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Relation between the Nature of the Components of Titanium-containing Ziegler Systems and Their Activity and Stereospecificity in the Polymerisation of Dienes

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Problems concerning the influence of ionic-coordination catalytic systems and of the structure of their individual components on their stereospecificity and activity in the polymerisation of dienes are considered in relation to titanium-containing catalysts. Modern ideas about the structure of the active centres and the factors determining their stereoregulating capacity are also examined.
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I. INTRODUCTION

The development of studies on catalytic processes using systems of the Ziegler–Natta type opens up new possibilities for the separation of stereoregular polymers both by employing hitherto uninvestigated monomers and by varying widely the composition and conditions in the formation of the catalyst. The literature on this question is enormous particularly when patents are included. The titanium-containing catalytic systems, which have been most thoroughly investigated and have been most widely used, are convenient systems for examining the influence of the composition of the catalyst on the stereospecificity of the systems and their activity as well as certain kinetic characteristics of the polymerisation of dienes, primarily butadiene and isoprene. These data made it necessary to resort to modern ideas about the structure of the active centres and the factors determining their stereoregulating capacity.

II. THE INFLUENCE OF THE STRUCTURE OF THE COMPONENTS OF TITANIUM CATALYTIC SYSTEMS ON THE CHARACTERISTICS OF THE POLYMERISATION OF DIENES

It is known that, depending on the nature of the transition metal, the polymerisation of dienes in the presence of metal complex catalysts results in the formation of polymers with different stereoregularities. For example, the $TiCl_4$–AlR_3 system (Al : Ti ≅ 1) yields preferentially 1,4-*cis*-polyisoprene[1], while 1,4-*trans*-polyisoprene is formed in the presence of VCl_4–AlR_3.[2]

Catalytic systems based on the same transition metal are also capable of manifesting different stereospecificities. This is primarily because the metal in the active centres of the growing chains ($P-MX_n$) can exist in various valence states and can contain particular groups X at their reaction centre. The state of the active centre also changes when the polymorphic modification of the transition metal compound is varied. Allowance for these factors opens up wide possibilities for the regulation of the stereospecificity of catalytic systems[3] by altering the nature of the transition metal, its valence, and the structure of the ligand X. Thus it has been shown in relation to chromium-containing catalysts[4] that the variation of the ligands makes it possible to realise all the conceivable microstructures of polybutadiene and polyisoprene.

Table 1. The microstructure of polybutadiene obtained in the presence of various titanium-containing catalytic systems.

Catalytic system	Content of units, %			Refs.
	1,4-*cis*	1,4-*trans*	1,2-	
$TiCl_4$–I_2–AlR_2H–AlR_3	95.6	1.2	3.2	[5]
TiI_4–AlR_3	93–95	2–4	2–5	[6–8]
$TiCl_4$–AlI_3–$AlHCl_2 \cdot OR_2$	95	—	—	[9]
$TiCl_3 \cdot L^*$–AlR_2I	94	2	4	[10]
$TiCl_4$–AlR_2I–AlR_3	92.7	—	—	[11]
$TiCl_4$–I_2AlR_3	92	4	4	[12]
TiI_2Cl_2–AlR_3	92	4	4	[3]
Polytitanate-I_2-AlR_3	90	—	—	[13]
$TiBr_4$–AlR_3	85	10	5	[6]
$TiCl_2(CNS)_2$–AlR_3	78	10	12	[14]
$Ti(acac)_3$**–AlI_3–AlR_3	72	23	5	[15]
$Ti(acac)_3$–$AlBr_3$–AlR_3	64	24	12	[15]
$Ti(OR')_4$+$AlRCl_2$(Al : Ti=5)	63.5	34.5	2	[16]
$TiCl_4$–AlR_3(Al : Ti≅1)	55–60	36–41	4	[6, 7, 17, 18]
$TiCl_2(acac)_2$–AlR_3	59	16	25	[14]
$Ti(acac)_3$–$AlCl_3$–AlR_3	53	34	13	[15]
$Ti(acac)_3$–AlR_2Cl	50	38	12	[19]
$TiCl_2(OCOR')_2$–AlR_3(R'>1)	53	15	32	[14]
TiF_4–AlR_3	35	—	—	[20]
$TiCl_2$–AlR_2Cl	32	64	4	[21]
$TiCl_2$–AlR_3	0	94.5	5.5	[21, 22]
$Ti(OR')_4$–$AlRCl_2$(Al : Ti=10)	4	94	2	[16]
$TiCl_4$–AlR_3(Al : Ti≥2)	0	98	2	[18]
$TiCl_3(\alpha, \gamma, \delta)$–$AlR_3$	—	****	—	[23]
$Ti(NR_2')_4$–$AlRCl_2$	—	****	—	[24]
$TiCl_2(OR')_2$–AlR_3	21	31	48	[14]
$TiCl_2(Ind)$***–AlR_3	22	18	60	[14]
$Ti(OR')_4$–AlR_3	2–12	0	88–98	[25]
$Ti(NR_2')_4$–AlH_2NR_2	—	—	89–93	[24]
$Ti(NR_2')_4$–AlR_3	—	—	****	[24]

*L = 2-methyltetrahydrofuran.
**acac = acetylacetone.
***Ind = indenyl.
****The polymer chain consists predominantly of units of the given type.

Such universality is characteristic also of titanium-containing catalytic systems. Titanium systems of the Ziegler type make it possible to obtain highly stereoregular polybutadienes with all possible microstructures (Table 1) and a similar picture is also observed when organometallic titanium compounds are used (Table 2). There are as a rule no 1,2-units in polyisoprene obtained in the presence of titanium systems of the Ziegler type (Table 3). Up to 6–7% of 1,2-units is formed only with benzyl derivatives (Table 4).

Table 2. The microstructure of polybutadiene obtained from titanium-containing compounds with a titanium–carbon bond (R = benzyl; solvent—toluene).

Catalytic system	Content of units, %			Refs.
	1,4-*cis*	1,4-*trans*	1,2-	
R_3TiI	97	1	2	[37—41]
$R_2TiI—AlR_3'$	96	2	2	[41]
$R_3Ti—AlR_2'I$	93	4	3	[41]
R_3TiI	91	7	2	[41]
$RTiI_2—AlR_3'$	90	7	3	[41]
R_3TiI*	81	15	4	[40]
RTiI	68	29	3	[41]
R_3TiBr	66	13	21	[40]
$(CH_3)_3SiCH_2TiCl_3—C_2H_5Li$	64	32	4	[42]
$(ClC_6H_4—CH_2)_4Ti$	60.4	22.2	17.4	[43]
R_2TiCl	54	8	38	[41]
R_3TiCl	35	19	46	[40]
$RTiI_2$	32	55	13	[41]
R_4Ti	26	15	59	[37, 38, 40]
R_3Ti	25	13	62	[44]
tris-π-Pentenyltitanium	—	—	60	[45]
$[(CH_3)_3SiCH_2]_3Ti$	15	18	67	[42]
$[C_3H_5(CH_3)_2SiCH_2]_3Ti$	0	17	83	[42]
$[(CH_3)_3SiCH_2]_4Ti—C_2H_5Li$	0	8	92	[42]
$(CH_3)_3SiCH_2TiCl_3$	—	88.8	—	[46]
$RTiCl_2$	0	90	10	[41]
$R_4Ti—AlCl_3$ (1 : 4)	0	100	0	[43]

*Solvent—hexane.

