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Organometallic Catalysis in Diene and Cyclo-olefin Polymerisation Processes. I. The Polymerisation and Copolymerisation of Dienes Under the Influence of Organometallic Transition Metal Compounds. The Stereoregulation Mechanism

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The results of experimental studies on the synthesis of individual organometallic transition metal compounds and of studies on their catalytic activity in stereospecific diene polymerisation and copolymerisation processes are surveyed. The kinetics of the polymerisation under the influence of various nickel-, chromium-, titanium-, and molybdenum-containing systems are examined. The stereoregulation mechanism and the principal characteristics of coordination copolymerisation are discussed on the basis of the experimental data.
The bibliography includes 125 references.

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I. INTRODUCTION

The question of the nature of the active centres affecting various types of stereoregulation and of the mechanism of their action has been at the centre of the attention of investigators from the instant of the establishment of the field of synthesis of rubbers by the polymerisation of dienes. This is mainly due to the fact that the properties of the polymers are directly related to the structure of the units in the polymer chain. Thus polybutadiene containing only 1,2-units has a glass point $t_g = -10$ °C, while the rubbers made from it are brittle already at 0 °C. *cis*-Polybutadiene is a highly elastic rubber with $t_g = -108$ °C, while *trans*-polybutadiene is a crystalline fibre with a melting point of ~+140 °C. In the polymerisation of isoprene the number of different variants of the microstructures of the units increases and new structures associated with the inhomogeneity of the distribution of 1,4-units in terms of the "head to tail" and "head to head" arrangements (1,4–1,4; 1,4–4,1; 4,1–1,4) appear. This also applies to other dienes.

Highly stereoregular butadiene and isoprene polymers of different structures were first obtained in the presence of Ziegler type catalysts consisting of transition metal compounds and organoaluminium compounds. Other components ensuring a higher selectivity of the action of the catalytic system and reproducibility of the results are added to them in in many instances.

Table 1 presents the compositions of systems characterised by the highest stereospecificity; some of them are of industrial importance. It is seen from the results presented that only lanthanide-containing systems are equally stereospecific for the formation of *cis*-units in the polymerisation of both butadiene and isoprene. The cobalt and nickel systems are stereospecific for butadiene and lead to the formation of a polyisoprene with a mixed structure. The $TiCl_4$–AlR_3 system is a stereospecific catalyst of the *cis*-polymerisation of isoprene, while in the polymerisation of butadiene many *trans*-units are formed. Vanadium systems based on $VCl_3(VOCl_3, VCl_4)$ are stereospecific in the formation of *trans*-units in the polymerisation of butadiene, while systems without a halogen cause the formation of 1,2(3,4)-units.

Table 1. Catalytic systems with stereospecific activity in the polymerisation of dienes.

Catalytic system*	Contents of units, %				Refs.
	cis-	*trans*-	1,2-	3,4-	
Butadiene					
TiI_4+AlR_3 (Al/Ti=4÷8)	95	2	3		[1–4]
$TiI_2Cl_2+AlR_3$(Al/Ti=4÷8)	90	—	—		[5]
$TiCl_4+AlR_3$	57—71	27—41	2		[6, 7]
$CoCl_2\cdot H_2O+R_2AlCl$ (Co : Al : H_2O = =1 : 150 : 10)	92	5	3		[2, 8]
$Ni(naphth)_2 + R_2AlCl$	92	5	3		[8]
$LnX_3.D + R_3Al$ (Al/Ln = 20)	98	1.5	0.5		[9, 10]
$Ln(OCOR)_3+R_2AlCl+R_3Al$**	97	2	1		[9, 10]
$VCl_3(VCl_4, VOCl_3)+R_3Al$	0	97—99	1—3		[12, 13]
$Rh(acac)_3+R_2AlCl$	—	98	—		[14, 15]
$V(acac)_3+R_3Al$	9—11	3—12	78—86		[16]
$Cr(acac)_3+R_3Al$	1—2	1—10	88—99		[17, 18]
$MoO_2(OR)_2+R_3Al$	—	—	98		[2]
$Ti(OR)_4+R_3Al$	—	—	88—98	—	[19, 20]
Isoprene					
$TiCl_4+AlR_3$(Al/Ti=1.2)	94—96	0	3—4	3	[7, 21]
$CoX_2+R_2AlCl+10H_2O$	up to 70	15—22	1—3	up to 31	[22, 23]
$LnX_3.D + R_3Al$ (Al/Ln = 20)	94—98	0	2—6	0	[10, 11]
$Ln(OCOR)_3+R_2AlC+R_3Al$**	94—95	0	5	0	[10, 11]
$VCl_3(VCl_4, VOCl_3)+R_3Al$	0	80—99	0	9	[12, 13]
$Ti(OR)_3[Ti(OR)_4]+R_3Al$	0	—	—	94—99	[19, 20]

