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Specific Features of Ethylene Polymerization on Self-Immobilizing Catalytic Systems Based on Titanium Bis(phenoxy imine) Complexes

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Abstract—The kinetics of ethylene polymerization on six methylalumoxane-activated self-immobilizing bis(phenoxy imine) complexes of titanium chloride with allyloxy groups in the *m*- and *p*-positions of the N-phenyl ring and with various substituents in the salicylaldehyde fragment was studied. The activity of the complexes in the temperature range 20–60°C and ethylene pressure of 0.4 MPa was evaluated.

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A significant problem in commercial implementation of catalytic polymerization is deposition of a polymer layer on the reactor walls. The most widely and successfully used way to overcome this problem is the use of polymerization catalysts applied onto various supports [1].

In the past decades, some other approaches to heterogenization of catalytic systems directly in the course of polymerization were suggested. Köppl and Alt [2] suggested using a heterogeneous cocatalyst. Also Alt et al. [3–5] studied catalytic systems based on functionalized metallocene complexes of Zr, Ti, and Hf, which allowed the ethylene polymerization to be performed with catalyst self-immobilization on the formed polyethylene (PE), owing to the possibility of copolymerization with the functionalized catalytic complex via the double bond in the functional group. In these papers, the catalysts studied were termed self-immobilizing systems.

The possibility of using the self-immobilization of post-metallocene catalytic systems was later demonstrated by Zhang et al. for Zr phenoxy imine systems [6, 7] and by Alt et al. [8] for Fe bis(imino) pyridine complexes.

Previously [9, 10] we studied ethylene polymerization using six methylalumoxane (MAO)-activated titanium chloride bis(phenoxy imine) complexes functionalized with allyloxy groups. We revealed the kinetic features of the polymerization and experimentally proved for the first time the self-immobilization mechanism for the catalytic systems studied.

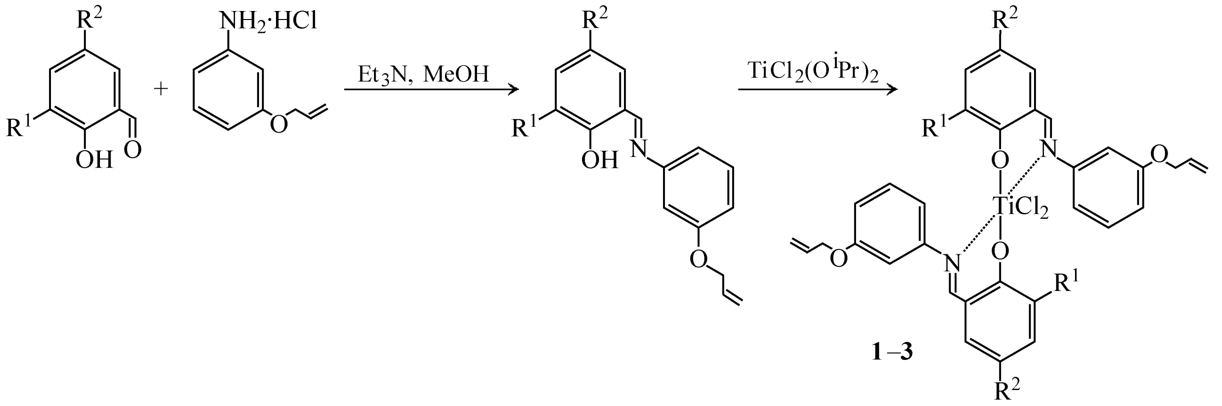
In this study we examined how the position of the functional group in the N-phenyl ring affects the self-immobilization, the polymerization kinetics, and the molecular characteristics of the polymers formed. The data obtained are useful for optimizing the structure of self-immobilizing catalytic systems for polymerization processes.

