Reviews

Ionic and coordination diene polymerization and organic derivatives of main group metals

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The effects of the nature of an organic derivative of a main group metal (cocatalyst), its composition, the cocatalyst : transition metal compound ratio, and the way of introducing the cocatalyst on the formation and operation of the active sites in the Ziegler—Natta catalytic systems in the polymerization of conjugated dienes are discussed. A correlation between the cocatalyst nature and the number and kinetic heterogeneity of the active sites is shown.

Key words: organic derivatives of main group metals, Ziegler—Natta catalysts, polydienes.

Introduction

Polymerization of conjugated dienes is distinct from olefin polymerization, *e.g.*, in a variety of microstructures formed when a monomer joins a growing chain. In the Ziegler polymerization of dienes, the course of the process, as well as the structure of the resulting polymer, depends on both the composition of a transition metal compound and the structure of an organic derivative of a main group metal (cocatalyst).[1—4] Compounds of Group I—III elements and, less often, Group IV elements (tin and silicon) are mainly used as cocatalysts. The cocatalyst based on an organic derivative of a main group metal is not necessarily required for ionic and coordination polymerization of dienes, yet significantly affecting the process features. When combined with a transition metal compound, it can fulfill various functions in a particular system (serving, *e.g.*, as an alkylating, reducing, and complexing agent; a stabilizer of active sites; a chain transfer agent; a reagent for binding unwanted impurities during the polymerization; *etc.*).[1—4]

Numerous data indicate that the yield and molecular parameters of polydienes are noticeably affected by the nature of substituents at the same metal in a cocatalyst, the cocatalyst : transition element ratio, and the way in which a main group metal derivative is introduced. Despite a variety of cocatalysts, main commercial catalysts for stereospecific diene polymerization are based on derivatives of Groups III transition metals (lanthanides), IV (titanium), and V (vanadium) and commonly used with organoaluminum compounds (OAC).[1—4]

Lanthanide-containing systems

Cocatalysts for lanthanide systems may contain lithium, zinc, tin, copper, boron, and magnesium, while

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OAC are preferred.[1,2] The catalyst efficiency is largely determined by the structure of an organic derivative of a main group metal and depends on the polymerization conditions. For the $LnCl_3 \cdot 3(BuO)_3PO—AlR_3$ system (Ln = Pr or Nd), the yield of polyisoprene at 25 °C decreases in the order $AlBu^i_3 > AlDec_3 > AlHex_3 > AlEt_3 > > AlBu^i_2H$, while at 80 °C, the order is quite the opposite. It is suggested[5] that the OAC associates decompose at this temperature and the active sites of a catalyst are generated with participation of the AlR_3 monomeric form. Similar activity series were found for the $Nd(OCOR)_3—AlR_2Cl—AlR'_3$ systems: $AlBu^i_3 > AlBu^i_2H > AlEt_3 \gg AlMe_3$.[6] In these systems, OAC are often used as a halogenating reagent, and such cocatalysts substantially affect the catalyst activity. For instance, for the $NdSt_3—AlR_2Hal—AlR_3$ system, the activity and *cis*-stereospecific effect decrease in the order $AlR_2Br > > AlR_2Cl > AlR_2I$ (content of 3,4-units in the resulting polyisoprene is 4, 7, and 12%, respectively), although these OAC are catalytically active in the same Hal : Nd ratio region (2 and 3).[7]

The cocatalytic activity of aluminum alkyls is also determined by its concentration affecting the associate—monomer equilibrium and the kinetic parameters of polymerization.[8] For systems with electron-donating ligands, OAC should remove basic ligands from the lanthanide complex. The monomer conversion in this reaction depends on both the concentration and nature of OAC. For instance, piperylene polymerization initiated by $NdCl_3 \cdot 3L^*$—OAC (L* is the optically active sulfoxide, OAC is $AlBu^i_3$, $AlEt_3$, or $AlBu^i_2H$) gives a polymer with a specific rotation value of −8.3°, −4.4° and 0°, respectively. The latter cocatalyst is assumed[9] to completely remove L* from the coordination sphere of the active sites.

Partial removal of ligands from the lanthanide coordination spheres in the complexes $Nd(Pr)Cl_2 \cdot n$THF can account for a significant increase in the content of *cis*-units in polybutadiene when OAC is added to these catalysts.[10]

Organoaluminum compounds substantially affect the molecular-mass characteristics of polydienes; one of the reasons is that they differ in chain transfer ability. For butadiene polymerization in the $LnCl_3 \cdot 3(BuO)_3PO—AlR_3$ system at 25 °C, the molecular weight (MW) and polydispersity of polybutadiene decrease in the following order of the AlR_3 groups: $AlBu^i_3 > AlEt_3 > > AlHex_3 > AlOct_3 > AlBu^i_2H$ for M_w and $AlEt_3 > > AlBu^i_2H > AlOct_3 > AlBu^i_3 > AlHex_3$ for M_w/M_n. Note that at 80 °C, the MW of the resulting polymer is virtually the same for any OAC.[11]

It was demonstrated[12] that the reactivity of active sites in the synthesis of polybutadiene and polyisoprene in the $NdCl_3 \cdot 3L$—OAC system is determined by the structure of AlR_3. The microstructure of the resulting polydienes varies with OAC (*e.g.*, the *cis*- to *trans*-unit ratio in polybutadiene decreases in the order $AlEt_3 > AlBu^i_3 > AlHex_3 > AlOct_3$), while the content of 1,2-units is maintained at a level of ~0.6%, except for $AlBu^i_2H$ (~1.8%).[13] At a decreased butadiene concentration (<0.5 mol L^{-1}) and at an elevated polymerization temperature, the amount of 1,4-*cis*-units becomes more sensitive to the AlR_3 structure.[14]

The above facts suggest that the cocatalyst is not merely an alkylating agent for a transition metal atom. Since the coordination sphere of a lanthanide is large, the OAC can be regarded as one of its ligands in the active site. The formation of bridged bimetallic complexes is also not improbable.[15,16] This is partly confirmed by the fact that isoprene polymerization is not initiated when AlR_3 is replaced by $LiAlR_3H$, $LiAlR_4$, or $NaAlR_4$, which alkylate transition metal chlorides but do not form bridged complexes.[15] The foregoing concept is consistent with the ratio Nd : Al = 1 : 1 in precipitates formed by the reaction of $NdCl_3 \cdot 3L$ with $AlBu^i_3$.[17] In conflict with this, butadiene is reported[18] to polymerize in the presence of a phosphorus-containing Ln derivative with a mixture of BuLi and $AlEt_3$. Most probably, the process involves the organolanthanide compound, since the resulting polybutadiene predominantly contains 1,4-*trans*-units. *trans*-Polymerization of isoprene in the $[(C_5HPr^i_4)Ln(BH_4)_2 \cdot (THF)]$—BuLi system (Ln = Sm or Nd; Li : Ln = 1.0) is attributed to a similar process.[19] Although, it is not improbable that polyisoprene forms in the boron—lanthanide system, while BuLi serves to remove THF from the coordination sphere of the *f* element.