*Ln = Nd, Pr, Ce, or La; D = complex-forming agent.
**$Ln(OCOR)_3$: R_2AlCl : R_3Al = 1 : 2–3 : 20.

An enormous number of studies have been made on the kinetics of the polymerisation of dienes and olefins under the influence of Ziegler systems. The experimental data, particularly the effective activation energies and the reaction orders with respect to the catalyst and the monomer, cannot be used to characterise the active centres, since the probability of the formation of new active centres based on more reduced compounds of the metal increases with increase of temperature or with increase of the concentration of the system components.

The authors of the early investigations assumed that the organoaluminium compound plays the main role in chain propagation steps. However, as research into this field developed, it became clear that the main role in the chain propagation steps is played by the transition metal compound. The concept of the two-centre (multicentre) stereoregulation mechanism in which the atoms of both the transition metal and aluminium are involved has become most widely adopted. The complexity of the composition of Ziegler-Natta catalytic systems and the wide variety of the reactions between their components precluded the finding of direct experimental approaches to the elucidation of the nature of the active centres and the stereoregulation mechanism. New possibilities for the solution of this problem have arisen as a result of the employment of individual organometallic compounds for the initiation of polymerisation.

II. THE SYNTHESIS OF ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS AND THE STUDY OF THE STEREOSPECIFICITY OF THEIR ACTION IN THE POLYMERISATION OF DIENES

The organic derivatives of transition metals with carbon–transition metal π-allyl and σ-bonds which have been synthesised and used in the polymerisation of dienes are listed in Table 2. Compounds having the general formula $\pi\text{-}R_nM$, where R = allyl, crotyl, or pentenyl and M = Ni^{2+}, Co^{3+}, Cr^{3+}, Cr^{2+}, V^{3+}, Nb^{3+}, or Rh^{3+}, were obtained from the corresponding alkenylmagnesium halides and metal chlorides in diethyl ether. Their stability increases in the sequence allyl < crotyl < pentenyl. We have shown[29,39,41] that the pentenyl complexes of many transition metals are stable at 0–20 °C, while the corresponding π-allyl complexes are stable below −20 °C.[24]

π-Alkenylnickel halides have been largely obtained by the Fischer method from nickel carbonyl and the corresponding alkenyl halide.

π-Oligodienylnickel chloride has been obtained by a new method of synthesis based on the interaction of nickel chloride and AlR_3 in the presence of small amounts of a diene (molar ratios Ni : Al : diene = 1 : 3–5 : 10–30),[26] for example:

$$NiCl_2 + R_3Al \rightarrow R_2AlCl + RNiCl \xrightarrow{C_4H_6} R(C_4H_6)_nNiCl.$$