EXPERIMENTAL

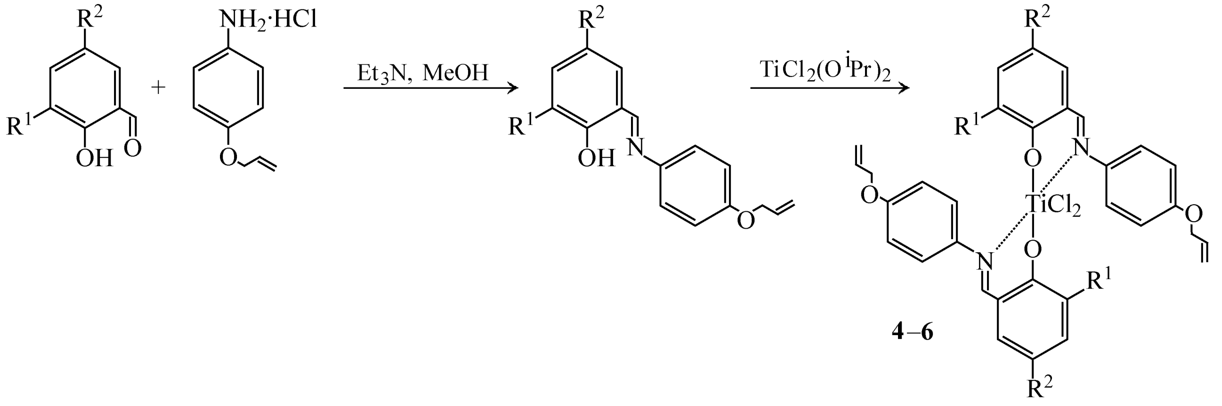
Ultrapure grade toluene was dried for 24 h over calcined Al_2O_3, distilled in an argon stream from sodium metal, and stored in the presence of sodium metal in an inert gas atmosphere. Chemically pure grade isopropyl alcohol was used without additional treatment.

Ethylene containing no less than 99.5% main substance and higher grade argon prior to feeding into the reactor were dried by passing through columns packed with calcined Al_2O_3, after which the moisture content of ethylene and argon did not exceed 10–20 and 10 ppm, respectively. Methylalumoxane (CK Witko GmbH) was used as 10% toluene solution without additional treatment.

Phenoxy imine ligands were prepared by the reaction of substituted salicylaldehydes with *m*- or *p*-allyloxyaniline hydrochloride in the presence of triethylamine in 87–97% yield. The corresponding complexes of dichlorotitanium(IV) (**1–3** with allyloxy group in *m*-position, **4–6** with allyloxy group in *p*-position) were prepared by the reaction of a $TiCl_2(O^iPr)_2$ solution with imines at room temperature[1] [9, 10]. The synthesis schemes are given below:



1–3



4–6

where R^1 = CMe_2Ph, R^2 = H (**1, 4**); R^1 = CMe_2Ph, R^2 = Me (**2, 5**); R^1 = *t*-Bu, R^2 = Me (**3, 6**).

The structures of the ligands and complexes were confirmed by elemental analysis and by ^1H NMR and IR spectroscopy.

Ethylene polymerization was performed in a 150-ml stainless steel reactor equipped with a detachable jacket and a magnetically driven propeller stirrer operating at pressures of up to 0.7 MPa and temperatures from 20 to 90°C. The pressure in the reactor was maintained automatically, and the temperature, by feeding water at the required temperature from an ultrathermostat to the reactor jacket. Prior to starting the polymerization, the reactor was evacuated to a residual pressure of 1×10^{-1} mm Hg at 150–170°C for 1 h, with threefold purging with dry argon. After cooling to room temperature, the calculated amount of toluene and the components of the catalytic system were loaded through the loading tube in an argon counterflow using medical syringes. The

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[1] Synthesized at the Vorozhtsov Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk.

reaction mixture was saturated with ethylene (0.4 MPa) with simultaneous heating to the working temperature of 20–60°C. After a definite time, the reaction was stopped by adding a mixture of isopropyl alcohol with 2% HCl. The liquid phase was separated on a Büchner funnel, and the polymer was washed twice with a mixture of isopropyl alcohol and H_2O and was vacuum-dried at 60°C to constant weight.