Catalysts based on lanthanide halides can be homogenized by special techniques with variation of the OAC nature. For instance, when $(AlBu^i_2)_2O$ is substituted for $AlBu^i_3$ or $AlBu^i_2H$ in a mixture with $NdCl_3 \cdot 3Pr^iOH$, up to 90% of the solid neodymium derivative passes into the liquid phase. Addition of piperylene (Nd : Al : diene = 1 : 18 : 20) makes this catalyst homogeneous, while the compositionally identical system but containing $AlBu^i_3$ is only quasi-homogeneous.[20]

Lanthanide catalysts containing aluminoxanes have other distinctive features. For instance, the Nd(neodecanate)$_3$—methylaluminoxane—Me_3CCl system initiates butadiene polymerization even without a halogenating agent (content of 1,4-*cis*-, 1,4-*trans*-, and 1,2-units in the resulting polybutadiene is 86, 11, and 3%, respectively), whereas the cocatalytic effect of $(AlBu^i_2)_2O$ is observed only in the presence of Me_3CCl. However, the halogen-containing catalytic systems involving $[AlBu^i_2]_2O$ are more efficient than those based on methylaluminoxane. The resulting 1,4-*cis*-polybutadiene is highly stereoregular, irrespective of the aluminoxane nature.[21]

The stereospecific effect of the $Nd(OCOR)_3—AlBu^i_3$ system is reversed when $AlBu^i_3$ is replaced by aluminoxane (*e.g.*, $(AlBu^i_2)_2O$). When this complex is prepared separately, the content of 1,4-*cis*-units in the resulting polyisoprenes and polybutadienes is up to 82%,[22] though the

same catalyst formed *in situ* initiates *trans*-polymerization of dienes.[23] The reaction mixture contains compounds with Al—O—Al bonds. This assumption is confirmed by the formation of *cis*-units (up to 94.6 and 87% in polybutadiene and polyisoprene, respectively) in the $Nd(OCOR)_3$—methylaluminoxane system.[24]

Methylaluminoxane exerts activating and *cis*-regulating effects on diene polymerization also in the presence of individual organolanthanides. It was found[25] that allyllanthanide derivatives $Ln(All)_3 \cdot nL$, $Ln(All)_2Cl \cdot nL$, and $Ln(All)Cl_2 \cdot nL$ (Ln = La or Nd; L is THF or dioxane) in combination with methylaluminoxane are efficient catalysts for the synthesis of polybutadiene. In the $Nd(All)_2Cl \cdot 1.5THF$ and $Nd(All)Cl_2 \cdot THF$ systems, the content of 1,4-*cis*-units in the polymer reaches 98%. The methylaluminoxane : Ln ratio is 30.

Aluminoxanes are also used in diene polymerization involving cyclopentadienyl and indenyl (Ind) derivatives of lanthanides. Ethene polymerization is initiated by the complexes Cp_2LnR (R = H or Alk) and $Cp_2Sm \cdot 2THF$ without any cocatalyst, while the synthesis of polybutadiene is possible only in the presence of aluminoxanes (methylaluminoxane and $(AlBu^i_2)_2O$). In this case, OAC prevents the formation of stable η^3-allyl complexes with diene, which are inactive in polymerization. The resulting polybutadiene is mainly composed of 1,4-*cis*-units (99%), $M_n = 5 \cdot 10^5$, $M_w/M_n = 1.8$.[26] Modified aluminoxane such as $(AlBu^i_2)_2O$) is more efficient. For $(AlBu^i_2)_2O$: Ln = 200, the complex $Cp^*_2Sm \cdot 2THF$ (Cp* is pentamethylcyclopentadienyl) is very active, and the conversion of butadiene reaches 20 000 mol per mole of lanthanide. When combined with methylaluminoxane, the complexes $(C_5H_9Cp)_2NdCl$, $(C_5H_9Cp)_2SmCl$, $(MeCp)_2SmOPh$, $Me_2Si(Ind)_2NdCl$, and $(Ind)_2NdCl$ are efficient in the polymerization of butadiene and isoprene.[27] The samaro- and neodymocene catalysts are more stereospecific toward butadiene (the content of 1,4-*cis*-units is 75%) than indenyl derivatives of neodymium, while the resulting polyisoprenes contain virtually equimolar amounts of 1,4-*cis*- and 1,4-*trans*-units (3,4-units account for 15 to 25%, depending on the catalyst composition).[27]

Such a changed stereospecific effect of the lanthanide—aluminoxane systems is explained by analogy with the formation of *cis*-polydienes in the presence of the reaction product of *trans*-regulating tris-π-allylchromium and the hydroxy groups at the Al_2O_3 surface.[28] Apparently, aluminoxanes can also serve as low-molecular carriers such as Al_2O_3.[29]

Organoaluminium compounds other than aluminoxanes are also capable of activating lanthanide derivatives of the $Cp^*_2Sm \cdot 2THF$ type. The latter, in combination with $AlBu^i_3 \cdot [Ph_3C][B(C_6F_5)_4]$, provides *cis*-polymerization of butadiene.[26] The process has no induction period, and the M_n of the polymer builds up in proportion to the monomer conversion, which is characteristic of "living" polymerization. The use of $AlMe_3$ or $AlEt_3$ instead of $AlBu^i_3$ in the above system virtually does not affect its efficiency, while the content of 1,4-*cis*-units in polybutadiene is reduced from 95 to 51 and 70%, respectively.

Cocatalytic functions of organic derivatives of main group elements depend on both the structures of substituents at the same metal and the nature of the metal. For instance, the $NdCl_3 \cdot 3(BuO)_3PO$—AlR_3 system is a *cis*-stereoregulating catalyst for the polymerization of butadiene and isoprene,[2] while the use of an organomagnesium compound instead of AlR_3 gives polymers mostly containing 1,4-*trans*-units.[30] The efficiency of the latter system is an extremum function of the Mg : Ln ratio, which is observed for OAC only when the catalysts contain reducible lanthanides (Ce and Eu).[31] Apparently,[32] LnR_3 serves as an active site, because the content of 1,4-*trans*-units in the polybutadiene obtained in the presence of such organolanthanide derivatives is 94 to 97%.[32] This assumption is quite reasonable since organomagnesium compounds are capable of completely alkylating *f*-metal halides.[33]

Usually, lanthanide catalysts containing organomagnesium derivatives are less efficient than systems with OAC.[34] The exception is butadiene polymerization in hexane at 50 °C; the yield of polybutadiene (content of 1,4-*trans*-units is 96.9%) in the Dm(neodecanate)$_3$—$MgBu_2$ system is nearly 40 times higher than its yield with $AlEt_3$ as cocatalyst, all other factors being equal.[35] The stereospecific effect of this system can be changed during polymerization by varying the cocatalyst nature: *e.g.*, sesquialuminum chloride added to the reaction mixture halogenates the terminal active site of a growing chain so that its subsequent growth involves only 1,4-*cis*-units.[35]