Table 3. The microstructure of polyisoprene obtained in the presence of various titanium-containing catalytic systems (R,R' = alkyl groups).

Catalytic system	Content of units, %			Refs.
	1,4-*cis*	1,4-*trans*	3,4-	
$TiCl_4—AlR_3$ (Al : Ti≃1)	95—99.5	—	—	[1, 6, 26, 27]
$TiCl_2(acac)_2—AlR_2Cl$	97.5	1.4	1.1	[28]
$Ti(OR')_4—Br_2—AlR_3$	97.1	0	2.9	[29]
$Ti(OR')_4—AlBr_3—AlR_3$	96—97	—	—	[30, 31]
$Ti(OR')_4—AlBr_3—AlR_2Cl$	97	0	3	[32]
$Ti(OR')_4—R_3Al_2Cl_3$	96.5	0	3.2	[33]
$Ti(OR')_4—AlRCl_2$ (Al : Ti=4)	96	0	4	[16, 34]
$TiI_4—AlR_3$	*	—	—	[6]
β-$TiCl_3—AlR_3$	85	0	15	[23]
β-$TiCl_3—AlR_2Cl$	85	0	15	[23]
$Ti(OR')_4—AlRCl_2$ (Al : Ti=10)	58	38	3	[16]
$TiCl_2—AlR_3$	0	88	12	[21]
$TiCl_3$(α, γ, δ)$—AlR_3$	0	91	9	[23, 35]
$Ti(O-t-R')_4-AlRCl_2$	—	*	—	[34]
$TiCl_4—AlR_3$ (Al : Ti=2)	—	*	—	[36]
$Ti(OR')_4—AlR_3$	—	—	93—99	[25]

*The polymer chain consists predominantly of units of the given type.

Table 4. The microstructure of polyisoprene obtained in the presence of titanium-containing compounds with a titanium–carbon bond (R = benzyl, solvent—toluene).

Catalytic system	Content of units, %				Refs.
	1,4-*cis*	1,4-*trans*	3,4-	1,2-	
Tris-π-pentenyltitanium-Al_2O_3	91	0	9	0	[45]
R_3TiI	87	0	13	0	[47]
R_3TiBr	69	0	27	4	[47]
$R_4Ti—Al_2O_3$	60	0	—	—	[48]
Tris-π-pentenyltitanium	24	43	30	3	[45]
R_3TiCl	19	36	39	6	[47]
R_4Ti	0	75	18	7	[47]
R_2TiBr_2	0	94	6	0	[47]

With the exception of piperylene (Table 5), studies on the polymerisation of two conjugated dienes have not been systematic and have not embraced a wide range of catalytic systems. It is therefore difficult to infer the stereoregulating selectivity of titanium systems in relation to these monomers.

Table 5. The microstructure of polypiperylene obtained in the presence of various titanium-containing catalytic systems.

Catalytic system	Content of units, %			Refs.
	cis-	*trans*-	3,4-	
$Ti(OR')_4—AlR_3$	80—85	9—15	3—5	[49—50]
$Ti(OC_{10}H_{19})_4—AlR_3$	73	17	10	[51, 52]
$TiBz_4—AlBz_3—C_{10}H_{19}OH$	66	23	11	[52]
$TiCl_4—AlR_3$	61	36	3	[53]
$TiBz_4—AlR_3$	57	42	1	[54, 55]
$TiBz_4—C_{10}H_{19}OH$	53	35	12	[52]
$CpTiCl_3—AlR_2Cl$	36	63	1	[56]
$TiI_4—AlR_3$	6	92	1	[57]

Notation: R' = alkyl; $C_{10}H_{19}OH$ = methanol; Bz = benzyl; Cp = cyclopentadienyl.

1. The Influence of the Ligand Environment at the Titanium Atom on the Stereospecificity and Activity of the Catalyst

There are at present no experimental data characterising the structure of the active centres of Ziegler catalysts but the specific features of the active centres can be inferred at least comparatively from the microstructures of the polydiene.

Table 1 shows that in the polymerisation of butadiene the titanium-containing system exhibits a high *cis*-regulating capacity only if it incorporates iodine and, for the optimum component ratio, the form in which this element is incorporated in the system is not very significant: in the initial titanium compound (TiI_4, TiI_2Cl_2), in the elemental form (I_2), or as part of the composition of other components (AlI_3, AlR_2I). The benzyl derivatives of titanium provide a remarkable example of the fact that the presence of iodine at the titanium atom in the active centre does not alone ensure a high *cis*-regulating capacity of the catalyst in the polymerisation of butadiene. Thus a sharp difference between the stereospecificities of R'_2TiI (91% of 1,4-*cis*-units) and $R'TiI_2$ (32% of 1,4-*cis*-units) has been observed[41]. It is extremely instructive that, when the $R'TiI_2—AlR_3$ system is judged on the basis of the microstructure of polybutadiene (Table 2), its active centres are apparently identical with those of the R'_2TiI catalyst.

The data on the microstructure of polybutadiene justify the hypothesis that, in all cases where iodine-containing Ziegler systems are used (Table 1), identical active centres are formed with iodine in the coordination sphere of the titanium atom. This is also confirmed by the results of the study of substances formed in the $TiI_4—AlR_3$ and $TiCl_4—I_2—AlR_3$ systems[58]. It has been observed that reduction and halogen exchange reactions take place in the ternary system and that the deposit contains organotitanium(III) iodide. When titanium tetrachloride is reduced by diethylaluminium bromide, the amount of bromine which is added to titanium is also appreciably greater than might have been expected on the basis of the statistical redistribution of the halogens[59]. The ease of replacement of chlorine at titanium by bromine or iodine has also been observed when $TiCl_3$ is treated with certain bromine- and iodine-containing compounds (AlI_3,

$AlRI_2$, AlR_2I, $AlBr_3$, $AlRBr_2$, and AlR_2Br), which is accompanied by a change in the stereospecificity of the action of the $TiCl_3$–AlR_2Cl system[60]. It has been suggested[61] that the ease of halogen exchange between $TiCl_4$ and AlR_2I is due to the fact that the larger titanium ion combines preferentially with the more polarisable (larger in size) iodide ion, while aluminium combines preferentially with the smaller halide ion (the chloride ion).

Judging from the microstructure of polydienes (Tables 1 and 3), such exchange reactions take place in those cases where the initial titanium compound in the catalytic system does not contain a halogen and is an alkoxide, an amide, or an acetylacetonate. Thus when the AlI_3, $AlBr_3$, and $AlCl_3$ additives are introduced into the $Ti(acac)_3$–AlR_3 system[15], the contents of the 1,4-*cis*-units in polybutadiene are 72, 64, and 53% respectively. These results confirm yet again the occurrence of exchange processes and the appearance of a halogen at the titanium atom in the active centre. Judging from the microstructure of polybutadienes[15], the exchange reactions leading to the formation of catalytic complexes based on titanium trihalides do not go to completion. One cannot rule out the simultaneous presence in the system of active centres of different types, particularly in the presence of $AlBr_3$ and $AlCl_3$, which can be inferred from the somewhat high number of 1,2-units in the polymer, characteristic of active centres formed on the basis of titanium compounds with a Ti–O bond.