The molecular weight of the polymers was determined viscometrically and was calculated by the equation [11]

$$[\eta] = 6.2 \times 10^{-4} M^{0.70}.$$

Thermal characteristics of the polymers were determined by scanning calorimetry with a Shimadzu DSM-60 device. The specific heats of phase transitions and the characteristic temperatures were measured with the same DSC device at a heating rate of 10 deg min^{-1} and a sample weight of 5–10 mg.

The content of terminal groups of the polymers was determined by IR Fourier spectroscopy with a Shimadzu FTIR-8300 device.

The results of ethylene polymerization on bis(phenoxy imine) complexes functionalized with the allyloxy group in the *m*- (structures **1**–**3**) or *p*-position (structures **4**–**6**) are given in the table. Figures 1–3 show the kinetic curves of polymerization on the six titanium complexes. Figure 4 shows how the molecular weight of the polymers depends on the polymerization temperature.

Experiments on polymerization at 20, 40, and 60°C (see table) on functionalized complexes **1** and

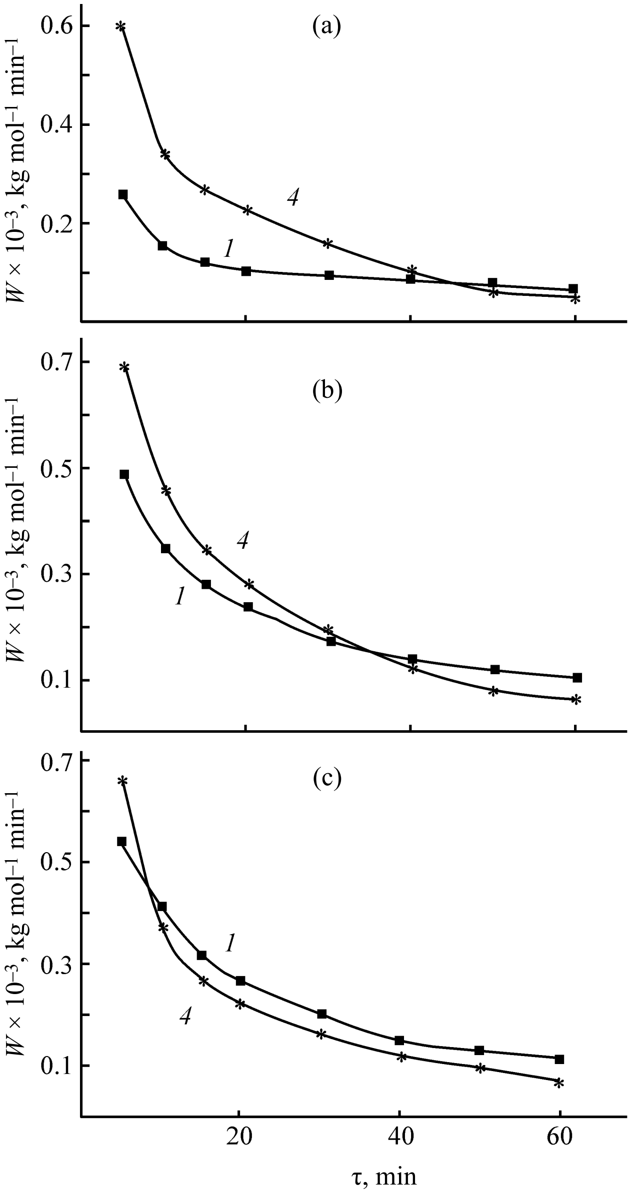

Fig. 1. Kinetic curves of ethylene polymerization on bis(phenoxy amine) complexes **1** and **4**. (*W*) Polymerization rate and (τ) time; the same for Figs. 2 and 3. *T*, °C: (a) 20, (b) 40, and (c) 60; the same for Figs. 2 and 3.