Diene polymerization can also be initiated by lanthanide alkoxides and carboxylates combined with MgR_2 and RMgHal.[36] The content of 1,4-*trans*-units in the resulting polybutadiene is 80 to 98% (even for halide-containing systems), M_w is up to $160 \cdot 10^3$, $M_w/M_n = 1.2$—4.0. Addition of Et_2AlCl or $Et_3Al_2Cl_3$ to the *trans*-regulating system composed of $Ln(OCOR)_3$ and an organic derivative of a main group metal reverses its stereospecific effect, while the highest yield of 1,4-*cis*-polydiene with OAC or dialkylmagnesium as cocatalyst is reached at Cl : Ln = 2 to 3 and 12 to 17, respectively.[35] This is indirect evidence for a deep alkylation of lanthanide by MgR_2, which competes with its halogenation. It should be noted that $MgCl_2$ formed in such a system (*e.g.*, according to the reaction $MgR_2 + Et_2AlCl \rightarrow MgCl_2 + Et_2AlR$) can serve as an active carrier. In the system $AlEt_3 + NdCl_3 \cdot n(BuO)_3PO$ applied to $MgCl_2$, the resulting polybutadiene has a mixed microstructure (57% and 42% for *cis*- and *trans*-1,4-units, respectively).[37] The lanthanide

complexes $(\pi\text{-All})_2LnCl_5Mg_2 \cdot 2L$ (Ln = La, Pr, Nd, or Sm) probably contain magnesium dichloride formed by an exchange reaction;[38] their formula should be rewritten as $(\pi\text{-All})_2LnCl \cdot 2MgCl_2 \cdot 2L$. The yield of polyisoprene in the presence of catalytic systems based on these complexes and AlR_3 (Al : Ln = 15—20) decreases in the order: $AlBu^i_3 > AlEt_3 > AlMe_3 > AlOct_3$.[39] The highest content of 1,4-*cis*-units (82%) was attained with $AlEt_3$ as cocatalyst; in the presence of the other OAC, the resulting polymer contains approximately equal amounts of *cis*- and *trans*-units (~50%).

Thus, the role of a magnesium-containing component is significant even when it is used as a carrier.

Titanium-containing systems

In systems based on transition metals, the efficiency of the catalyst is often an extremum function of the cocatalyst content, which is due to the polyfunctional effect of the cocatalyst, *e.g.*, OAC. This was most clearly demonstrated for Ti^{IV}-containing complexes. It is universally accepted[1—4] that active sites of such catalysts bear alkylated derivatives of Ti^{III} and that the polydiene chain grows at the transition metal—carbon σ-bond formed and stabilized in the presence of an organic derivative of a main group metal. The microstructure of polyisoprene obtained in the $TiCl_4$-based systems only slightly varies with the cocatalyst nature; in all cases, *cis*-polymers were obtained (Table 1).

Aluminum halohydrides are low-efficiency cocatalysts at relatively high Al : Ti ratios.[42] Nitrogen-containing OAC also form inactive catalysts.[43] Cocatalysts based on polyiminoalanes $[—AlH—NR—]_n$ allow prompt synthesis of highly stereoregular polydienes with high MW and a low gel content.[44] The cocatalytic efficiency of polyiminoalanes depends on the structure of radical R, being the highest when OAC contains a secondary C atom in the α- or β-position relative to the N atom.

Table 1. Dependence of the polyisoprene microstructure on the cocatalyst nature in the $TiCl_4$-based catalytic system

Cocatalyst	Al : Ti	1,4-*cis*-Units (%)	References
AlR_3	≥1	95—99.5	40, 41
$AlH(Hal)_2 \cdot Et_2O$	1.5—2.2	95—96	42
$AlHCl_2 \cdot NR_3$	1.4—1.7	95—96	43
$AlH_2Cl \cdot NR_3$	0.5—0.6	96	43
$AlH_3 \cdot NR_3$	0.35—0.5	94—95	43
$AlH_2(NR_2)$	0.55—0.7	95—96	43
$AlH_2(OR) \cdot NMe_3$	0.6—0.7	94—96	43
Polyiminoalanes	1.4—1.8	94—96	44
$[CaEt]_n \cdot ZnEt_2$	0.6—1.5	95—96	45
R_3SnH	≥1	95—97	46
$R_3SiOR' — AlR_2''Cl$	0.5—1	97	47
$R_3SnH — AlR_2'Cl$	0.5—0.6	97	48
CdR_3	0.5	90	49
AlB_3H_{12}	0.7—1.5	80	50
MgR_2	0.8	75	51

The $TiCl_4—[CaEt_2]_n \cdot ZnEt_2$ complex is impractical because the yield and MW of the resulting polymer are low;[45] apparently, this is due to the tendency of dialkylzinc toward chain transfer reactions. For instance, the use of $ZnEt_2$ instead of $AlEt_3$ in a $\alpha\text{-}TiCl_3$-based catalyst gives polybutadiene and polyisoprene with dominant branch vinyl bonds and noticeably reduced molecular weights.[52]

Organotin, -silicon, and -cadmium compounds favor the formation of *cis*-polyisoprene; however, the MW of the polymers is also low.[46—49] In isoprene polymerization, catalysts containing aluminum borohydride[50] and organomagnesium compounds are least stereospecific;[51] the content of *cis*-units in the resulting low-molecular polymers is at most 80%. The $TiCl_4—MgR_2$ system is most active at Mg : Ti = 2.0, and *trans*-units are dominant in the polyisoprene.

The effect of the cocatalyst nature on the working parameters of a catalyst has been most thoroughly investigated for the $TiCl_4—AlR_3$ system. The yield of polyisoprene in this system was found[53] to increase in the order $AlMe_3 < AlEt_3 < AlPr_3 < AlBu_3 < AlHex_3$, which is the same as for the decreasing alkylating ability of OAC and the increasing concentration of active sites because the higher OAC have a milder reducing and stronger stabilizing effects on the active sites. The reactivity and stereospecific effect of these active sites do not depend on the OAC structure. The catalyst efficiency is affected by both the carbon chain length and the structure of radicals: OAC with branched alkyl groups are more active than OAC with unbranched alkyls. The efficiency of aluminum isoalkyls grows with an increase in the number of carbon atoms in the alkyl group (*e.g.*, $AlHex^i_3$ is more efficient than $AlBu^i_3$).[53] For OAC bearing linear and cyclic radicals, it was shown[54] that the isoprene polymerization rate increases and the total energy of activation decreases with an increase in the carbon chain length. The AlR_3-containing systems (R is a saturated radical) are less efficient than those with unsaturated R, especially when the conjugated double bonds are involved, which is attributed to the growing number of more stable active sites. Among OAC containing the same number of carbon atoms, the polymerization rate for OAC with cyclic radicals is lower than for those with linear radicals. The rate constant of the chain growth and the microstructure of the resulting polyisoprene are independent of the AlR_3 structure.