For a titanium system ensuring a 1,4-*trans*-polymerisation of butadiene and isoprene, the presence of a halogen in a particular component is also obligatory. One should not the $TiCl_4$–AlR_3(Al : Ti > 2), α-, γ-, and δ-$TiCl_3$–AlR_3, and $TiCl_2$–AlR_3 systems, which are highly stereospecific in the *trans*-polymerisation of butadiene and isoprene. However, the appearance of such isotypical regulating capacity regardless of the nature of the monomer is by no means observed in all cases. Thus the $Ti(n\text{-}OR')_4$–$AlRCl_2$ (Al : Ti = 10) system leads to the formation of crystalline 1,4-*trans*-polybutadiene, whereas polyisoprene containing only 38% of the 1,4-*trans*-units is formed under the same conditions[16]. With decrease of the Al : Tl ratio to 4–6, the above system becomes *cis*-regulating in relation to isoprene and yields polybutadiene with a mixed microstructure.

Data on the chemical analysis and X-ray diffraction of the products of the reaction between $Ti(n\text{-}OR')_4$ and $AlRCl_2$ showed that, for Al : Ti = 4, the insoluble component consists almost entirely of β-$TiCl_3$ crystals[16]. NMR data have led to the conclusion that the exchange reaction $Ti(OR')_4 + AlRCl_2 \rightarrow TiCl_4 + AlR(OR')Cl$ takes place in the homogeneous phase and precedes the reduction of titanium. The EPR spectrum of the reaction mixture in which insoluble compounds have already been formed shows a broad signal with a *g*-factor of 1.959, which has been attributed to titanium(III) chloride with an adsorbed aluminium alkyl. Consequently, active centres identical in their structure to those in the $TiCl_4$–AlR_3. .(Al : Ti ≅ 1) catalytic system are formed in the $Ti(n\text{-}OR')_4$–$AlRCl_2$ system with the ratio Al : Ti ≅ 4. This is also supported by the microstructures of polybutadiene and polyisoprene formed in such cases.

An unusual feature of the $Ti(OR')_4$–$AlRCl_2$ systems consists in the dependence of their stereospecificity and the nature of the group OR' and the solvent[34]. Titanium tetraalkoxides with both linear and branched primary substituents form *cis*-regulating systems regardless of the nature of the solvent, while titanates with tertiary substituents lead to the formation of *trans*-polyisoprene. The most interesting results have been obtained for titanates with secondary substituents: *cis*-polyisoprene is formed in aliphatic solvents, while the use of aromatic solvents results in the inversion of the stereospecificity and the formation of *trans*-polyisoprene. The results of the study of these systems in various solvents by EPR have been interpreted[34] as evidence for the formation of crystalline α- or β-modifications of $TiCl_3$, because the structure of the titanates in solution (monomeric or polymeric form) is influenced both by the structure of the substituent OR' and by the nature of the solvent[62]. In all cases where the initial alkoxide has the polymeric form, 1,4-*cis*-polymerisation takes place and the monomeric alkoxides lead to the formation of 1,4-*trans*-polyisoprene. The Ti–Ti bonds are shorter for the polymeric form of the alkoxides and it is believed[34] that, after the reaction with $AlRCl_2$, the difference is maintained, which is consistent with various modifications of $TiCl_3$ in which the distances between the titanium atoms are 3.54 and 2.91 Å for the α- and β-forms respectively[63]. In other words, the "seed" for the formation of the α- and β-forms of $TiCl_3$ is already present in the initial solution of the alkoxide and predetermines the stereospecificity of the $Ti(OR')_4$–$AlRCl_2$ catalyst.

Presumably analogous $TiCl_3$ formation reactions occur also in the $Ti(NR'_2)_4$–$AlRCl_2$ systems[24].

The presence of a halogen at the titanium atom is not always obligatory for the formation of a polydiene having a predominantly 1,4-structure. Thus 1,3-pentadiene gives rise to an isotactic polymer containing mainly 1,4-*cis*-units in the presence of the $Ti(OR')_4$–AlR_3 systems[50]. On the other hand, the use of a titanium halide does not always ensure the formation of 1,4-polydiene either. The polymerisation of 4-methylpenta-1,3-diene in the presence of the $TiCl_4$–AlR_3 or α-$TiCl_3$–AlR_3 systems leads to the formation of a crystalline polymer having the 1,2-structure; the $Ti(OR')_4$–AlR_3 system likewise gives rise to the 1,2-polymer but this is amorphous[64].

Thus, while there is an abundance of different varieties of highly stereospecific titanium systems, the set of active centres formed (not only as regards the selectivity of their action but also their composition and structure) is apparently much narrower. The results which might have confirmed directly the identity of active centres in many systems are so far not available. Nevertheless data on the microstructures of polydienes, the interaction of the system components, and the compositions of the corresponding products justify this conclusion. The data accumulated on various titanium systems confirm yet again the view[65] that there are no "specialised" atoms or groups responsible for the stereospecificity in the polymerisation of dienes in the presence of metal complex catalysts. Because of this, catalytic systems in fact manifest a wide variety of stereoregulating capacities, particularly when the monomer is varied. This feature hinders significantly the search for ways of regulating the stereospecificity of these catalysts. Nevertheless, certain characteristics can be traced fairly clearly. In the first place this concerns the influence of halogens on the stereospecificity.

The nature of the halogen in the $TiHal_4$–AlR_3 systems determines the microstructure of polybutadiene: the content of *cis*-units is a maximum for iodine-containing systems and a minimum for fluorine-containing systems. The decrease in the number of *cis*-units is then caused by the increased amount of *trans*-structures, while the fraction of 1,2-units hardly changes. The stereoregulating capacity of monohalide derivatives of tetrabenzyltitanium also depends on the nature of the halogen. As in systems of the Ziegler type, the maximum number of *cis*-units are formed in the presence of iodine-containing derivatives (Table 2). However, in this case the decrease of the number of *cis*-units in the macrochains corresponding to the series of iodine-, bromine-, and chlorine-containing catalysts occurs primarily due to the increase of the fraction of 1,2-units. The absence of a halogen in titanium derivatives with a Ti–C bond (Table 2) leads to the formation of a polymer in which 1,2-units predominate

and, as can be seen from the microstructure of polybutadiene obtained in the presence of $(ClC_6H_4-CH_2)_4Ti$,[43] the preferential 1,2-combination of units requires the obligatory presence of the Ti–Hal bond. The introduction of chlorine into the aromatic ring also alters significantly the stereoregulating capacity of tetrabenzyltitanium. The results obtained in the polymerisation of butadiene in the presence of systems of the Ziegler type based on $TiCl_2(OCOCCl_3)_2$ and $TiCl_2(OCOCF_3)_2$ are also consistent with this[14]. The contents of the *cis*-units in the polymer are then 60 and 38% respectively, while the number of 1,2-units remains at the same level. Thus the halogen has an appreciable influence on the stereoregulating capacity of the catalyst by altering the electron density on titanium also when the latter is part of the titanium component but is not directly involved in a Ti–Hal bond.

One must note that the influence of the nature of the halogen on the stereospecificity of titanium systems in the polymerisation of butadienes differs somewhat from that in systems with other transition metals (V, Cr, Co, Ni, Mn, Fe). The effects of these metals (M) have been compared in the $M(acac)_n-AlR_3-AlX_3$ (X = Cl, Br, or I) systems; the content of 1,4-*cis*-units in polybutadiene increases in all cases, except for titanium, in the sequence Cl > Br > I, other conditions being equal[15]. It was established[15] that the content of 1,4-*cis*-units in polybutadiene obtained in the presence of titanium systems decreases linearly with increasing electron affinity (*eV*) of the halogen present in the system. In compounds of other metals (V, Cr, Co, Ni) a direct relation is observed between *eV* and the content of units with the *cis*-structure in polybutadiene. The unusual behaviour of titanium has also been noted[66] in the study of the NMR spectra of halide derivatives of biscyclopentadienyltitanium: the opposite sequence was observed for the halogens when the apparent energies of the abstraction of electrons from the titanium atom were estimated.