At the end of the reaction the hydrocarbon solution was washed with an aqueous solution of acid to remove completely the organoaluminium compound. The π-alkenylnickel chloride remained entirely in the hydrocarbon solution, the yield amounting to ~90% of theoretical. The oligodienylnickel chloride is more stable than $\pi\text{-}C_3H_5NiCl$ and $\pi\text{-}C_4H_7\text{.NiCl}$. The π-allyl compounds π-RNiOY have been obtained from $\pi\text{-}R_2Ni$ and the corresponding acid (CCl_3COOH, $CH_3C_6H_4OSO_2H$, and *o,o*-dinitrophenol).[27]

Tribenzyltitanium and tris(trimethylsilymethyl)titanium can be obtained from $TiCl_3$ and the corresponding organolithium compounds at temperatures in the range −30° to −40 °C in 50–60% yield[37]. However, TiR_3 and other transition metal compounds can be synthesised more conveniently in a more reduced state by a method which we proposed[36] on the basis of the reaction

$$MR_{n+1} + LiC_2H_5 \rightarrow LiR + MR_nC_2H_5 \rightarrow MR_n + 0.5C_2H_4 + 0.5C_2H_6 \quad ,$$

where R = benzyl, trimethylsilylmethyl, or allyl. The reaction is carried out in a hydrocarbon solvent and the yield of MR_n is nearly quantitative. Trimethylbenzyltitanium is fairly stable at 20 °C in solution in aromatic and aliphatic hydrocarbons; the presence of even small amounts of an electron donor [tetrahydrofuran (THF), ether] reduces sharply the stability of the compound. In hydrocarbon solutions tribenzyltitanium is associated and the concentration of paramagnetic species is only 2–3% of the total content of Ti^{3+}, in contrast to tri-π-allyltitanium, which is monomeric in solution and the concentration of the paramagnetic species corresponds to that of Ti^{3+}.[52] Benzyltitanium halides are stable only below −30 °C, disproportionating quantitatively on raising the temperature with formation of equivalent amounts of titanium(II) and titanium(IV) compounds[37]. The occurrence of this reaction precludes the synthesis of TiR_3 from $TiCl_3$ + RMgCl(RLi) above −20 °C.[53] The disproportionation reaction is fully suppressed in the presence of small amounts of diene[51]. It has been shown that butadiene is inserted in the Ti–benzyl bond with formation of trioligodienyltitanium. A similar compound has also been obtained by the reaction of $TiCl_3$ with oligodienyl-lithium in solution in toluene[52]. Tri-π-oligodienyltitanium is monomeric in solution and the concentration of paramagnetic species corresponds to that of Ti^{3+} determined by reaction with Fe^{3+}; the compound is stable for a long time at room temperature[52].

Table 2. The organometallic compounds synthesised and used as catalysts of the polymerisation of dienes.