Apart from the nature of the ligand in OAC, diene polymerization is significantly affected by the cocatalyst content. In the $TiCl_4—AlR_3$ system, the highest content of Ti^{III} is observed at nearly equimolar Al : Ti ratios for $AlBu^i_3$ and at Al : Ti > 1 for the higher trialkylaluminum

compounds.[54] The maximum efficiency of the system in isoprene polymerization virtually corresponds to the highest content of Ti^{III}. However, these two parameters most often differ significantly both for titanium and other catalysts,[1—4] especially with monosubstituted aluminum alkyls as cocatalysts (*e.g.*, for $TiCl_4$—$AlBu^i_2H$ or $AlBu^i_2Cl$ in isoprene polymerization).[55] It should also be noted that the microstructure of polydienes is sensitive to the ratio of the catalyst components. A typical example is the dependence of the stereospecific effect of $TiCl_4$—AlR_3 on the OAC concentration in butadiene polymerization.[56]

When organomagnesium compounds (MgR_2 or RMgCl) are combined with $TiCl_4$, the resulting catalytic systems have approximately equal stereospecific effects on the polymerization of both butadiene and isoprene (content of 1,4-*trans*-units is 60 to 80%).[51] With PhMgBr as cocatalyst (instead of MgR_2), 1,4-*cis*-units account for 95% of the polyisoprene obtained. Here, the cocatalyst acts as a halogenating agent as well.[57] Replacement of OAC by dialkylmagnesium in systems based on TiI_2Cl_2 and $Ti(OBu)_4$ noticeably changes the stereospecific effect of the catalysts and reduces their efficiency in butadiene polymerization. The latter is due to the decreased reactivity of an active site.[58] At the same time, magnesium derivatives can be used[59] to prepare active supported catalysts for the synthesis of polyolefins. *trans*-Polymerization of butadiene and isoprene in the presence of titanium—magnesium catalysts based on $TiCl_4$ and supported on silica gel was studied with $AlBu^i_3$ as cocatalyst.[60,61] The yields and microstructures of polydienes (content of 1,4-*trans*-units is 85—94%) are determined by the Al : Ti ratio and the polymerization temperature. It is supposed[62] that $MgCl_2$-type carriers enlarge the catalyst surface and favor the formation of $TiCl_3$ in the α-, δ-, or γ-modification required for diene trans-polymerization. Titanium—magnesium complexes containing nickel or zirconium compounds also afford *trans*-polybutadiene.[63] By varying the catalyst composition and the polymerization temperature, one can obtain virtually stereoregular *cis*- or *trans*-polymers. For instance, the content of 1,4-*trans*-units in polybutadiene obtained in the presence of $TiCl_4/MgCl_2$—$Al(OEt)Et_2$—$NiCl_2$ increases from 6 to 83% with an increase in the temperature from 20 to 60 °C, while the content of 1,4-*cis*-units decreases. Apparently, magnesium derivatives can serve as active carriers regulating the stereospecific effect of these catalysts.

Aluminoxanes should also be classified under cocatalysts tuning the stereoregulating effect of titanium systems. For instance, the microstructure of polybutadiene in the presence of $Ti(OR)_4$—aluminoxane significantly depends on the nature of the alkyl group in OAC and the Al : Ti ratio (Table 2). In combination with aluminoxanes, cyclopentadienyl- and indenyltitanium derivatives have a *cis*-stereoregulating effect on the polymerization of butadiene and isoprene. As in the synthesis of polyolefins, high Al : Ti ratios are required. For instance, polybutadiene and polyisoprene with a *cis*-unit content of 85 and 90% were obtained on the $CpTiCl_2$ and $CpTiCl_3$ catalysts with methylaluminoxane as cocatalyst for Al : Ti = 500 and 1000, respectively.[65,66] Catalytic systems with pentamethylcyclopentadienyl and indenyl ligands, which are most efficient and stereospecific in the synthesis of polyolefins, are much less active and stereospecific in butadiene polymerization than catalysts with an unsubstituted Cp group. In the presence of the former, the resulting polybutadiene contains an increased amount of 1,2-units because the content of *cis*-units decreases.[67] The efficiency of the $CpTiX_n$—aluminoxane systems is affected by the presence of $AlMe_3$ in methylaluminoxane and the nature of the alkyl group in OAC. It is assumed[68] that $AlMe_3$ deactivates the active site of a catalyst. The efficiency of $MeCpTiCl_3$ is enhanced in the presence of modified methylaluminoxane; however, the content of *cis*-units decreases from 85 to 75%, while that of 1,2-units grows.[67] As noted above, polymerization with methylaluminoxane as cocatalyst is efficient at very high Al : Ti ratios. At the same time, polybutadiene was obtained[69] in a high yield with the use of the methylaluminoxane—$AlBu^i_3$—$CpTiX_3$ system (X = Cl or OPh) for Al : Ti (for both OAC) = 400 : 1 and 100 : 1, respectively. When combined with AlR_3, the cyclopentadienyl derivatives of titanium fail in diene polymerization. However, the efficiency and *cis*-stereospecific effect of $CpTiCl_3$ in the presence of $AlBu^i_3$ or $AlEt_3$ modified with borate $Ph_3CB(C_6F_5)_4$ (Al : B : Ti = 200 : 1.5 : 1) are even higher than those for the catalytic systems with modified methylaluminoxane.[67] This is indirect evidence for the presence of Ti^{III}-based cationic active sites in the above systems containing methylaluminoxane.[70]

Table 2. Dependence of the polybutadiene microstructure on the aluminoxane nature in the $Ti(OR)_4$-based catalytic system[64]

R´	Al : Ti	Polybutadiene microstructure (%)		
		1,4-*cis*-units	1,4-*trans*-units	1,2-units
Me	440	94.6	3.0	2.4
Me	220	80.6	7.8	11.4
Et	370	12.4	0	87.6
Bu^i	208	6.6	12.2	81.2

Note. R´ is an alkyl group in the aluminoxane.