The data presented in Table 6 confirm that the influence of the halogen on the stereospecificity of ionic-coordination systems is varied and is determined by the nature of the transition metal. Only the stereospecificity of systems based on *f* elements is independent of the nature of the halogen.

Table 6. The influence of the nature of the halogen on the stereoregularity of the polybutadiene obtained in the presence of catalytic systems containing halogeno-derivatives of *d* and *f* elements.

Halogen	Content of 1,4-*cis*-units				
	Ti	Co [67]	Ni [67]	Nd [68]	U [69]
F	35	93	98	95.7	—
Cl	55	98	85	96.2	99.0
Br	85	91	80	96.8	98.5
I	95	50	10	96.7	98.5

Note. The microstructure of polybutadiene obtained in the presence of the $TiHal_4-AlR_3$ systems is indicated in accordance with the data in Table 1.
The numbers in square brackets denote references (Ed. of Translation).

Sharp differences between the microstructures of the polymer have not been observed as a function of the halogen in the polymerisation of isoprene in the presence of titanium systems of the Ziegler type. However, in the presence of tetrabenzyltitanium monohalide derivatives (Table 4) the overall variation of the number of units with the *cis*-structure in polyisoprene on passing from iodine-, to bromine-, and chlorine-containing derivatives is consistent with the relation observed in the polymerisation of butadiene in the presence of the same compound.

The replacement of the halogen atoms in $TiHal_4$ by substituents of another chemical type alters significantly the stereoregulating capacity of the catalytic systems. Individual examples of this are presented in Tables 1, 3, and 5. The replacement of the Ti–Hal bonds in the titanium component by Ti–O bonds increases the contribution of the 1,2-addition in polybutadiene. Thus the contents of the 1,2-units in the polymers for systems based on $TiCl_4$, $TiCl_2(OCOCH_3)_2$, and $TiCl(OCOCH_3)_3$ are 14, 21, and 42% respectively[14]. The same type of variation is manifested in the $TiCl_4$, $TiCl_2.(OC_4H_9)_2$, and $Ti(OC_4H_9)_4$ series—14, 48, and 73% of 1,2-units respectively[14]. A sharp decrease in the rate of polymerisation is observed in the series indicated. The step involving the addition of 1,2-units takes place approximately 300 times more slowly than for the 1,4-*cis*-units, which is indicated by a comparison of the rate constants for the chain propagation of polybutadiene when catalytic systems based on $Ti(OR')_4$ and TiI_2Cl_2 are used[70].

Data obtained for systems based on dichloroacetoxytitanium derivatives have shown that the content of 1,4-*cis*-units in polybutadiene diminishes with increase of the electronegativity of the acido-ligand[14]. An analogous picture has been noted also for titanium dichloride derivatives containing the anions of butyric acid or its chloro-derivatives. In all these cases the content of 1,4-*cis*-units diminishes due to the formation of *trans*-structures, while 1,2-addition in the chain is maintained at the same level regardless of the presence and nature of the halogen in the acido-ligands.

Presumably the change in the chemical nature of the substituents at the transition metal atom (and not the accompanying steric factors, which nevertheless must be taken into account) have in fact the primary influence on the catalytic characteristics of the active centres. Thus an increase in the length or bulk of the substituent of one chemical type at the titanium atom does not affect the stereospecificity of the catalyst[14,70]. It has been shown for the $Ti(OR')_4-AlR_3$ systems[70] that, when the substituents R' are varied within a homologous series, the microstructure of polybutadiene and the rate constant for chain propagation do not vary. The reactivity of the active centres is maintained, but the reactivity of the systems diminishes with increase in the size of R' as a result of the decrease of the number of these centres, the latter being related primarily to the steric hindrance in the interaction of the components of the catalytic system.

In considering the possibility of regulating the stereospecificity of catalytic systems of the ionic coordination type, one must also deal with results obtained in the study of these systems in the presence of modifying electron-donating additives. The nature of the variation of the stereospecificity of Ziegler systems following the introduction of an electron donor is determined by the nature of the transition metal. It has been shown for the $M(acac)_n-AlR_2Cl$ (M = V, Cr, Co, Ni, Ti) systems[19] that the influence of bases is most notable for the titanium systems; the extent of the changes in the microstructure is smallest when bases are introduced into a nickel-containing system.

The introduction of ethers, thioethers, and tertiary amines into the highly stereospecific *cis*-regulating TiI_4-AlR_3 system impairs the microstructure of polybutadiene as a result of the increase of the content of the 1,4-*trans*-unit, while the number of 1,2-units hardly changes[71,72]. The influence of ethers on the microstructure of the polymer varies in the sequence dimethyl ether > ethyl methyl ether > diethyl ether > dibutyl ether, which agrees with the variation of the capacity of the ethers for complex formation. A similar picture has been

observed also after the introduction of electron donors into another *cis*-regulating system: $TiCl_4$–AlI_3–$AlHCl_2OR_2$.[9] The content of the *trans*-units in polybutadiene reaches 80% (without change in the content of the 1,2-structures) when amines are introduced into the $TiCl_4$–AlR_3 system[73], which gives rise to a polymer with a mixed microstructure in the absence of these additives. With the aid of electron donors, it is sometimes possible to achieve the almost complete inversion of the stereospecificity of the catalyst. Thus the addition of tetrahydrothiophen to the $TiCl_3.3AlI_3$–AlR_3 system leads to the formation of polybutadiene containing 88% of the 1,4-*trans*-units, while in the absence of a Lewis base the system exhibits a high *cis*-regulating capacity[74].

The addition of electron donors to systems based on titanium halides does not alter the ratio of the sums of 1,4-units and 1,2-units in the polybutadiene chain but drives the process towards a more intense formation of the 1,4-*trans*-units. On the basis of the concept of the *anti–syn* isomerisation of the terminal unit[75], it has been suggested that bases displace the equilibrium towards the formation of the *syn*-complex responsible for the appearance of units with the *trans*-structure in the chain.

The influence of the structure of the electron donors on the stereospecificity of the $TiCl_4$–AlR_2 systems in the polymerisation of isoprene has been traced[76] in relation to a series of tetra-alkyldiamines and, by altering the amount of *N,N,N',N'*-tetramethyldiamino-4,4'-diphenylmethane, it has been possible to regulate smoothly the stereospecificity of the system.

In contrast to the *cis*-regulating halogen-containing titanium systems of the Ziegler type, the addition of electron donors to tribenzyltitanium iodide in toluene enriches polybutadiene in the 1,2-units and polyisoprene in the 3,4-units[40,47].

Table 7. Dependence of the stereospecificity of systems based on titanium tetrachloride on the nature of the cocatalyst in the polymerisation of isoprene.

