) are very fast and irreversible [31–34]. At high [Al] : [Ti] ratios, the alkylations of titanium compounds generally continue:

$$X_3Ti–\mathbf{R} + AlR_3 \ (or \ AlR_2Cl)$$
$$\rightarrow X_2TiR_2 + AlR_2X \ (or \ AlRXCl). \qquad (3)$$
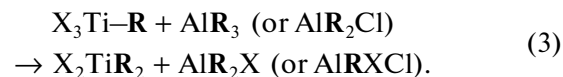
2. In some cases, $X_3Ti–R$ are involved in condensations. If $R = C_2H_5$, the condensation leads to the formation of binuclear Ti complexes:

$$2X_3Ti–C_2H_5 \rightarrow X_3Ti–CH_2–CH_2–TiX_3 + C_2H_6. \quad (4)$$
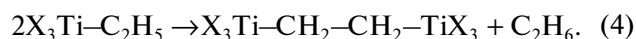
3. Reduction of organotitanium compounds $X_3Ti^{IV}–R$ and $X_2Ti^{IV}R_2$ with aluminoorganic compounds to $Ti^{III}X_3$ and $X_2Ti^{III}–R$. All the Ti complexes formed in reactions (2)–(4) and reductions generate numerous complexes with one or two AlR_2X or $AlRXCl$ molecules. Some of the soluble binuclear and trinuclear Ti^{III} complexes such as $[TiX_3] \cdot 2AlR_2X$, $[TiX_3]AlR_2X$, and $[X_2Ti–R]AlRXCl$ were characterized in detail [30–33].

The Ti complexes with bidentate and multidentate ligands can be represented by the general formula $LTiCl_2$ or L_2Ti. When these complexes are mixed with the AlR_2Cl/MgR_2' combinations at a ratio of [Al] : [Mg] > 2.5, they are quickly alkylated to $LTi(Cl)–R$ or $LTiR_2$ by the reactions similar to (3).

The efficiency of the AlR_2Cl and MgR_2' combinations as cocatalysts can be explained by two factors. The first factor is that AlR_2Cl and MgR_2' quickly react, forming the finely dispersed $MgCl_2$, whose surface has Lewis acidity [1, 2]:
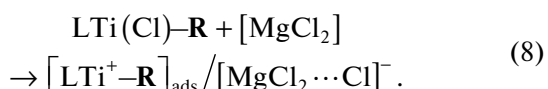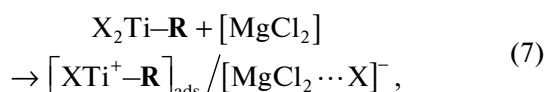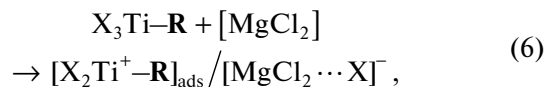
Table 11. Molecular weight and structural characteristics of PP obtained for PMC complexes of Ti and its fractions

Sample	Content, %	M_w	M_w/M_n	[mmmm], %[a]	A_{998}/A_{973}[b]	A_{841}/A_{973}[b]	T_m, °C[c]	ΔH_f, J/g[c]	χ, %[c,d]
I−MAO									
Total polymer		319000	19.8		0.44	0.32	152	23.9	14/11
Insoluble fraction	24	676000	5.4	58			154	58.2	35/26
Soluble fraction	76	298000	13						
I−Al(C2H5)2Cl/Mg(C4H9)2									
Total polymer		150000	110		0.48	0.43	152	36.2	21/13
Insoluble fraction	32	272000	104	586			156	66.5	40/33
Soluble fraction	68	92500	86						
II−Al(C2H5)2Cl/Mg(C4H9)2									
Total polymer		235000	11.0		0.51	0.42	151	32.1	20/15
Insoluble fraction	46	272000	10.4	52.5			153	54.5	32/25
Soluble fraction	54	108000	13.3						
III−MAO									
Total polymer		174800	3.2	~8	–	–	–	–	–
III−Al(C2H5)2Cl/Mg(C4H9)2									
Total polymer		83300	3.6	34.4	0.49	0.41	151	17.2	10
Insoluble fraction	34	120000	6.4	49.3			153	40.6	24/20
IV−MAO									
Insoluble fraction	25	407300	10.3	36.8	0.45	0.45			10
Soluble fraction	75	221300			0.14	0.17			~1
IV−Al(C2H5)2Cl/Mg(C4H9)2									
Insoluble fraction	19	356700	6.8	74.7	0.81	0.62			41/32
Soluble fraction	81				0.29	0.24			~4
V−Al(C2H5)2Cl/Mg(C4H9)2									
Total polymer		20400	2.7		0.46	0.37	153	18.8	11
Insoluble fraction	20	420000	7.5	74	0.89	0.63	159	89.7	53