Organometallic compound	Methods and conditions of synthesis	Refs
$\pi\text{-}R_2Ni$(R = allyl or crotyl)	$NiCl_2$ + RMgCl; ether; −30–−40°	[24]
π-RNiX (R = allyl, crotyl, pentenyl, or cyclohexadienyl; X = Cl, Br, or I	$Ni(CO)_4$ + RCl; benzene; 60–65°	[25]
$\pi\text{-}RNiCl$ [$R = R'(diene)_n$]	$NiCl_2 + AlR_3' + C_4H_6(C_5H_8)$ (1 : 2÷5 : : 10÷30); 0°	[26]
π-RNiOY (R = allyl or crotyl)	$\pi\text{-}R_2Ni$ + HOY; toluene; −30°; OY = CCl_3COO, CF_3COO, *o,o*-dinitrophenoxy, or $CH_3C_6H_4OSO_2$	[27]
$\pi\text{-}R_3Cr$ (R = allyl, pentenyl, or crotyl)	$CrCl_3$ + RMgX; ether; −20°	[28, 29]
$\pi\text{-}R_2Cr$ (R = allyl or pentenyl)	$CrCl_2$ + RMgX; ether; 0-20°	[29]
$\pi\text{-}R_2CrOSi\|SiO_2$	$\pi\text{-}R_3Cr + HOSi\|SiO_2$	[30]
$\pi\text{-}RCr(OSi)_2\|SiO_2$	$\pi\text{-}R_3Cr + HOSi\|SiO_2$	
π-RCr(OAl)(OAl)|Al_2O_3	$\pi\text{-}R_3Cr + HOAl\|Al_2O_3$	[30]
$\pi\text{-}R_2CrCl$	$\pi\text{-}R_3Cr$ + HCl; toluene; −30°	[31]
$(C_6H_5CH_2)_4Ti$	$TiCl_4$ + RMgCl; ether + heptane; −25°	[32, 33]
$(C_6H_5CH_2)_3TiI$	$TiR_4 + I_2$; toluene + benzene; −20°	[33]
$(C_6H_5CH_2)_3TiBr$	$TiR_4 + Br_2$; toluene + benzene; −20°	[33]
$(C_6H_5CH_2)_3TiCl$	TiR_4 + HCl; toluene; −16°	[33]
$[(CH_3)_3SiCH_2]_nTiCl_{4-n}$	$TiR_4 + TiCl_4$	[34, 35]
$(C_6H_5CH_2)_3Ti$	$(C_6H_5CH_2)_4Ti + LiC_6H_5 \rightarrow [(C_6H_5CH_2)_3TiC_2H_5] \rightarrow TiR_3$	[36]
$(C_6H_5CH_2)_2TiI$	$TiR_3 + 0.5I_2$; toluene + benzene; −35°	[37]
$(C_6H_5CH_2)_2TiCl$	TiR_3 + HCl; toluene + benzene; −35°	[37]
$C_6H_5CH_2TiCl_2$	TiR_3 + 2HCl; toluene + benzene; −20–−35°	[37]
$C_6H_5CH_2TiI_2$	$TiR_3 + I_2$; toluene + benzene; −35°	[37]
$[(CH_3)_3SiCH_2]_3Ti$	$TiCl_3 + LiCH_2Si(CH_3)_3$; ether; −50°	[37]
$(C_3H_5)_3Ti$, $(C_4H_7)_3Ti$	$TiCl_3$ + RMgX; ether; −30°	[1, 38]
$(C_5H_9)_3Ti$	$TiCl_3$ ($TiCl_4$) + RMgX; ether	[39]
$[C_3H_5(C_4H_6)_n]_3Ti$ ($n = 2 \div 10$)	TiR_3 + (2–10)C_4H_6; toluene; −20°	[40]
$(C_5H_9)_3V$	$VCl_4 + C_5H_9MgX$; ether; −30°	[41]
$[(CH_3)_3SiCH_2]_3V$	$VCl_3 + (CH_3)_3SiCH_2Li$; ether + heptane	[42]
$(\pi\text{-}C_3H_5)_4Mo$(W, Zr)	$MCl_4 + C_3H_5MgX$	[43, 45]
$(C_3H_5)_nMo$(W, Zr)X_{4-n}	$M(C_3H_5)_4 + HX$	[46]
$(C_3H_5)_3Nb$	$NbCl_3 + C_3H_5MgX$; ether	[47]
$(C_3H_5)_2NbCl$	NbR_3 + HCl	[47]
$(C_3H_5)_3Rh$	$RhCl_3 + C_3H_5MgCl$	[47]
$(C_6H_5CH_2)_3Nd$	$NdCl_3 + LiCH_2C_6H_5$; ether; −25°	[48]
$RLnCl_2$(R = $C_6H_5CH_2$, $(C_6H_5)_3C$)	Ln + RCl; THF; 20–40°	[49, 50]

Tribenzylneodymium is stable only below −20 °C, but in the presence of dienes it is stabilised and induces their polymerisation at 50 °C. All three Nd–benzyl bonds are involved in the polymerisation process and the active centre is a trioligodienyl derivative of neodymium, which proved to be fairly stable[48].