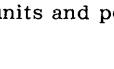
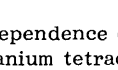
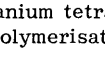
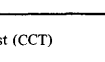
Cocatalyst (CCT)	CCT : $TiCl_4$	1,4-*cis*-units, %	Refs.
AlR_3	⩾1	95—99.5	[1, 6, 26, 27]
$AlH(Hal)_2 \cdot O(C_2H_5)_2$	1.5—2.2	95—96	[77]
$AHCl_2 \cdot NR_3$	1.4—1.7	95—96	[78]
$AlH_2Cl \cdot NR_3$	0.5—0.6	96	[78]
$AlH_3 \cdot NR_3$	0.35—0.5	94—95	[78]
$AlH_2(NR_2)$	0.55—0.7	95—96	[78]
$AlH_2(OR) \cdot N(CH_3)_3$	0.6—0.7	94—96	[78]
Polyiminoalanes	1.4—1.8	94—96	[79, 80]
AlR_2F	2—50	96	[81]
$[Ca(C_2H_5)_2]_n \cdot Zn(C_2H_5)_2$	0.6—1.5	95—96	[82]
R_3SnH	⩾1	95—97	[83, 84]
$R_3SiOR'—AlR_2''Cl$	0.5—1	97	[85]
$R_3SnH—AlR_2'Cl$	0.5—6.0	97	[86]
$R_3SnH—AlBr_3$	2—4	95.4	[87]
CdR_2	0,5	90	[88]
AlB_3H_{12}	0.7—1.5	80	[89]
MgR_2	0.8	75	[90]

2. The Influence of the Nature of the Organometallic Component on the Activity and Stereospecificity of the Catalyst

Mainly organic derivatives of Group I–III metals are used as the organometallic components (cocatalysts) in Ziegler systems. Despite the wide variety of cocatalysts, organoaluminium compounds (OAC) are most widely used in the polymerisation of butadiene and isoprene. Although the presence of a cocatalyst is not always obligatory for the occurrence of ionic-coordination polymerisation, it can have a significant influence on the process characteristics.

The microstructure of the polyisoprene obtained in the presence of titanium tetrachloride (Table 7) does not depend significantly on the nature of the organometallic compound, *cis*-polymerisation occurring in all cases. A distinctive feature of systems based on the OAC is their high catalytic activity combined with a high stereoregulating capacity (Tables 7 and 8).

Table 8. The influence of the nature of the organoaluminium compound on the microstructure of polydienes ($TiCl_4$ and TiI_2Cl_2 catalysts for isoprene and butadiene respectively)[91].

No.	OAC	Content of 1,4-*cis*-units, %	
		polybutadiene	polyisoprene
1	Al (iso-C_4H_9)$_3$	91	95
2	Al (C_7H_{15})$_3$	90	96
3	Al ($C_{10}H_{21}$)$_3$	90	96
4	Al ($C_{15}H_{31}$)$_3$	91	96
5	Al 	90	96
6	Al	90	95
7	Al 	92	96
8	Al 	92	95
9	Al 	—	97
10	Al 	91	96
11	OAC based on 1,2-polybutadiene	92	96
12		92	97
13	(iso-C_4H_9)$_2$Al—N (C_2H_5)$_2$	93	96
14	(iso-C_4H_9)$_2$Al—N	92	—
15	(iso-C_4H_9)$_2$Al—N	91	—
16	[(CH$_3$)$_3$Si—CH—]$_2$Al—CH_2Si (CH$_3$)$_3$	92	97
17	(iso-C_4H_9)$_2$Al—C≡C—C_6H_5	92	96

The role of electron-donating additives has been adequately elucidated. In many cases they (for example, water and alcohols) can react both with the transition metal compound and with the organometallic cocatalyst. On the other hand, the main cause of the effect of bases on the stereospecificity of the system is probably associated with their ability to be coordinated to the transition metal atom, to alter its ligand environment (electron density), and consequently to influence the reactivity of the active centre.

Aluminium tetrahydroborate and organomagnesium compounds are least stereospecific as cocatalysts in the polymerisation of isoprene. In their presence, low-molecular-weight polymers containing not more than 80% of *cis*-units are obtained. The polymerisation of butadiene in the presence of TiI_4, TiI_2Cl_2, and organomagnesium cocatalysts[92,93] involves the formation of polymers whose stereoregularity is as high as that of the polymers obtained using AlR_3. Organosilicon and organotin compounds occupy a special place among cocatalysts

(Table 7). They permit the use of a wide range of component ratios of the catalytic system, but the molecular weight of the polymers is low. Cocatalysts based on polyiminoalanes $[-AlH-NR-]_n$ [80] cause a rapid polymerisation of the diene and the polymers obtained under these conditions exhibit a high stereoregularity and have high molecular weights and a low content of the gel fraction. The activity of polyiminoalanes as cocatalysts in the polymerisation of isoprene in the presence of $TiCl_4$ depends on the structure of the group R, the greatest activity being attained for groups with a secondary carbon atom in the α- or β-position relative to the nitrogen atom.

More detailed data are available concerning the influence of the structure of the OAC on the characteristics of the catalytic systems for the polymerisation of dienes. In the first place one should note that a change in the structure (chain length, degree of branching, degree of cyclisation, and degree of unsaturation) of the hydrocarbon groups in AlR_3 does not entail a change in the stereospecificity of the catalytic system (as shown in experiments using titanium halides and tetraalkoxides[91,94–97]). The replacement of alkyl groups by groups containing heteroatoms (N, O, Si) is also not reflected in the microstructure of polydienes (Table 8). However, in contrast to their stereoregulating capacity, the activity of titanium systems in the polymerisation of both butadiene and isoprene depends significantly on the structure of the group in the organoaluminium component. The following main characteristic features have been discovered.

With increased length of the alkyl group within the limits of the homologous series of the OAC, the rate of polymerisation initially rises and then tends (Fig. 1) to a limiting value for OAC in which the chain length of the group exceeds C_{12}.[91,94–97] Here the region of catalytic activity shifts (Fig. 2) towards higher Al : Ti ratios with increase in the size of R.[91,96,97] AlR_3 with branched alkyl groups are more reactive than those with linear groups. However, among OAC with substituents having the iso-structure the activity also increases with increase of the number of carbon atoms in the group[94].

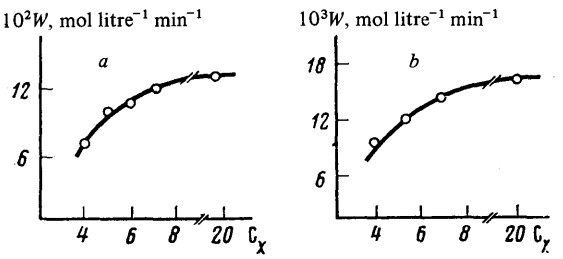


Figure 1. Dependence of the rate of polymerisation W of butadiene in the presence of TiI_2Cl_2–AlR_3 (*a*) and isoprene in the presence of $TiCl_4$–AlR_3 (*b*) on the number of carbon atoms C_X in the alkyl group R; solvent–toluene; t = 20 °C; $[TiI_2Cl_2] = 1.5 \times 10^{-3}$ M; $[TiCl_4] = 2.7 \times 10^{-3}$ M; $[C_4H_6]$ = 0.82 M; $[iso\text{-}C_5H_8]$ = 1.0 M.[91]

For the same number of carbon atoms, the rate of polymerisation is higher for aluminium trialkyls with linear substituents than for AlR_3 with cyclic substituents. With increase of the bulk of the cyclic substituent, the activity of the system falls. For the same number of carbon atoms in R, the rate of polymerisation is higher for AlR_3 with double bonds in the group than for saturated substituents, the presence of conjugated double bonds resulting in a still greater increase in the rate (Fig. 3).[91,97]

The replacement of alkyl groups in AlR_3 by substituents containing heteroatoms (N, O, Si) decreases the activity of the catalytic systems[91,97]. Consequently the increase in the activity of the titanium catalytic systems suggest the usefulness of employing organoaluminium compounds containing 8–10 carbon atoms in the hydrocarbon substituents and double bonds, in particular conjugated double bonds. It may be hoped that, when gel-immobilised OAC are used, it will be possible to increase still further the activity of the catalysts while retaining their high stereospecificity, particularly since a recent communication[98] confirms this possibility.