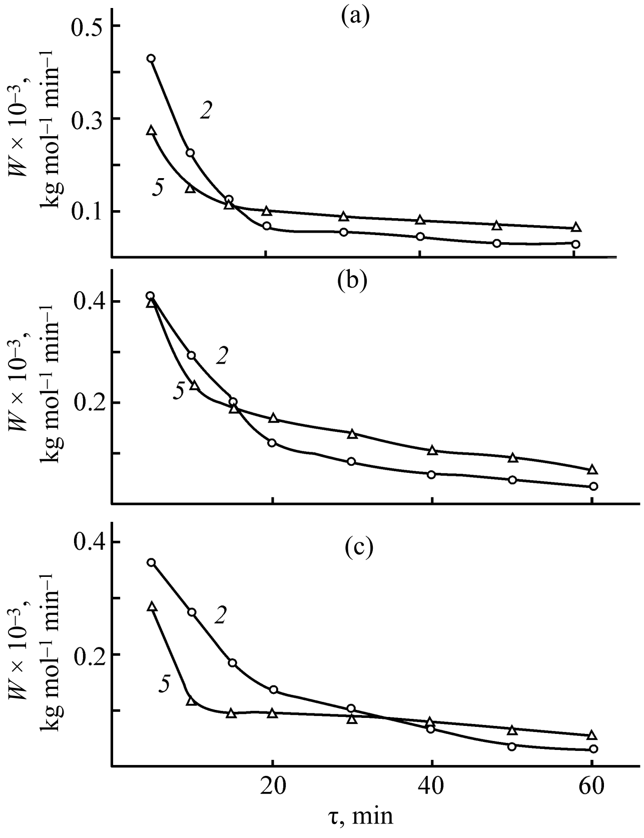

Fig. 2. Kinetic curves of ethylene polymerization on bis(phenoxy amine) complexes **2** and **5**.

Results of ethylene polymerization on complexes 1–6. Polymerization conditions: 50 ml of toluene, ethylene pressure 0.4 MPa, MAO : Ti = 500 : 1, τ_{pol} = 60 min

Complex	T_{pol}, °C	Ti, μmol	Yield, g	Activity A, $kg_{PE}\ (mol_{cat})^{-1}\ MPa^{-1}\ h^{-1}$	$M_\eta \times 10^{-6}$	–CH$_3$	–CH=CH$_2$	T_m, °C	*K*, %
(1)	20	0.698	4.785	17140	4.3	0.05	0.065	142.7	76
	40	0.523	6.093	29130	3.0	0.05	0.09	142.3	79
	60	0.465	6.466	34760	2.5	0.2	0.09	142.7	80
(2)	20	1.41	8.795	15590	3.0	~0	0.06	142.0	78
	40	1.13	8.957	19820	2.8	0.05	0.07	142.8	75
	60	1.3	10.291	19790	3.7	~0	0.08	143.2	77
(3)	20	1.18	4.155	8800	2.4	0	0.035	142.2	80
	40	0.917	4.979	13570	1.8	0	0.04	143.4	81
	60	0.917	5.100	13900	1.3	~0	0.06	141.6	79
(4)	20	0.523	6.041	28900	2.8	0	0.05	141.7	75
	40	0.523	7.37	35230	5.9	0	0.04	144.3	77
	60	0.47	5.833	31030	8.7	0	0.03	144.1	78
(5)	20	1.0	6.74	22470	4.0	0	0.04	143.3	76
	40	1.0	8.83	29430	6.21	0	0.035	143.2	80
	60	1.0	5.752	19170	8.2	0	0.025	143.2	81

4 with the allyloxy group in the *m*- and *p*-positions of the N-phenyl ring, respectively, and with the *o*-cumyl substituent in the salicylaldehyde ring show that the relative performance of the catalysts depends on the polymerization conditions. At 20°C, the activity is lower by 70% for the system with the allyloxy substituent in the *m*-position, compared to the *p*-substituted derivative. In addition, the course of kinetic curves in Fig. 1a indicates that self-immobilization at low temperatures occurs more intensely for catalytic systems with the allyloxy group in the *m*-position, compared to the *p*-substituted derivatives. At higher temperatures, the self-immobilization rate and the catalyst activity depend on the position of the allyloxy group less significantly (see table; Figs. 1b, 1c).