[a] ^{13}C NMR;
[b] IR;
[c] DSC;
[d] XRD.

$$MgR'_2 + 2AlR_2Cl \rightarrow [MgCl_2] + 2AlR_2R'. \quad (5)$$

All the cocatalysts used were prepared at a ratio of [Al] : [Mg] > 2.5. Thus, the titanium compound TiX_4 or the complex $LTiX_2$, which were added to the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ mixture at the last stage of catalyst preparation, can react both with an excess of AlR_2Cl and with AlR_2R' formed in reaction (5). When the products $X_3Ti^{IV}-R$, $X_2Ti^{III}-R$, and $LTi(Cl)-R$ or their complexes with organoaluminum compounds are adsorbed on the acid surface of $MgCl_2$, they can be ionized, forming cation centers containing the Ti^+-C bond:

$$X_3Ti-R + [MgCl_2]$$
$$\rightarrow [X_2Ti^+-R]_{ads}/[MgCl_2\cdots X]^-, \quad (6)$$

$$X_2Ti-R + [MgCl_2]$$
$$\rightarrow [XTi^+-R]_{ads}/[MgCl_2\cdots X]^-, \quad (7)$$

$$LTi(Cl)-R + [MgCl_2]$$
$$\rightarrow [LTi^+-R]_{ads}/[MgCl_2\cdots Cl]^-. \quad (8)$$

Table 12. GPC analysis of the PP samples obtained for complex I

| System | | **I–MAO** | | **I–Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$** | |
| | | $M_w^{av} = 319\,000$; $M_w/M_n = 19.8$ | | $M_w^{av} = 150\,000$; $M_w/M_n = 11$ | |
sample	Flory component	M_w	content, %	M_w	content, %
Insoluble fraction	I			9300	4.1
	II	40800	5.9	32800	17.8
	III	106300	18.7	92400	30.8
	IV	347100	41.0	289600	30.8
	V	1208000	34.0	905000	16.5
Soluble fraction	I	2200	1.0	1800	2.4
	II	9100	5.4	7600	11.1
	III	30300	19.0	25500	32.0
	IV	85100	29.5	69400	34.0
	V	260900	28.0	208400	17.5
	VI	1135000	17.1	850600	2.8

Table 13. Polymerizations of higher linear 1-alkenes in the presence of complex IV with various cocatalysts

Cocatalyst	[1-alkene], mol	[Ti] × 10^3, mol	[Al] : [Ti], mol/mol	[Al] : [Mg], mol/mol	Conversion, %	[η], dL/g	$M_\eta × 10^{-3}$	[mmmm], ^{13}C NMR
				1-Decene				
MAO	0.210	0.022	76		20.4	1.63	690	0.53
Al(C$_2$H$_5$)$_2$Cl	0.213	0.022	106		6.9	2.95	1500	0.60
Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$	0.213	0.022	117	3.2	69.3	3.30	1730	
				1-Octene				
MAO	0.210	0.022	76		92.3	2.02	920	0.50
Al(C$_2$H$_5$)$_2$Cl	0.214	0.022	90		7.5	2.64	1300	0.52
Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$	0.210	0.022	106	2.4	70.6	1.50	620	
				1-Hexene				
MAO	0.219	0.022	70		84.6	3.10	1596	
Al(C$_2$H$_5$)$_2$Cl	0.226	0.022	90		23.7	4.25	2404	0.62
Al(C$_2$H$_5$)$_2$Cl/Mg(C$_4$H$_9$)$_2$	0.220	0.009	175	3.1	76.9	1.04	386	