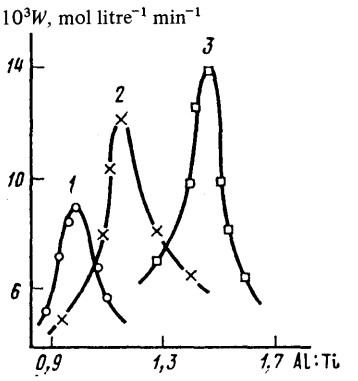


Figure 2. Dependence of the rate of polymerisation of isoprene on the Al : Ti ratio in the $TiCl_4$–AlR_3 systems with R = iso-C_4H_9 (curve *1*), n-C_7H_{15} (curve *2*), and n-$C_{10}H_{21}$ (curve *3*); solvent—toluene; $[TiCl_4] = 2.7 \times 10^{-3}$ M; [monomer] = 1.0 M; t = 20 °C.[91]

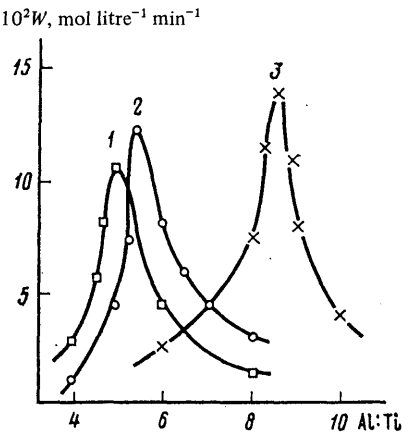
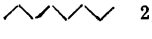
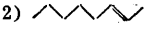
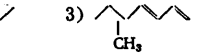


Figure 3. Dependence of the rate of polymerisation of butadiene in the presence of the TiI_2Cl_2–AlR_3 systems with different Al : Ti ratios on the structure of the group R:

1)  2)  3) 

solvent—toluene; t = 20 °C; $[TiI_2Cl_2] = 1.5 \times 10^{-3}$ M; [monomer] = 0.82 M.[91]

Thus, when substituents at the aluminium atom in the cocatalysts are varied within the limits of a homologous series, the stereospecificity of ionic-coordination systems remains constant in the polymerisation of dienes, but their activity changes, as in the case where substituents are varied similarly at a transition metal atom. Such variation results in the formation of active centres with identical structures and reactivities. This is supported, apart from the microstructure data, by the following facts. The form of the EPR spectra of the reaction product in the TiI_2Cl_2–AlR_3 and $Ti(OR')_4$–AlR_3 systems is independent of the length of the group R.[96] The activation energy for the chain propagation reaction is likewise independent of the length and structure of the hydrocarbon group in the polymerisation of isoprene in the presence of $TiCl_4$–AlR_3 and amounts to 5–6 kcal mol^{-1}.[91,99] All the changes in the activity of the catalytic systems associated with the differences between the structures of the substituent in the OAC and unaccompanied by a change in the microstructures of the polymers are due to the different concentrations of the active centres, while the reactivity of these centres (k_p) remains unchanged (Table 9).

Table 9. The influence of the structure of AlR_3 on the rate constant for the propagation reaction (k_p), the content of active centres (C_a), and the constant for chain transfer to AlR_3 (k_o^{Al}) in the polymerisation of butadiene and isoprene in the presence of the titanium-containing $TiHal_4$–AlR_3 systems (solvent—toluene; t = 25 °C).[97]

Reaction conditions	AlR_3	$10^{-3}k_p$, litre mol^{-1} min^{-1}	$C_a/C_{Ti}\cdot10^2$	$10^{-3}k_o^{Al}$ litre mol^{-1} min^{-1}
TiI_2Cl_2; Al:Ti = 7, butadiene	Al (iso-C_4H_9)$_3$	7.4	1.5	3.4
	Al (–C_2H_4–)$_3$	7.4	3.6	1.5
$TiCl_4$; Al:Ti = 1.1; isoprene	Al (iso-C_4H_9)$_3$	1.0	0.3	0.2
	Al (–C_2H_4–)$_3$	1.0	0.7	0.1
	Al ()$_3$	1.0	1.0	0.1

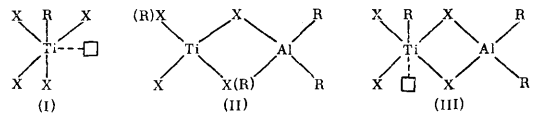
The increased molecular weights of the polydienes when higher AlR_3 are used are associated with the increase of the macrochain propagation time as a result of the decrease of the constant for chain transfer to AlR_3 with increase in R (Table 9).

III. THE STRUCTURE OF ACTIVE CENTRES AND THEIR STEREOREGULATING CAPACITY

The study of the mechanism of the stereospecific polymerisation of dienes is related directly to the structure of the active centres.

It is generally accepted that polymerisation involves the transition metal–carbon bond and that the cocatalyst plays the role of a complex-forming agent, a reductant, and an alkylating agent. However, the question whether or not the organometallic compound is incorporated in the composition of the active centre for polymerisation, i.e. the question of the mono- or bi-metallic structure of the active centres, still remains controversial.

There exists a view[100–103] that the active centre (I) includes only the alkylated transition metal compound. However, this structure of the active centre does not explain the influence of the nature of the organometallic compounds on the stereospecificity of the catalytic systems.



□ - vacant site, X-ligand, R-alkyl group

The bimetallic structure of the active centres (II) presupposes an important role of the organometallic compounds in their creation[104–107], a more important role than simple stabilisation of the alkylated transition metal compound via halide bridges[108,109]. Thus Minsker and co-workers[106,107,110] demonstrated by quantum-chemical calculations the high probability of the propagation of the polymer chain with participation of the $\overset{-}{Al}$–R–$\overset{\delta+}{Ti}$ group, while Cossee's mechanism[101,102] presupposes chain propagation solely via the Ti–R bond. It is believed[106,107,110] that the OAC coordinated to the titanium compounds is directly involved in the addition of the monomer to the growing chain via the simultaneous electrophilic (from the side of the Ti atom) and nucleophilic (from the side of the Al atom) attack on the monomer.

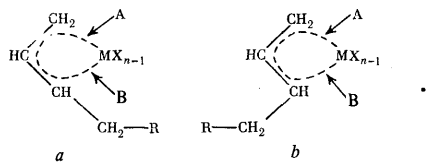
In conformity with the schematic representation of the active centre (III), the propagation of the polymer chain takes place at the transition metal, while the aluminium compound is one of the ligands of the transition metal[111–113]. According to Avdeev et al.[112], the OAC, present in the second coordination sphere of the transition metal, cannot influence appreciably the reactivity of the active centre in this case. Thus the third type of active centres, where the leading role of the transition metal compound is assumed, also takes into account the appreciable role of the OAC in the formation and stabilisation of the active centres. Active centres of type (III) made it possible to explain[114] why the reactivity of the active centres is independent of the nature of the OAC in the ionic-coordination polymerisation of α-olefins. Our set of investigations[91,97,99], using a large number of aluminium trialkyls of different structures, showed that active centres of type (III) are most probably formed also in the polymerisation of dienes, since the reactivity of the active centres of titanium systems is independent of the structure of the organoaluminium component.