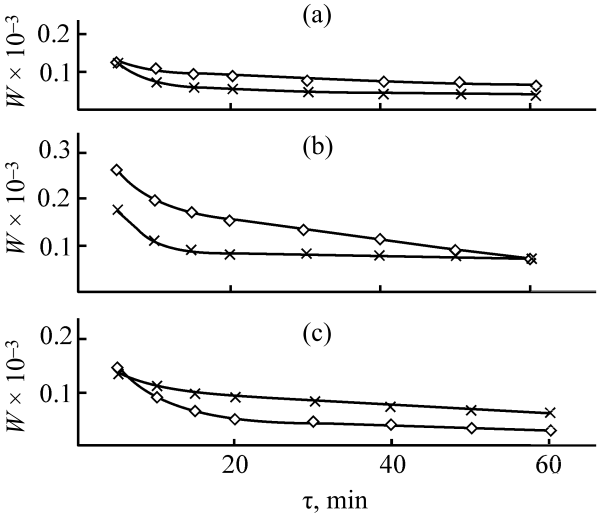

Fig. 3. Kinetic curves of ethylene polymerization on bis(phenoxy amine) complexes **3** and **6**. (*W*) Polymerization rate, kg mol^{-1} min^{-1}.

Figures 2 and 3 show the polymerization kinetic curves for catalytic complexes differing in the nature and position of substituents in the salicylaldehyde ring. As can be seen, the kinetic curves at different polymerization temperatures are fairly similar.

Of particular interest are data on the molecular weight (MW) of the polymers obtained on the self-immobilizing systems at different temperatures and different positions of the allyloxy group in the N-phenyl ring (Fig. 4). As can be seen, in going from *m*- to *p*-allyloxy derivatives, the influence of temperature on the MW of the PE formed changes cardinally (Fig. 4a). For the catalytic systems with the allyloxy group in the *p*-position, MW of the polymer increases with temperature, whereas for the *m*-substituted derivatives it depends on temperature insignificantly. For the complexes with different substitution pattern in the salicylaldehyde ring (Fig. 4b, compounds **2** and **5**; Fig. 4c, compounds **3** and **6**), the molecular weight varies with temperature to a lesser extent or is almost independent of temperature.

As shown in [12], among bis(phenoxy imine) complexes substituted in the salicylaldehyde ring, the complexes containing the *o*-cumyl substituent exhibit the highest catalytic activity. This can be seen when considering complexes **1** and **4**. Evaluation of the capability of complexes **1** and **4** for self-immobilization showed that, in ethylene polymerization at 20°C, about 70% of the catalytic complex undergoes self-immobilization on the PE formed (determined with an SF-2000 spectrophotometer from variation of the solution color in the range 400–500 nm [10]).