Thus it has been established in relation to Ti^{3+}, Nd^{3+}, and other ions that the oligodienyl derivatives of transition metals are much more stable than the corresponding π-allyl, benzyl, etc. derivatives. This finding has been explained[52] on the basis of the idea of the stabilising action of the π-complexes of the transition metal with the double bonds of the oligodienyl chain.

Arylalkyl-lanthanide dichlorides have been obtained by the oxidative addition of arylalkyl halides to the metallic lanthanide (Nd, Pr, Ho, or Gd) in THF.[49,50] A distinctive feature of the compounds formed is their ability to metallate THF.

The reaction involving the addition of dienes and olefins to the M–H bond is a source of the formation of organometallic compounds. Thus the interaction of dienes with nickel, cobalt, and chromium hydrides leads to the formation of the corresponding π-allyl complexes, which can participate in polymerisation like the compounds described above[54]. In essence, this type of reaction obtains in systems of the Ziegler type when hydrogen is used to regulate the molecular weight:

$$pMX_n + H_2 \rightarrow pH + HMX_n \xrightarrow{C_4H_6} \pi\text{-}C_4H_7MX_n \xrightarrow{C_4H_6} \text{chain propagation},$$

where p is the polymer chain.

An effective system for the polymerisation of dienes is formed under the influence of nickel and other metal subhalides obtained by heating *in vacuo*.[55] In this case a very small amount of paramagnetic NiCl species, incorporated in the mass of nickel chloride, is produced. These species become organometallic active centres initiating the polymerisation of butadiene, particularly after the extinction of the paramagnetic signal by hydrogen (the formation of $HNiCl|NiCl_2$). In a number of instances metal hydrides can serve as a convenient source in which active centres are formed. In view of the lower stability of σ bonds compared with π-allyl bonds in olefins (styrene and ethylene), the reaction of the latter usually terminates with formation of oligomers and the active centre propagating the chain in HNiX:[56]

$$HNiX + H_2C{=}CHC_6H_5 \rightarrow H_3C{-}CH(C_6H_5)NiX \xrightarrow{H_2C=CHC_6H_5}$$
$$\rightarrow H_3C{-}CH(C_6H_5)CH_2{-}CH(C_6H_5)NiX \rightarrow H_3C{-}CH(C_6H_5)CH{=}CHC_6H_5 + HNiX\ .$$

Studies have established that organometallic compounds of transition metals are the true active centres for the polymerisation of dienes and the stereospecificity of their action is determined by the nature of the metal and the ligands surrounding it.

Table 3 presents experimental data characterising the stereospecificity of the action of various organometallic compounds in the polymerisation of butadiene and isoprene. Polymerisation proceeds in all cases throughout the addition of the monomer to the carbon–transition metal bond. The active centre of the growing chain is an organometallic compound of the alkenyl type with a π-allyl or σ bond depending on the nature of the transition metal. π-Allylnickel halides are *trans*-regulating catalysts leading to the formation of crystalline *trans*-polybutadiene and *trans*-polyisoprene[57–59,65]. π-Allylnickel iodide is the most active in the π-allylnickel halides. One should note that the π-alkenylnickel halides are as a rule dimeric and the order of the polymerisation reaction with respect to the catalyst is 0.5.[57] It follows from this that only small numbers of monomeric forms, which exist in equilibrium with the associated species, participate in the polymerisation reaction.

It is seen in relation to $\pi\text{-RNiOCOCCl}_3$ as an example that the substitution of the halogen by a more electronegative group reverses the stereospecificity of the action of the catalyst (from *trans*- to *cis*-). The most effective and stereospecific, in relation to *cis*-stereoregulation in the polymerisation of butadiene, are the products of the interaction of π-RNiX with electron acceptors (A_1 and A_2); charge-transfer complexes (CTC) and complexes with the transfer of an anion (ATC):

$$\underset{\vdots\ A_1^-}{\pi\text{-}R\overset{+}{N}iCl} \qquad \underset{\text{ATC}}{\pi\text{-}R\overset{+}{N}i\,[ClA_2]^-}$$
CTC

Table 3. The stereospecificity of the action of organometallic compounds of transition metals in the polymerisation reactions of butadiene and isoprene.