Although the hypothesis that the structure of the active centres in the polymerisation of dienes is modelled by the π-allyl complexes of transition metals is generally accepted, the question of the causes of stereoregulation, i.e. of the factors responsible for the formation of polydiene macrochains with 1,4-*cis*-, 1,4-*trans*-, 1,2-, or 3,4-units remains controversial. Two concepts predominate in the literature on this topic.

The concept of the *cis*–*trans* geometrical control[115–117] takes into account the presence of two double bonds in the conjugated dienes. If the diene is coordinated to the active centre via two double bonds, then its subsequent incorporation in the growing chain entails the formation of a unit with the 1,4-*cis*-configuration. For the monodentate coordination of the diene, it is possible to obtain polymers containing 1,4-*trans*- or 1,2-units. Thus the coordination of the monomer and hence the stereoregularity of the polymer depend on the matrix effect of the catalyst. Active centres with a single vacancy (a single coordination site), for example α-$TiCl_3$, permit the possibility of employing only one double bond of the diene in the *S*-*trans*-form, while on centres with two vacancies (for example, the crystal lattice of β-$TiCl_3$), the diene molecules can be coordinated using either one or

two double bonds (the *S-cis*-form)[118]. Furukawa[65] suggested that the microstructure of the polydienes, determined by the mode of coordination of the monomer, depends on the electron density at the transition metal atom. The probability of the mono- and bi-dentate coordination of the monomer is determined, according to Furukawa[119], by the difference between the energy levels of the orbitals of the transition metal involved in bonding with the π-orbitals of the diene and the highest occupied orbitals of the latter. In conformity with the proposed mechanism, 1,4-*cis*-polydienes are obtained when the energy levels of the bonding orbitals of the metal and the highest occupied orbitals of the monomer are close to one another; when there is a large difference between the energy levels, polymers with the 1,2- or 1,4-*trans*-structures are formed. The electronegativity of the ligands, which influences the positions of the energy levels of the transition metal orbitals, is an important stereoregulation factor.

According to the other concept, the stereoregularity of the polymer chain is determined by the π-alkenyl polymer–transition metal linkage and not the coordination of the monomer to the active centre, *the* anti-form *a* corresponding to *cis*-addition and the *syn*-form *b* corresponding to the *trans*-units:



a *b*

It is believed[116,119] that the *anti–syn* orientation should depend on the coordinating capacity of the double bond adjoining the π-alkenyl linkage at the end of the macromolecule (i.e. on the penultimate double bond), while the geometrical configuration of the π-alkenyl end of the growing chain is unimportant. However, the stereospecificity of the action of the catalyst has been attributed[75,120–125] to the configuration of the π-alkenyl unit of the growing chain. This version is supported by data obtained in a study[126] where it was shown by ^{1}H NMR that there is only a very slight possibility of the coordination of the penultimate double bonds of the growing chain.

According to a number of investigations[75,122,124,125], a conjugated diene always behaves as bidentate ligand, which is favoured by energy factors for conjugated dienes, and the primary steps involving the addition of the monomer therefore lead solely to the *anti*-configuration of the π-alkenyl centre. The content of the 1,4-*cis*- or 1,4-*trans*-structures is determined by the ratio of the rates of chain propagation and *anti–syn* isomerisation of the active centre: a higher rate of chain propagation results in the formation of a polymer with the 1,4-*cis*-structure of the units on insertion of the monomer in the π-alkenyl linkage of the *anti*-complex formed initially, while at low rates of chain propagation the role of the *anti–syn* isomerisation reaction of the active centres increases and the thermodynamically more stable *syn*-π-complexes, giving rise to units with a 1,4-*trans*-structure, are formed. Such interconversions of the structures take place fairly readily for simple compounds[127]; the *anti–syn* isomerisation of the π-alkenyl complexes of certain transition metals has been observed also in the polymerisation of dienes[128–131], the rate of reaction depending on the structure of the alkyl substituent in the diene.

The coordinated diene molecule can enter the growing chain either from side A, whereupon polymer chains with 1,4-units are formed, or from side B, which leads to the formation of polymers with a 1,2-structure of the units.

Very little is known about the factors directing the stereospecific polymerisation towards the formation of the 1,4- or 1,2(3,4)-polymer, nevertheless experimental data show indirectly that these factors may depend both on the monomer and on the catalyst. Thus comparison of the results of the polymerisation of butadiene and 4-methylpenta-1,3-diene in the presence of α-$TiCl_3$–AlR_3 showed[132] that in both cases the monomer is inserted in the same Ti–C bond of the π-allyl complex at the end of the chain, which contains the least substituted and hence the most reactive carbon atom. However, this approach cannot explain the formation of 1,2-polybutadiene. On the grounds that in the majority of polybutadienes in which the 1,2-units predominate, including those obtained in the presence of $Ti(OR')_4$–AlR_3, the residual units have almost exclusively the 1,4-*cis*-structure, the authors[132] believe that the monomer in these systems is always coordinated as a bidentate ligand and the π-allyl complex at the end of the chain has the *anti*-structure. However, in such systems one assumes a geometry of the catalytic complex such that the terminal, carbon atom of the coordinated monomer can be closer (at a distance equal to a single bond length) to the more substituted although less reactive third carbon atom in the π-allyl group. As a result of this, the monomer is inserted preferentially in the B direction and 1,2-polybutadiene is formed.

This approach, which takes into account the rigorously steric, geometrical characteristics of the active centre, should apparently be regarded as useful. Indeed the presence of bulky substituents at the titanium atom promotes in all cases and, what is most important, independently of their chemical nature the appearance of 1,2-units in the polybutadiene chain. The greater the number of such ligands at the titanium atom, the larger the fraction of 1,2-junctions. This is indicated by the results of the polymerisation of butadiene in the presence of catalytic systems consisting of $Ti(OR')_4$,[25,70] $Ti(NR_2)_4$,[24] $TiCl_2(indenyl)_2$,[14] $TiCl_2(fluorenyl)_2$,[14] $TiCl_2(OR')_2$,[14] and $TiCl_2(OCOR')_2$ [14] in combination with AlR_3.

The causes of the formation of a polymer with a mixed microstructure can be accounted for also by factors other than the *anti–syn*-isomerisation of the active centre, a difference in the modes of incorporation of the monomer in the growing chain, or an alteration of the geometry of the catalytic complex. The question whether the polymerisation involving the formation of polydienes with a mixed microstructure occurs on the same active centres or on non-identical active centres with different activities and stereospecificities still remains open. The latter possibility is not ruled out if only because even when the Al : Ti ratio is altered only slightly in systems based on titanium halides, the microstructure of the polydienes begins to change. Unfortunately, there are almost no literature data which would make it possible to follow the qualitative and quantitative variation of the active centres as a function of the component ratio in catalytic systems. Thus it has been shown in a study[133] of the polymerisation of butadiene in the presence of TiI_4–$Al(iso\text{-}C_4H_9)_3$ that the propagation rate constant increases sharply when the Al : Ti ratio is raised from 1.5 to 5.5, but a clear-cut correlation between the concentration of active centres and the Al : Ti ratio was not found.