Vanadium-containing systems

Organic derivatives of main group metals in Ziegler vanadium catalysts function as in the titanium systems. A distinctive feature of the former is that the *trans*-stereospecific effect of complexes based on vanadium ha-

lides is slightly dependent on the structure and content of OAC. It is believed[4,71] that V^{IV} or V^{V} compounds are easier than Ti^{IV} derivatives to reduce with OAC. Even an equimolar amount of $Al_2Et_3Cl_3$ very rapidly (within 1 to 2 s) and virtually completely alkylates VCl_4 into VCl_3R, which undergoes prompt reductive dealkylation to give a V^{III} compound. A study of the reactions of VCl_4 with $Alk_nAl_2Cl_{6-n}$ (n = 2—6) showed that the rates of vanadium alkylation and reduction decrease with a decrease in the number of alkyl groups in OAC. Cocatalysts with smaller radicals react faster (Me > Et > Bu^i).[71]

Comparison of data on the effect of the nature of vanadium compounds and OAC and their ratio on the oxidation state of the transition metal and the maximum efficiency shows that OAC is often taken greater amounts than are necessary to reach the highest concentration of V^{III}. This is primarily due to the functions of OAC as a cocatalyst in a catalytic system. As in titanium catalysts, the optimum (as regards efficiency) Al : V ratio depends on the nature of both a vanadium derivative and OAC. It was found[72] that the amount of V^{III} is maximum at an equimolar ratio between $VOCl_3$ and $AlBu^i_3$. This system is most efficient in isoprene polymerization for Al : V = 1.5 to 2.0, the microstructure of polyisoprene and the chain growth rate constant being sensitive to the ratio between the catalyst components.[73] This is associated with the presence of several types of active sites containing different OAC in the ligand environment of V^{III}. In butadiene polymerization, the $VOCl_3$—OAC systems are most efficient when $AlBu^i_2H$, $AlBu^i_3$, and $AlBu^i_2Cl$ are used in excess (2.0, 3.8, and 4.0, respectively). This is primarily due to different reducing abilities of these OAC.[74] Moreover, the nature of OAC affects the reactivity of active sites, which is associated with both the structure of the latter and the interaction of free OAC molecules with the V—C bond responsible for chain growth. Similar reasons account for a substantial change in the rate constant of chain growth in the *trans*-polymerization of butadiene in the $VOCl_3$-containing system with dialkylmagnesium used instead of $AlBu^i_3$.[75] Thus, the main group metal derivatives are involved both in the generation and operation of the active sites of these catalysts and affect their reactivities. The microstructure of a polymer obtained in the vanadium systems can vary with the cocatalyst. When aluminum alkyls are replaced by aluminoxanes in the systems based on vanadium halides, the stereospecific effect remains unchanged.[76] The pattern is different for $V(acac)_3$-based systems. With $AlEt_3$ as cocatalyst, the resulting polymer is 1,2-polybutadiene,[77] while the polymer obtained in the $V(acac)_3$—methylaluminoxane system for Al : V = 30 and 1000 contains *trans*-1,4-units (90 [78] and 100%,[76] respectively). At the same time, the stereospecific effect of vanadium systems largely depends on the nature of alkyl in aluminoxane (Table 3).

The *cis*-stereospecific effect is also exhibited by Cp complexes of vanadium in combination with methylaluminoxane. In the presence of the $CpVCl_3$-, Cp_2VCl-, and Cp_2VCl_2-based catalysts at Al : V = 1000, the content of 1,4-*cis*-units in the resulting polybutadiene is 90 to 91%.[66,81] Polyisoprene obtained in the Cp_2VCl—methylaluminoxane system consists of 1,4-*cis*- (82%) and 3,4-units (18%).[76] As for the titanocene systems, the $CpVCl_3$ catalyst containing $Ph_3CB(C_6F_5)_4$-modified $AlEt_3$ is more efficient and stereospecific than the $CpVCl_3$—methylaluminoxane system. The highest yield of polybutadiene is attained at B : V = 1.3 to 1.5 (catalyst is inactive without the borate) and $AlEt_3$: V = 200, while methylaluminoxane : V should be 1000 for this effect to be produced.[66,81] The resulting polybutadiene contains 1,4-*cis*- (90.3%), 1,4-*trans*- (1.3%), and 1,2-units (8.4%); $M_w = 2.03 \cdot 10^6$, $M_w/M_n = 2.80$. Supposedly, active sites contain cations $[CpV - Me]^+$.[76]

Variation of active site types in Ziegler—Natta systems with cocatalyst nature

Different types of active sites are known in Ziegler catalysts[82] for catalytic systems containing structurally different cocatalysts (both initial and formed *in situ* from its components). The probable formation of several types of active sites differing in stereospecific effect can be, among other things, responsible for the effect of the relative content of OAC on the polymer microstructure. Variation in the nature and amount of a cocatalyst can give rise to

Table 3. Dependence of the polydiene microstructure on the composition of the catalytic $V(OR)_4$—aluminoxane systems

Diene	OR	R´	Al : V	Polymer microstructure (%)				References
				1,4-*cis*-units	1,4-*trans*-units	1,2-units	3,4-units	
C_4H_6	OBu^t	Me	10	55	0	45	—	79
C_4H_6	OPr^i	Bu^i	50	30	0	70	—	80
C_5H_8	OBu^t	Me	10	0	5	15	80	79
C_5H_8	OPr^i	Bu^i	100	10	3	27	60	80

Note. R´ is the alkyl group in aluminoxane.

different active sites: (1) OAC structure affects the completeness of removal of ligand L from the coordination sphere of the transition metal in $LnCl_3 \cdot 3L$ complexes;[9] (2) lanthanide in $Ln(OR)_3—AlR'_nHal_{3-n}—AlR'_3$ [7] or $LnCl_3 \cdot 3L—AlR_3$ systems is differently halogenated or alkylated, respectively;[83] (3) cocatalyst structure is changed by reactions between the components of the $Nd(OCOR)_3—AlR'_3$ system;[22] and (4) active sites involve derivatives of different main group metals in the $Nd(OCOR)_3—AlR'_nHal_{3-n}—MgR''_2$ system.[41] For systems based on reducible *d* elements, variation in the nature and amount of a cocatalyst can result in the generation of active sites containing the transition metal in different oxidation states.[4]

The Monte-Carlo method was used to investigate[84] the generation of active sites in heterogeneous Ziegler catalysts prepared by reactions of α-(β-, γ-, and δ-)$TiCl_3$, $CrCl_3$, $CoCl_3$, and $TiCl_2$ with Mg, Zn, Al, and Be alkyl halides. The fractions of structurally different active sites were estimated. It was shown that the molecule of a cocatalyst (*e.g.*, OAC) can either be fixed at the catalyst surface or freely change its position, depending on the catalytic system. During physical adsorption of OAC at the surface of titanium or vanadium trichlorides, active sites are generated and distributed by composition and stereoregulating effect. Since the polymerization active sites are unstable and not numerous, it is difficult to estimate their true distribution in Ziegler—Natta catalysts, *viz.*, to determine the number, kinetic parameters, and stereospecific effect of each type of the active sites.