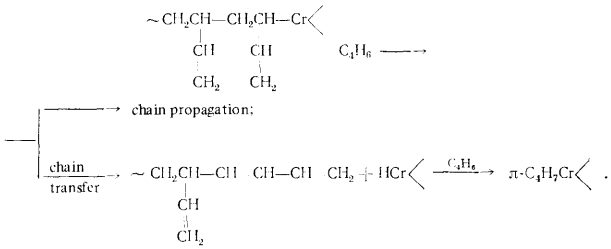
Organometallic compound	Contents of units, %				Refs.
	cis-	*trans*-	1,2-	3,4-	
Butadiene					
π-RNiX (X=Br, I)	0	95	5		[57–59]
$\pi\text{-RNiOCOCCl}_3$	92–95	3–6	2		[27]
	93.5	4.5	2		[27]
$\pi\text{-RNiOSO}_2C_6H_4CH_3$	48	45.5	3.5		[27]
π-RNiX·A* (X=Cl, Br, I)	90–97	2–5	1–3		[60, 61]
π-R_3Cr (R = allyl, crotyl, or pentenyl)	0	20	80		[31]
$\pi\text{-R}_2\text{CrOC}_4\text{H}_9$	12	14	74		[62]
$\pi\text{-RCr(OC}_2\text{H}_5)_2$	6	19	75		[62]
π-R_2CrOSi|SiO_2 (aluminosilicate)	0	92–97	3–8		[30]
$\pi\text{-RCr(OAl)}_2|\text{Al}_2\text{O}_3$	86	9	5		[62]
$\pi\text{-R}_2\text{CrOCOCCl}_3$	93	4	3		[31]
π-R_2Cr+HCl (1 : 2)	90	5.5	4.5		[31]
$(C_6H_5CH_2)_4Ti$	20	20	60		[33]
$(C_6H_5CH_2)_3TiCl$	35	19	48		[63]
$(C_6H_5CH_2)_3TiBr$	66	13	21		[63]
$(C_6H_5CH_2)_3TiI$	97	1	2		[63]
$(C_6H_5CH_2)_3Ti$	22	18	60		[40, 64]
$(C_6H_5CH_2)TiCl$	54	8	38		[40, 64]
$(C_6H_5CH_2)_2TiI$	91	7	2		[40, 64]
$C_6H_5CH_2TiCl_2$	0	90	10		[40, 64]
$C_6H_5CH_2TiI_2$	32	55	13		[40, 64]
$(C_3H_5)_4Nb$	0	0	100		[47]
$(C_3H_5)_2NbCl$	91	5.5	3.5		[47]
$(C_3H_5)_3Rh$	0	94	6		[47]
$(C_3H_5)_2RhCl$	0	93	7		[47]
$(C_3H_5)_3MoOCOCCl_3$	0	2	98		[44, 46]
$(C_3H_5)_3MoCl$	2	11	87		[44, 46]
$(C_3H_5)_3MoI$	0	2	98		[44, 46]
$(C_3H_5)_3WCl$	0	8	92		[45]
$(C_3H_5)_3WOCOCCl_3$	0	13.5	86.5		[45]
$(\pi\text{-}C_3H_5)_4Zr$	55	7	38		[45]
$(C_6H_5CH_2)_3Nd$	0	95	5		[48]
Isoprene					
π-RNiI	0	95	0	5	[65]
π-RNiX·A*	23–55	27–66	1–2	10–20	[66]
π-R_3Cr	17.5	18	28.5	36	[30]
π-R_2Cr	0	0	47.5	52.5	[29]
π-R_2CrOSi|SiO_2	0	97	0	3	[62]
$\pi\text{-R}_2\text{CrOC}_4\text{H}_9$	25	22	29	22	[62]
$\pi\text{-R}_2\text{Cr(OAl)}_2|\text{Al}_2\text{O}_3$	95	0	0	5	[62]
$(C_6H_5CH_2)_4Ti$	0	75	7	18	[67]
$(C_6H_5CH_2)_3TiCl$	19	36	6	39	[67]
$(C_6H_5CH_2)_3TiBr$	69	0	4	27	[67]
$(C_6H_5CH_2)_3TiI$	87	0	0	13	[67]
$(C_6H_5CH_2)_3Nd$	0	95	0	5	[48]