Nevertheless, certain results can be interpreted only on the assumption of the simultaneous presence in a particular system of active centres of different types and with different reactivities. Thus the separation of the products of the polymerisation of butadiene in the presence of $TiCl_4$–AlR_3 by extraction with different solvents made it possible to isolate from the overall reaction mass a highly stereoregular 1,4-*cis*-polybutadiene[134]. In the polymerisation in the presence of β-$TiCl_3$ the formation of two polymers separable by extraction (1,4-*cis*-, and 1,4-*trans*-polybutadienes) in comparable

amounts was also noted[135]. Even when highly stereospecific catalytic systems such as TiI_2Cl_2–AlR_3 (monomer = butadiene) and $TiCl_4$–AlR_3 (monomer = isoprene) were used, an increase of the content of the 1,4-*cis*-units was observed in all the fractions of rubbers with increase in the molecular weight of the fraction; a particularly marked decrease of the amount of *cis*-units is observed in the region of molecular weights below 20000.[27] This phenomenon is regarded as a consequence of the presence in the catalyst of different active centres with different propagation and *anti–syn* isomerisation constants, polymers with a higher molecular weight and a higher content of 1,4-*cis*-units being formed on the more active centres. It is believed[136] that EPR data confirm the hypothesis of the existence of two forms of active centres in iodine-containing titanium systems: monomeric paramagnetic centres with a high catalytic activity lead to the formation of a high-molecular-weight 1,4-*cis*-polydiene, while associated diamagnetic centres are much less reactive and the decrease of the content of the 1,4-*cis*-units in the polymer probably depends on them.

One can therefore assume that the significant difference between the stereoregulating capacities of the $TiCl_4$–AlR_3 system (Al : Ti $\geq$ 1) in the polymerisation of butadiene and isoprene is due to the fact that in the case of butadiene the polymerisation takes place simultaneously on two types of active centres (*cis*- and *trans*-regulating), which in fact leads to a mixed microstructure of the polymer. On the other hand, the polymerisation of isoprene hardly takes place on the less active *trans*-regulating centres (if only by virtue of the steric hindrance to coordination) and the entire polymerisation process occurs on the *cis*-regulating active centres. Quantum-chemical calculations[137,138] agree with these ideas.

It is difficult to obtain experimental data on the structure and the active centres in ionic-coordination polymerisation of dienes because of their high sensitivity to impurities, the complexity of their composition, and their low concentrations. Thus the degree of conversion of the initial titanium halide into the catalytically active compounds by its reaction with AlR_3 does not exceed several per cent[70,91,97,99,133,139–142]. This parameter is even lower (<1%) for systems based on titanium alkoxides[70,143].

The lack of experimental data on the structure of the active centres is partly compensated by quantum-chemical studies. The relevant calculations have the following aspects: the nature of the metal–monomer and metal–alkyl bonds, the coordination of the monomer to the active centre, and its insertion in the metal–carbon bond. There have been almost no detailed calculations of the structure of the active centres for the polymerisation of dienes in the presence of Ziegler–Natta catalyst and of the potential energy surfaces for the addition of the diene to the active centre (of the kind carried out, for example, for α-olefins[110,112,114,144]).

Quantum-chemical calculations on the anionic polymerisation of dienes in the presence of organometallic derivatives of alkali metals modelling the structure of the terminal unit of the growing macromolecule linked to the transition metal have been published in a number of communications[145–150] and a computer study of the formation of active centres and of the mechanism of the polymerisation of α-olefins and dienes in the presence of heterogeneous Ziegler–Natta catalysts has been described[137]. According to calculations[137], the role of the organometallic compound MR consists in building up the crystal lattice of the catalyst, in the formation of a Ti–R–M bridge bond, and in the formation of an unusual structure of the active centre by the groups R and the metal atoms ("tunnel"), which has an orienting effect at the monomer coordination stage.

Attention has been concentrated in semiempirical[114] and non-empirical[151] calculations on the estimation of the electronic structures of various titanium–aluminium–olefin complexes and their alteration in the addition of the olefin to the Ti–C bond. As a rule, the choice of the model of the active centre is based on the available experimental data. Models of active centres have been obtained by the computer calculation of the random absorption of AlR_3 on the surface of $TiCl_3$ crystals in only a few studies[110,137,151]; this made it possible to predict different forms of active centres and to select the most probable.

A hypothesis concerning the mechanism of catalytic polymerisation is impossible without the elucidation of the nature of the lability of the transition metal–carbon bond. In terms of this aspect, the data of L'vovskii and Erusalimskii[152,153], who investigated the equilibrium properties and the electronic nature of the lability of the Ti–C σ-bond in a series of alkyl halide derivatives of quadrivalent titanium, are of great interest. L'vovskii used the unrestricted version of the Hartree–Fock–Roothaan (UHFR) for quantum-chemical calculations and compared it with the restricted version (RHFR) in the CNDO approximation. Calculations on the homolytic dissociation of the Ti–C bonds in $TiCl_3CH_3$ and the Al–C bonds in $AlCl_2CH_3$ by the UHFR method showed[153] that there is a very much smaller energy barrier to the dissociation of the Ti–C bond than to the dissociation of the Al–C bond. The electronic correlation has a much greater influence on the lability of the Ti–C bond and this influence is determined mainly by the properties of the *d* orbitals of the transition metal[153], which explains the difference between the energy barriers to the homolytic dissociation of the Ti–C and Al–C bonds. It is also of interest to note that calculations[153] indicate an increase of the energy barrier to the dissociation of the Ti–C bonds in the sequence $TiCl_3C_2H_5 < TiCl_3CH_3 < (\eta^5\text{-Cp})_2.TiClCH_3$, which agrees with the variation of the thermal stability of these compounds.

However, all the known calculations on reaction pathways have been carried out within the framework of the RHFR method, where, in the light of the results of L'vovskii and Erusalimskii[152,153], some caution is needed in assessing the energy barriers obtained and hence also the correctness of the choice of both the rate-limiting stage and the single- and two-stage mechanisms of chain propagation.

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The general level of the results achieved at the present time in the field of the ionic-coordination polymerisation of dienes is fairly high. Extensive experimental data have accumulated on various aspects of this field and further studies are being vigorously prosecuted. However, despite the advances made, the state of knowledge on a number of questions is still merely empirical. A particular consequence of the lack of a profound theoretical basis is that new catalytic systems are selected, as regards both composition and the formation conditions, by a purely experimental procedure. In view of the complexity of the physicochemical picture of the formation and functioning of the active centres, the characteristic features of the polymerisation of a particular diene in the presence of a given transition metal cannot always be extended to other systems and other monomers. This applies in the first place to the stereospecificity of the action of ionic-coordination systems, which is indicated by the analysis of the literature data presented in this review. On the other hand, one can assume, on the basis of modern ideas about the structure of the active centres, that the lack of an effect by the structure of the organoaluminium component on the stereospecificity of the titanium system apparently obtains

also in other systems of the Ziegler type. As regards the question of the influence of the structure of the OAC on the activity of the systems, the characteristics discovered for the titanium systems can hardly hold in all other cases in view of the wide variety of the functions of the organoaluminium compound in the Ziegler system, particularly when account is taken of their reducing and alkylating capacities.

Thus there is an evident necessity for further studies designed to accumulate new experimental facts which would serve as a basis for the development of methods for the specific control of processes involving the stereospecific polymerisation of dienes.

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