Quantum-chemical calculations showed[85] that diene polymerization initiated by lanthanide catalysts can involve at least six types of active sites differing in the nearest environment of the lanthanide atom (in the content of Cl and C atoms), the amount of the Ln—C bonds involved in polymer chain growth, and the stereospecific effect. The ratio between these sites depends on the nature and concentration of a cocatalyst. When a catalyst contains several types of active sites, the molecular weight distribution (MWD) of the resulting polymer should broaden.

The authors[86] proposed to use Tikhonov´s regularization method[87] to find the active site distribution function from the probability of macrochain termination, which is calculated from the total MWD of the polymer. This method was applied to diene polymerization in the $NdCl_3 \cdot 3(BuO)_3PO—OAC$ systems.[88] It was found, with the use of experimental MWD curves of polybutadiene, that the process involves four types of active sites differing in the ratio between the rate constants of the chain growth and chain transfer, irrespective of the starting diene and polymerization conditions. Both this ratio and the number of active sites of each type depend on the OAC structure. The regularization method was also used to study the effect of the OAC nature on the kinetic heterogeneity of active sites in vanadium-containing catalysts for butadiene polymerization. With any cocatalyst in the $VOCl_3—AlBu^i_2X$ system (X = Bu^i, Cl, or H), polymerization involves three types of active sites differing in the MW of the resulting polybutadiene. Only in the case of $AlBu^i_2H$ under certain conditions, active sites of the fourth type are involved. The kinetic activity of sites of different types depends on the OAC nature and polymerization conditions;[89] *e.g.*, the polybutadiene microstructure noticeably varies with the Al : V ratio. The relative contribution from each type of active sites to the overall polymerization can be estimated by comparatively analyzing the dependences of the efficiency and stereospecific effect of catalytic systems on various factors and the conventionally determined constants of elementary polymerization steps, on the one hand, and data on the changed calculated distribution curves of active sites in kinetic activity, on the other hand. This was done for the $NdCl_3 \cdot 3(BuO)_3PO—AlBu^i_3$ [88] and $VOCl_3—OAC$[90] systems in butadiene polymerization.

Thus, organic derivatives of main group metals in Ziegler catalysts fulfill various functions (complexing, alkylating, halogenating, or reducing agent; ligand in an active site; stabilizer of an active site; chain transfer agent; *etc.*) during both the active site generation and polymerization. This is manifested by the noticeable effect of the nature of the main group element, the structure of substituents in the cocatalyst, the way of introducing this derivative into a catalytic system, and its concentration on the yield and molecular parameters of polydienes. A variety of types of active sites based on the same transition metal is partly associated with the nature of an organic derivative of a main group metal.

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References

1. I. J. Boor, *Ziegler Natta Catalysis and Polymerization*, Academic Press, New York—San Francisco, 1979, 660.
2. Yu. B. Monakov and G. A. Tolstikov, *Kataliticheskaya polimerizatsiya 1,3-dienov* [*Catalytic Polymerization of 1,3-Dienes*], Nauka, Moscow, 1990, 211 (in Russian).
3. *The Stereo Rubber*, Ed. W. M. Saltman, Wiley, New York, 1977, 492.
4. N. M. Chirkov, P. E. Matkovskii, and F. S. D´yachkovskii, *Polimerizatsiya na kompleksnykh metalloorganicheskikh katalizatorakh* [*Polymerization on Complex Organometallic Catalysts*], Khimiya, Moscow, 1976, 416 (in Russian).
5. D. H. Lee and T. O. Ahn, *Polymer*, 1988, **29**, 713.
6. G. Ricci, S. Italia, F. Cabassi, and L. Rorri, *Polym. Commun.*, 1987, **28**, 223.