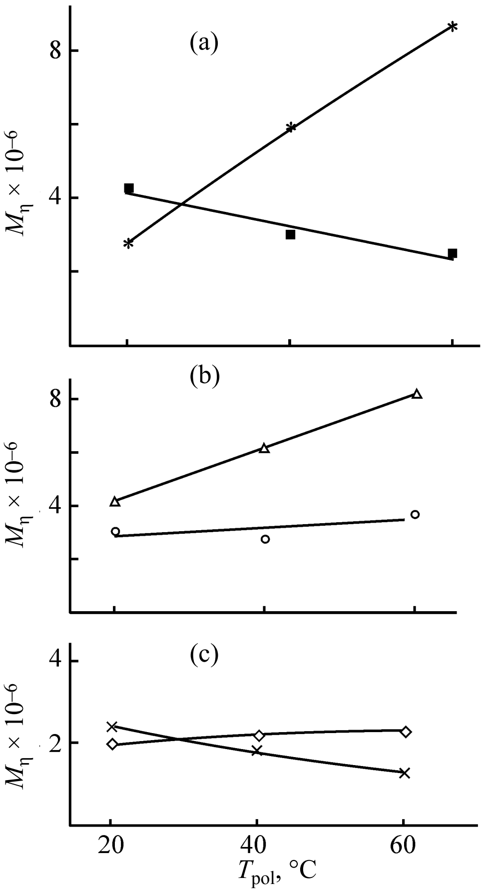

Fig. 4. PE molecular weight M_η as a function of polymerization temperature T_{pol} for complexes (a) 1 and 4, (b) 2 and 5, and (c) 3 and 6. Numerals at curves are complex nos.

It is known that a bulky substituent in the *o*-position of the salicylaldehyde ring in bis(phenoxy imine) complexes ensures steric protection of these complexes from the MAO cocatalyst always present in excess in the polymerization system. It also favors efficient separation of the active cationic species and anionic fragments of the cocatalyst [12]. Therefore, an electron-donor methyl group in the *p*-position of the salicylaldehyde phenoxy group in complexes **2** and **5**, which also contain a cumyl group in the *o*-position, should not affect the catalyst activity and the kinetic features of the polymerization (see table; Figs. 2a–2c).

Smaller substituents in the *o*-position of the salicylaldehyde phenoxy group (e.g., *tert*-butyl group instead of cumyl), with the methyl group in the *p*-position, decrease the catalyst activity and the polymerization rate at 20, 40, and 60°C (Fig. 3, complexes **3** and **6**). The data obtained also showed that, at all the temperatures, the MW of the product obtained with complex **6**, as well as with complex **3**, is lower than with complexes **4** and **5**. Evaluation of the capability of complexes **3** and **6** for self-immobilization also showed that, in ethylene polymerization at 20°C, about 40% of the catalytic complex is immobilized on the PE obtained [10]. This fact determines a decrease in the activity and MW.

Experiments on ethylene polymerization on similar complexes containing the allyloxy group in the *o*-position failed to yield the polymer. Apparently, in such complexes close location of the allyloxy group prevents the monomer access to the active center.

Zhang and Jin [6] studied structurally related bis(phenoxy imine) complexes of Zr and Ti and suggested a self-immobilization mechanism in formation of PE macrochains. They assume that several catalytic complexes can be incorporated into one PE macromolecule. To check this assumption, we determined the molecular-weight distribution of the isolated polymerized catalyst, which allowed calculation of its "molar" yield. We found that, in all the cases, there is approximately one number-average PE macromolecule [M_w ~(150–300) × 10^3, $M_w : M_n = 2.0$–2.6] per loaded catalyst molecule. This fact indicates that incorporation of two or more catalytic complexes into one PE macromolecule is hardly probable, and in the second step of the polymerization, when the self-immobilized complexes act as catalyst, the number of macromolecules per catalytic center can increase to two and more [9].

Thus, comparison of the features of ethylene polymerization on titanium chloride bis(phenoxy imine) complexes functionalized with allyloxy groups in *m*-position (complexes **1–3**) and *p*-position (complexes **4, 5**) of the N-phenyl ring shows that, with the *m*-substituted derivatives, the MW of the resulting PE is lower.

By varying the position of the allyloxy group in the N-phenyl ring (*p*- or *m*-), it is possible to obtain PE in the presence of complexes **1**, **4** and **2**, **5** with acceptable kinetic characteristics and satisfactory MW without MW-controlling additives, using the self-immobilization effect.

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