*A = acceptor—chloranil, chloral, CCl_3COOH, CCl_3COCl, $M(OCOCCl_3)_2$ (M = Zn, Ni, or Mg), $TiCl_4$, AlX_3, $NiCl_2$, $CoCl_2$, etc.

Chloranil, *fluoranil*, *chloral*, *trichloroacetic acid*, *etc.* have been investigated as the acceptors A_1 and various metal salts playing the role of Lewis acids ($AlCl_3$, zinc trichloroacetate,

$ZnCl_2$, $NiCl_2$, and other salts) have been studied as the acceptors A_2.[60,61,68-70] In both cases (CTC and ATC) the increase of the efficiency of the action of the system is associated with the increase of the positive charge on the nickel atom. Some of the catalytic systems investigated proved to be extremely effective even at -15 °C. Investigations have established that, when π-RNiX interacts with acceptors, side reactions take place and lead to the decomposition of a considerable proportion of the organonickel compound, as a result of which the amount of the effective active centres propagating the polymerisation reaction is 10–15% of the π-RNiX introduced[71-73]. In all cases the reaction is of first order with respect to the catalyst.

Organochromium compounds (π-R_3Cr and π-R_2Cr) lead preferentially to the formation of 1,2(3,4)-units in the polymerisation of dienes[29,31]. In all cases low-molecular-weight polymers are formed (the average degree of polymerisation is 25–30) containing a conjugated system of double bonds at one end of the chain. The molecular weight of the polymer is independent of the monomer concentration although the propagation reactions have been shown to be of first order with respect to the monomer[31]. Hence it follows that not only the propagation reaction but also the chain transfer reaction proceeds with participation of the monomer:



The quantitative Diels–Alder reaction of polymer chains with maleic anhydride indicates the *trans*-conformation of the diene end of the chain (analogue of *trans*-piperylene). The use of π-allyl compounds of chromium thus leads to the possibility of obtaining oligomeric unsaturated products with the functional group at one end of the chain.

In contrast to the comparatively unstable π-alkenyl derivatives of chromium, the organometallic compounds of chromium(II) and chromium(III), bound chemically to the SiO_2 or aluminosilicate surface, are fairly stable, propagating the polymerisation process via the "live" chain mechanism even at ~70 °C. These systems are extremely stereospecific for the formation of *trans*-units in the polymerisation of various dienes[30,62]. The *trans*-conformation of the units is fully retained in the copolymerisation of dienes. The above systems can be used to obtain the corresponding crystalline homopolymers (butadiene and isoprene) as well as amorphous *trans*-copolymers. All the groups bound to the chromium atom participate in the polymerisation reaction and the molecular weight of the polymer increases continuously with the degree of polymerisation. The similarity of the copolymerisation constants (r_1 and r_2) for butadiene, isoprene, and piperylene must be noted. The identity of the microstructures of the polymers and the identify of the constants of the copolymerisation of butadiene with isoprene permitted the conclusion that the chromium oxide catalyst known previously (CrO_3 on a carrier) acts via analogous stages involving organochromium compounds[30].