7. Yu. B. Monakov, Ya. Kh. Bieshev, A. A. Berg, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR*, 1977, **234**, 1125 [*Dokl. Chem.*, 1977 (Engl. Transl.)].
8. I. G. Savel´eva, Ph.D. (Chem.) Thesis, Inst. Khim. BFAN SSSR, Ufa, 1982, 148.
9. Yu. B. Monakov, N. G. Marina, O. I. Kozlova, F. Ya. Kanzafarov, and G. A. Tolstikov, *Dokl. Akad. Nauk SSSR*, 1987, **292**, 405 [*Dokl. Chem.*, 1987 (Engl. Transl.)].
10. A. A. Sanyagin and V. A. Kormer, *Dokl. Akad. Nauk SSSR*, 1985, **283**, 1209 [*Dokl. Chem.*, 1985 (Engl. Transl.)].
11. V. G. Kozlov, K. V. Nefed´ev, N. G. Marina, Yu. B. Monakov, A. V. Kuchin, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR*, 1988, **299**, 652 [*Dokl. Chem.*, 1988 (Engl. Transl.)].
12. S. V. Bubnova, A. I. Tverdov, and V. A. Vasil´ev, *Vysokomol. Soedin., Ser. A*, 1988, **30**, 1374 [*Polym. Sci. USSR*, *Ser. A*, 1988, **30** (Engl. Transl.)].
13. Yu. B. Monakov, N. G. Marina, and G. A. Tolstikov, *Polymery*, 1989, **34**, 263.
14. Yu. B. Monakov, N. G. Marina, and G. A. Tolstikov, *Chemia Stosowana*, 1988, **32**, 547.
15. Yu. B. Monakov, Ya. Kh. Bieshev, A. A. Berg, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR*, 1977, **234**, 1125 [*Dokl. Chem.*, 1985 (Engl. Transl.)].
16. Y. Jin and Y. Sun, *J. Ouyang*, *Gaofenxi Tongxun*., 1984, 358; *Chem. Abstr.*, 1985, **102**, 185562a.
17. Z. G. Shamaeva, N. G. Marina, Yu. B. Monakov, and S. R. Rafikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 846 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1982, **31** (Engl. Transl.)].
18. Pat. 02-60907 Jpn, 1990; *Chem. Abstrs.,* 1990, **113**, 600078t.
19. D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann, and M. Visseaux, *Eur. J. Inorg. Chem.*, 2000, 2333.
20. V. S. Bodrova, E. P. Piskareva, L. F. Shelokhneva, and I. A. Poletaeva, *Vysokomol. Soedin., Ser. A*, 1998, **40**, 1741 [*Polym. Sci., Ser. A*, 1998, **40** (Engl. Transl.)].
21. D. J. Wilson, *Polym. Int.*, 1996, **39**, 235.
22. E. I. Tinyakova, N. N. Kostitsyna, O. K. Sharaev, and G. N. Bondarenko, *Vysokomol. Soedin., Ser. B*, 2002, **44**, 1582 [*Polym. Sci., Ser. B*, 2002, **44** (Engl. Transl.)].
23. N. N. Chigir, O. K. Sharaev, E. I. Tinyakova, and B. A. Dolgoplosk, *Vysokomol. Soedin., Ser. B*, 1983, **25**, 47 [*Polym. Sci. USSR*, *Ser. B*, 1983, **25** (Engl. Transl.)].
24. L. Porri, A. Giarrusso, and G. Ricci, *Macromol. Chem., Macromol. Symp.*, 1993, **66**, 231.
25. R. Taube, H. Windisch, S. Maiwald, and H. Hemling, *J. Organomet. Chem.*, 1996, **512**, 49.
26. S. Kaita, Z. Hou, and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 9078.
27. L. Cui, X. Ba, H. Teng, L. Ying, K. Li, and Y. Jin, *Polym. Bull.*, 1998, **40**, 729.
28. B. A. Dolgoplosk, E. I. Tinyakova, N. N. Stefanovskaya, I. A. Oreshkin, and V. L. Shmonina, *Eur. Polym. J.*, 1974, **10**, 605.
29. J. Cihlar, J. Mejzlik, O. Hamrik, P. Hudec, and J. Majer, *Macromol. Chem. Phys.*, 1981, **182**, 1127.
30. N. G. Marina, N. V. Duvakina, Z. M. Sabirov, V. S. Glukhovskoi, Yu. A. Litvin, and Yu. B. Monakov, *Vysokomol. Soedin., Ser. B*, 1997, **39**, 163 [*Polym. Sci., Ser. B*, 1997, **39** (Engl. Transl.)].
31. H. L. Hsieh and H. C. Yeh, *Rubber Chem. Technol.*, 1985, **56**, 117.
32. E. N. Zavadovskaya, O. K. Sharaev, G. K. Borisov, Yu. P. Yampol´skii, E. I. Tinyakova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1984, **274**, 333 [*Dokl. Chem.*, 1984 (Engl. Transl.)].
33. K. H. Thiele, R. Opitz, and E. Kohler, *Z. Anorg. Allg. Chem.*, 1977, **435**, 45.
34. Yu. B. Monakov, N. G. Marina, N. V. Duvakina, and V. L. Zolotarev, *Vysokomol. Soedin., Ser. A*, 1997, **39**, 787 [*Polym. Sci., Ser. A*, 1997, **39** (Engl. Transl.)].
35. D. K. Jenkins, *Polymer*, 1985, **26**, 152.
36. Pat. 4 931 376 USA, 1990.
37. L. Xu, J. Hu, C. Zhong, and X. Tang, *Petrochem. Technol.*, 1993, **22**, 799.
38. S. Zhuang, W. Qiu, and Z. Huang, *J. Fudan Univ. Nat. Sci.*, 1993, **32**, 98; *Ref. Zh., Khim.*, 1994, 1 C111 [*Abstr. J., Chem.* (in Russian)].
39. Y. Jin, F. Li, F. Wang, and Y. Sun, *Macromolecules*, 1994, **27**, 4397.
40. V. I. Valuev, A. S. Estrin, R. A. Shlyakhter, I. V. Garmonov, A. S. Khachaturov, and E. E. Avstriiskaya, *Vysokomol. Soedin., Ser. B*, 1978, **20**, 512 [*Polym. Sci. USSR*, *Ser. B*, 1978, **20** (Engl. Transl.)].
41. N. Kh. Minchenkova, Ph.D. (Chem.) Thesis, Inst. Khim. BFAN SSSR, Ufa, 1978, 140.
42. W. Marconi, A. Mazzei, S. Cucinella, and M. de Malde, *Macromol. Chem.*, 1964, **71**, 118.
43. W. Marconi, A. Mazzei, S. Cucinella, and M. de Malde, *Macromol. Chem.*, 1964, **71**, 134.
44. A. Balducci, M. Bruzzone, S. Cucinella, and A. Mazzei, *Rubber Chem. Technol.*, 1975, **48**, 736.
45. W. Marconi, A. Mazzei, S. Cucinella, and M. de Malde, *Chim. Ind.*, 1962, **44**, 121.
46. Pat. 38 072 Jpn, 1970; *Chem. Abstr.*, 1971, **74**, 88523.
47. Pat. 1 550 042 France, 1968.
48. Pat. 38 073 Jpn, 1970; *Chem. Abstr.*, 1971, **74**, 65253.
49. J. Furukawa, T. Tsuruta, T. Saegusa, A. Onishi, A. Kawasaki, and T. Fueno, *J. Polym. Sci.*, 1958, **28**, 450.
50. Pat. 3 901 865 USA, 1975.
51. W. Cooper and G. Vaughan, *Progr. Polym. Sci.*, 1967, **1**, 91.
52. V. A. Khodzhemirov, E. V. Zabolotskaya, A. R. Gantmakher, and S. S. Medvedev, *Vysokomol. Soedin., Ser. A*, 1971, **13**, 329 [*Polym. Sci. USSR*, *Ser. A*, 1971, **13** (Engl. Transl.)].
53. E. Schoenberg, D. L. Chalfant, and T. L. Hanlon, *Adv. Chem. Ser.*, 1966, **52**, 7.
54. Yu. B. Monakov, S. R. Rafikov, G. A. Tolstikov, N. G. Marina, N. Kh. Minchenkova, and I. G. Savelieva, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 2697.
55. C. Vyroubal and J. C. Trneny, *Collect. Czech. Chem. Commun.*, 1968, **33**, 2983.
56. N. G. Marina, Yu. B. Monakov, S. R. Rafikov, and V. I. Ponomarenko, *Usp. Khim.*, 1983, **25**, 2103 [*Russ. Chem. Rev.*, 1983, **25** (Engl. Transl.)].
57. L. S. Bresler, K. V. Kisin, A. V. Lubnin, and N. N. Marasanova, *Vysokomol. Soedin., Ser. A*, 1983, **36**, 1607 [*Polym. Ssi. USSR*, *Ser. A*, 1983, **36** (Engl. Transl.)].
58. Yu. B. Monakov and I. R. Mullagaliev, *Int. J. Polym. Mater.*, 2001, **50**, 1.
59. B. A. Krentsel´ and L. A. Nekhaeva, *Vysokomol. Soedin., Ser. A*, 1994, **36**, 1607 [*Polym. Sci., Ser. A*, 1994, **36** (Engl.

