Design of Post-Metallocene Arylimine Type Catalytic Systems for the Polymerization of Olefins

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Abstract

Results of the recent decade are generalized with respect to joint research work of the Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, and the Branch of the Institute of Catalysis, SB RAS (St. Petersburg), concerning the development of scientific foundations for designing post-metallocene arylimine type catalytic systems. Post-metallocene complexes have been for the first time obtained, whose structure could provide a high activity at the temperature values of 70-90 °C and possibility to use them for the synthesis of high-molecular polythene in the process of gas phase polymerization.

Key words: catalysts, polymerization, postmetallocenes

By the beginning of the 21st century, equipping Russian domestic polyolefin industry with the newest prospective catalysts has become an urgent problem since the basis of polythene and polypropylene manufacture in Russia is formed by gas phase technologies based on import catalysts purchased in 1970ths years. In this connection in 1999 under the direction of Corresponding Member of RAS S. S. Ivanchev and Academician G. A. Tolstikov at the Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS (NIOC), and the Branch of the Institute of Catalysis, SB RAS (St. Petersburg), research works aimed at the creation of novel catalytic systems capable of polymerization at an elevated temperature had been expanded.

The intensive development of basic research and the application of metallocene catalysts to practice have resulted in understanding the necessity of the development of more perfect catalytic systems [1]. As a consequence, data concerning novel catalytic systems referred as "postmetallocene catalysts" began to appear in the literature already since the end of 1990s [2].

Owing to a set of attractive properties the complexes of imine structural type 1-3 occupy a highly important place in the series of postmetallocene catalysts being much more perfect in comparison with metallocenes. Nevertheless, they are not devoid of disadvantages the main of those consists in a low thermal stability whereby the increase in temperature results in a considerable reduction of the catalytic activity and the molecular mass of the polymer formed [3] (Scheme 1).

It is known that the processes determining a low thermal stability of metallocene and post-



Scheme 1.

metallocene catalysts are sensitive to the changes in the ligand environment. Hence, the creation of novel prospective catalysts is possible *via* the modification of already known structures.

In order to synthesize novel complexes we have proposed to introduce cycloalkyl substituents with the cycle size of 5, 6, 8 and 12 carbon atoms into the ortho position of the phenyl ring of iron bis(arylimino)pyridine complexes and nickel bis(arylimino)acen aphtene complexes [4]. Complexes 4 and 5 modified in such a fashion appeared highly active at the temperature of 80 °C as well as capable of the formation of high-molecular linear polythene, whereas the initial complex 6 lost its catalytic activity already at 40 °C [5, 6] (Scheme 2).

With the introduction of cycloaliphatic substituents into the structure of iron and nickel bis-arylimine complexes there is a shift of maximum activity observed towards the region of increased temperature values. Due to this fact postmetallocene complexes could be used for gas phase polymerization. The results of testing the samples of novel supported catalysts using a laboratory-scale installation for gas-phase polymerizations of Kazanorgsyntez JSC with the use of commercial ethylene indicated that there are no obstacles for practical application of the novel catalytic systems [6, 7].

The gas-phase polymerization with the application of the catalysts developed is attractive from the economic point of view, too, since this process unites the advantages of using metallocenes and Ziegler-Natta catalysts (the obtaining of high-molecular polymer and the simplicity of technology). Nobody succeeded in realizing such a thing before our works concerning post-metallocene systems.

Varying the ligand structure in the phenoxyimine complexes **3** could result in changing in the mechanism of polymerization, since it influences the steric load and electron density at the active centre of the catalyst [8]. The maximal activity of the complex can be exhibited only with balancing the ensemble of substituents.

In order to reveal the character of variation in the activity of complexes at various combinations of bulky substituents in the positions 3 and 5 of the ligand against the background of various substituents at the imine nitrogen atom we have synthesized novel phenoxyimine chelate complexes of titanium dichloride 7-9[9, 10] (Scheme 3).

With the use of catalysts containing cyclic substituents with cycle size of 5, 6, 8 and 12 carbon atoms under the conditions of the suspension polymerization at 30–70 °C we obtained super-high-molecular polythene $((3.6-5.4) \cdot 10^6)$ wherein the CH₃ and vinyl groups were almost absent, with melting temperature >140 °C inherent in polythene monocrystals. At the same time, according to data from the literature, the catalysts of this type do not exhibit such ability. It has been established that the complexes with the substituents such as R = cyclohexyl, $R^1 = \alpha$ -cumyl, $R^2 = Me$, α -cumyl demonstrate a maximal catalytic activity (64 000 $kg_{polym}/$ $(mol_{cat} \cdot h \cdot bar))$, three-fold exceeding the activity of the complex with $R^1 = R^2 = {}^tBu$ [10].

The linkage of imine substituents with various bridges results in the formation of di- or polynuclear complexes those should demonstrate



Scheme 2.