These cation centers are generally regarded in the literature as catalytically active sites in polymerizations in the presence of Ziegler–Natta catalysts [24]. The second possible reason for the high efficiency of AlR$_2$Cl/MgR$_2'$ combinations used as cocatalysts is the formation of contact ion pairs [MgR']$^+$ [R$_2$R$_2'$Al]$^-$ and [MgR']$^+$ [RR'AlCl···AlRR$_2'$]$^-$. These ion pairs can transform the alkylated products X$_3$Ti^{IV}–R, X$_2$Ti^{III}–R, or LT(Cl)–R into cation active centers of another type, for example:

$$X_3Ti–R + [MgR']^+\left[R_2R_2'Al\right]^- \tag{9}$$
$$\rightarrow \left[X_2Ti^+–R\right]\left[R_2R_2'Al\right]^- + MgR'X,$$

$$X_3Ti–R + [MgR']^+\left[RR'\,AlCl···AlR'R_2\right]^- \tag{10}$$
$$\rightarrow \left[X_2Ti^+–R\right]\left[RR'\,AlCl···AlR'\,R_2\right]^- + MgR'X,$$

$$LTi(Cl)–R + [MgR']^+\left[R_2R_2'Al\right]^- \tag{11}$$
$$\rightarrow [LTi^+–R]\left[R_2R_2'Al\right]^- + MgR'X.$$
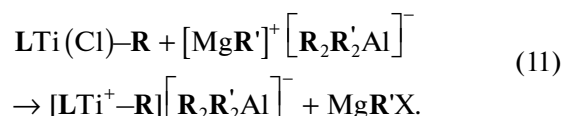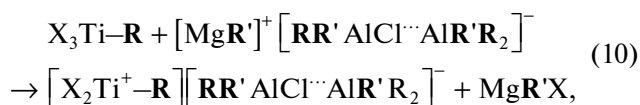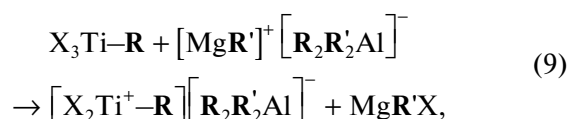
All the catalytic systems consisting of $TiCl_4$, $Ti(OR)_4$, or PMC complexes of Ti and AlR_2Cl/MgR_2' binary cocatalysts contain active centers of various types, which differ in the kinetic parameters, stereospecificity, and copolymerizing ability. It can be assumed that these active sites form in reactions (2)−(11) from various compounds: $X_xTi−\mathbf{R}$, X_yTiR_2, and $\mathbf{L}Ti(Cl)−\mathbf{R}$ containing both Ti^{IV} and Ti^{III}.

CONCLUSIONS

1. The $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ combination at a molar ratio of [Al] : [Mg] > 2.5 is an effective cocatalyst for titanium compounds such as $TiCl_4$ and $Ti(Oi\text{-}C_3H_7)_4$ and for PMC complexes of Ti in polymerizations of ethylene, propylene, and higher 1-alkenes and in copolymerizations of ethylene with 1-alkenes.

2. The efficiency of the $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ combination as a cocatalyst in 1-alkene polymerizations is explained by the in situ formation of finely dispersed $MgCl_2$ and immobilization of cation active centers on its surface.

3. The products of polymerizations are highly molecular linear PE; mostly amorphous atactic PP; highly molecular polymers of higher 1-alkenes (1-hexene, 1-octene, and 1-decene); and copolymers of ethylene with higher 1-alkenes.

4. The active centers of these catalytic systems differ in the kinetic parameters, stereospecificity, and copolymerizing ability.

5. The chain growth reaction on the isospecific centers proceeds according to the enantiomorphic mechanism typical of propylene polymerizations in the presence of heterogeneous Ziegler−Natta and metallocene catalysts.

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