Transl.)].
60. E. A. Mushina, I. F. Gavrilenko, I. A. Borodina, E. I. Tinyakova, E. M. Antipov, G. N. Bondarenko, Yu. Ya. Podol´skii, V. M. Frolov, M. S. Gabutdinov, and B. A. Krentsel´, *Vysokomol. Soedin., Ser. A*, 1996, **38**, 453 [*Polym. Sci., Ser. A*, 1996, **38** (Engl. Transl.)].
61. H. Jidong, H. Baochem, J. Feng, Z. Jianzhong, and T. Xueming, *China Synth. Rubber Ind.*, 1996, **19**, 37.
62. H. Maciejewska and Z. Wietrzynska-Lalak, *Polymery*, 1989, **34**, 303.
63. E. M. Antipov, E. A. Mushina, I. F. Gavrilenko, B. F. Shklyaruk, I. V. Razumovskaya, S. A. Kuptsov, Yu. Ya. Podol´skii, and M. S. Gabutdinov, *Vysokomol. Soedin., Ser. A*, 1997, **39**, 639 [*Polym. Sci., Ser. A*, 1997, **39** (Engl. Transl.)].
64. L. A. Nekhaeva, S. A. Kuptsov, B. F. Shklyaruk, B. A. Krentsel´, V. M. Frolov, N. A. Konovalenko, I. A. Tikhomirova, and E. M. Antipov, *Vysokomol. Soedin., Ser.* A, 1997, **39**, 1939 [*Polym. Sci., Ser. A*, 1997, **39** (Engl. Transl.)].
65. R. Longo, R. Oliva, A. Proto, and A. Zambelli, *Gazz. Chim. Ital.*, 1996, **126**, 377.
66. M. Suzuki, N. Tsuimoto, J. Yamashita, and S. Ikai, *Int. Symp. on Metallorganic Catalysts for Synthesis and Polymerization*, Hamburg, 1998, 83.
67. S. Ikai, J. Yamashita, Y. Kai, M. Murakami, T. Yano, Y. Qian, and J. Huang, *J. Mol. Catal., A: Chem.*, 1999, **140**, 115.
68. A. Miazawa, T. Kase, and K. Soga, *Polym. Prepr.*, 1999, **40**, 109.
69. Z. Lin Huang, *Acta Polym. Sinica*, 2001, **5**, 580.
70. G. Ricci, S. Italia, A. Giarrusso, and J. Porri, *J. Organomet. Chem.*, 1993, **451**, 67.
71. S. Datta and F. T. Morrar, *Macromolecules*, 1992, **25**, 6430.
72. A. A. Pozdeeva, N. A. Vakhrusheva, I. R. Mullagaliev, V. G. Martsina, R. A. Sadykov, and Yu. B. Monakov, *Zh. Prikl. Khim.*, 1980, **53**, 42 [*J. Appl. Chem. USSR*, 1980, **53** (Engl. Transl.)].
73. Yu. B. Monakov, S. R. Rafikov, N. Kh. Minchenkova, I. R. Mullagaliev, and K. S. Minsker, *Dokl. Akad. Nauk SSSR*, 1981, **258**, 892 [*Dokl. Chem.*, 1981 (Engl. Transl.)].
74. N. N. Sigaeva, E. A. Shirokova, I. A. Ionova, I. R. Mullagaliev, and Yu. B. Monakov, *Zh. Prikl. Khim.*, 2001, **74**, 300 [*Russ. J. Appl. Chem.*, 2001, **74** (Engl. Transl.)].
75. Yu. B. Monakov, I. R. Mullagaliev, and E. Yu. Kharitonova, *Vysokomol. Soedin., Ser. A*, 2002, **44**, 220 [*Polym. Sci., Ser. A*, 2002, **44** (Engl. Transl.)].
76. G. Ricci, A. Panagia, and L. Porri, *Polymer*, 1996, **37**, 363.
77. A. Mazzei, S. Cucinella, and W. Marconi, *Chim. Ind.*, 1969, **51**, 374.
78. G. Ricci, S. Italia, and L. Porri, *Macromol. Chem. Phys.*, 1994, **195**, 1389.
79. L. A. Nekhaeva, I. F. Gavrilenko, S. V. Rykov, V. L. Khodzhaeva, E. M. Antipov, B. A. Krentsel´, V. M. Frolov, N. A. Konovalenko, and I. A. Tikhomirova, *Vysokomol. Soedin., Ser. A*, 1996, **38**, 594 [*Polym. Sci., Ser. A*, 1996, **38** (Engl. Transl.)].
80. L. A. Nekhaeva, V. L. Khodzhaeva, S. A. Kuptsov, V. M. Frolov, B. F. Shklyaruk, N. A. Konovalenko, I. A. Tikhomirova, and E. M. Antipov, *Vysokomol. Soedin., Ser. A*, 2000, **42**, 1344 [*Polym. Sci., Ser. A*, 2000, **42** (Engl. Transl.)].
81. S. Ikai, M. Suzuki, Y. Iwamoto, S. Yuasa, J. Yamashita, M. Murakami, Y. Kai, and T. Yano, *Metallorganic Catalysts for Synthesis and Polymerizations. Recent Results by Ziegler-Natta and Metallocene Investigations*, Ed. W. Kaminsky, Springer, Berlin, 1999, 558.
82. Yu. B. Monakov and N. N. Sigaeva, *Vysokomol. Soedin., Ser. C*, 2001, **43**, 1667 [*Polym. Sci., Ser. C*, 2001, **43** (Engl. Transl.)].
83. Yu. B. Monakov, Z. M. Sabirov, V. N. Urazbaev, and V. P. Efimov, *Vysokomol. Soedin., Ser. A*, 2002, **44**, 389 [*Polym. Sci., Ser. A*, 2002, **44** (Engl. Transl.)].
84. K. S. Minsker, M. M. Karpasas, and A. M. El´yashevich, *Vysokomol. Soedin., Ser. A*, 1990, **32**, 1902 [*Polym. Sci., Ser. A*, 1990, **32** (Engl. Transl.)].
85. Yu. B. Monakov, Z. M. Sabirov, V. N. Urazbaev, and V. P. Efimov, *Vysokomol. Soedin., Ser. B*, 2002, **44**, 1587 [*Polym. Sci., Ser. B*, 2002, **44** (Engl. Transl.)].
86. V. P. Budtov, E. G. Zotikov, E. L. Ponomoreva, and M. I. Gandel´sman, *Vysokomol. Soedin., Ser. A*, 1985, **27**, 1094 [*Polym. Sci. USSR, Ser. A*, 1985, **27** (Engl. Transl.)].
87. A. N. Tikhonov, A. V. Goncharskii, V. V. Stepanov, and A. G. Yagola, *Chislennye metody resheniya nekorrektnykh zadach* [*Numerical Methods of Solving Ill-Conditioned Problems*], Nauka, Moscow, 1990, 232 (in Russian).
88. N. N. Sigaeva, T. S. Usmanov, V. P. Budtov, S. I. Spivak, and Yu. B. Monakov, *Vysokomol. Soedin., Ser. A*, 2000, **42**, 112 [*Polym. Sci., Ser. A*, 2000, **42** (Engl. Transl.)].
89. N. N. Sigaeva, E. A. Shirokova, I. R. Mullagaliev, I. A. Ionova, V. P. Budtov, and Yu. B. Monakov, *Vysokomol. Soedin., Ser. A*, 2000, **42**, 1269 [*Polym. Sci., Ser. A*, 2000, **42** (Engl. Transl.)].
90. N. N. Sigaeva, E. A. Shirokova, I. R. Mullagaliev, and Yu. B. Monakov, *Bashkir. Khim. Zh.*, 2003, **10**, 22.

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