 $\begin{array}{ll} R^1 = CMe_2(Ph), \ R^2 = Me, \ ^tBu, \ CMe_2(Ph), \ Tr; \\ R^1 = {}^tBu, \ R^2 = CMe_2(Ph), \ Tr; \\ R^1 = 2\text{-}isobornyl, \ R^2 = H, \ Me, \ ^tBu, \ CMe_2(Ph). \end{array}$





Scheme 3



Scheme 4.

a greater stability during the deactivation process. In order to synthesize polynuclear oligomeric complexes **10** and **11**, we used diaminodiphenylmethanes containing cycloalkyl substituents [11] (Scheme 4).

The synthesis of polythene in the presence of novel multifunctional bis-arylimine complexes with iron chloride allows one to carry out the process of ethylene polymerization with a higher activity at increased temperature (60– 90 °C). In this case, as against similar monofunctional systems **12** and **13**, polythene obtained is characterized by high molecular mass values [11].

Binuclear complexes with tetradentate bis(phenoxyimine) ligands $L_2(MCl_2)_2$ should be much more stable with respect to thermal deactivation. Owing to the effect of "active centres cooperation" observed for binuclear complexes, the use of the latter in the polymerization process offers considerable scope for



 $R^{1} = R^{2} = H; R^{1} = CMe_{2}(Ph), R^{2} = Me; {}^{t}Bu, CMe_{2}(Ph), Tr; R^{1} = {}^{t}Bu, R^{2} = H, {}^{t}Bu, CMe_{2}(Ph), Tr; R^{1} = 2-isobornyl, R^{2} = H, Me, {}^{t}Bu, CMe_{2}(Ph).$

Scheme 5.

obtaining absolutely new polymeric materials those could not be obtained employing mononuclear analogues [12] (Scheme 5).

The studies on the kinetics of ethylene polymerization in the presence of complexes with novel tetradentate ligands **14** and **15** has allowed us to reveal the complexes with an unprecedentedly high activity (140 000 kg_{polym}/(mol_{cat} \cdot h \cdot bar) at 30 °C) [13]. The results of our investigations indicate that binuclear complexes even at 70 °C allow one to obtain with very high efficiency super-high-molecular linear polythene characterized by an increased melting point.

The process whereby a homogeneous catalyst containing an alkenyl group capable of copolymerization is converted into a heterogeneous one with no alien carrier used is referred to as "autoimmobilization" (the system itself produces a substrate and performs applying a catalyst onto the substrate). Such an approach is of interest being an additional tool for the process to control, since the activity of the heterogeneous catalyst obtained as well as the molecular mass of the polyolefin formed could be determined by the length of an alkenyl substituent [14].

The polythenes formed with the catalytic systems based on complexes **16** and their polymerized forms capable of self-immobilizing, are characterized by very high molecular mass values $((2-6) \cdot 10^6)$, a good morphology of parti-

cles and the absence of particle sticking onto the walls of a reactor. A considerable increase in the molecular mass of polyolefin in the course of polymerization indicates that there is a realization of a "living" nature of the polymerization observed in the systems under consideration [15] (Scheme 6).

Generalizing the results of research work concerning the development of scientific bases for designing post-metallocene arylimine type catalytic systems performed by joint efforts of the NIOC, SB RAS, and the Branch of the IC, SB RAS (St. Petersburg), one should note the following: since 1999 a considerable backlog was formed and important results were obtained those indicate the absence of any ob-



 $\begin{array}{l} {\rm R}^1={}^t{\rm Bu},\;{\rm R}^2={\rm H},\;{\rm Me},\;{}^t{\rm Bu},\;{\rm CMe}_2({\rm Ph}),{\rm Tr};\\ {\rm R}^1={\rm CMe}_2({\rm Ph}),{\rm R}^2={\rm H},\;{\rm Me},\;{}^t{\rm Bu},\;{\rm CMe}_2({\rm Ph}),\;{\rm Tr};\\ {\rm R}^1={\rm CHMe}(n{-}^t{\rm BuC}_6{\rm H}_4),\;{\rm R}^2={\rm H},\;{\rm Me},\;{}^t{\rm Bu},\;{\rm CMe}_2({\rm Ph}),\;{\rm Tr}.\\ {\rm Scheme}\;6. \end{array}$

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stacles for practical application of novel catalytic systems.

The further perfection of novel catalytic systems represents a very important problem and offers the prospects of controlling not only the molecular structure of polymers formed, but also the supramolecular structure and nanostructure of polymeric systems. It should be emphasized that the timeliness of expanding the studies aimed the creation of new high-efficiency polymerization catalysts adapted to the conditions of real industrial production, as well as the validity of the strategy chosen have allowed us to provide the productivity and priority in the creation and application of novel non-infringing catalytic systems of the indicated type [6, 13].

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