π-Alkenylchromium compounds, bound chemically in Al_2O_3, are *cis*-stereoregulating catalysts in the polymerisation of butadiene and isoprene, in contrast to the compounds described above. However, they rapidly lose their activity at a comparatively low degree of polymerisation[62]. The most important distinctive feature of this system is the formation of a polymer with a very high molecular weight even at a low degree of conversion, which indicates a very high rate of chain propagation. When the allyl groups in π-R_3Cr are substituted by electronegative groups, the system becomes *cis*-stereoregulating[31].

Like polyallylchromium compounds, tetrabenzyltitanium induces the formation of mainly 1,2(3,4)-units. The substitution of one benzyl group by a chlorine, bromine, or iodine atom increases the content of *cis*-units (in the sequence indicated). Tribenzyltitanium iodide is a highly stereospecific catalyst for the synthesis of *cis*-polybutadiene. The somewhat smaller content of *cis*-units in the polyisoprene formed can be due to the contamination of the system by a very small amount of oxygen-containing impurities. It has been established that the addition of small amounts of THF or diethyl ether to $(C_6H_5CH_2)_3TiI$ reverses the stereospecificity of the action of the system from 1,4-*cis*-specificity to 1,2-stereoregulation, as in the case of organolithium compounds. Only one benzyl group participates in polymerisation steps under the influence of $(C_6H_5CH_2)_4Ti$ and $(C_6H_5CH_2)_3TiI$; this is illustrated by the data in Fig. 1, which presents the yields of toluene in the decomposition of the polymerisation mixture by an aqueous solution of acid at the end of the polymerisation reaction[33],

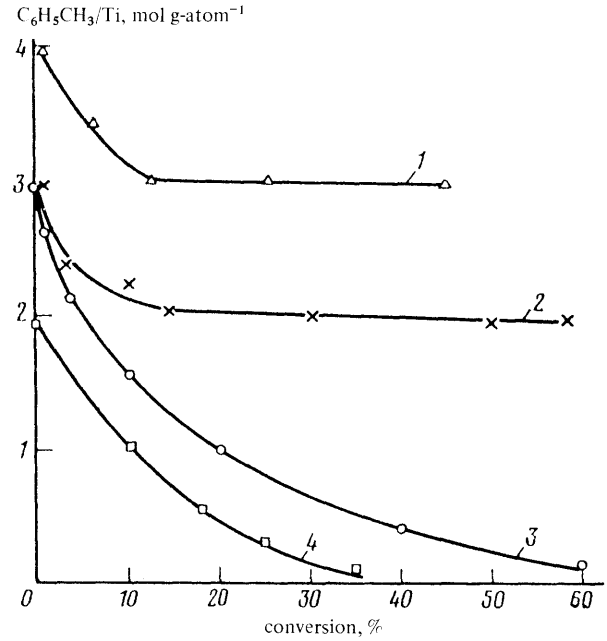


Figure 1. The consumption of benzyl groups in the polymerisation of butadiene {$[C_4H_6]$ = 5 M} under the influence of benzyl derivatives of titanium(IV) and titanium(III):[33,37,40]
1) $(C_6H_5CH_2)_4Ti$, [Ti] = 5 × 10^{-3} M, 50 °C, *o*-xylene;
2) $(C_6H_5CH_2)_3TiI$, [Ti] = 1.5 × 10^{-3} M, 25 °C, *o*-xylene;
3) $(C_6H_5CH_2)_3Ti$, [Ti] = 10 × 10^{-3} M, 50 °C, toluene;
4) $(C_6H_5CH_2)_2TiI$, [Ti] = 3 × 10^{-3} M, 25 °C, toluene.

It is important to note that tetrabenzyltitanium remains in the quadrivalent state throughout the polymerisation process. Titanium(III) compounds have so far been investigated only

in the polymerisation of butadiene. Tribenzyltitanium leads to the preferential formation of 1,2-units and, in contrast to tetrabenzyltitanium, all the benzyl groups are involved in the polymerisation reaction (Fig. 1). Among all the halogeno-derivatives of tervalent titanium, only $(C_6H_5CH_2)_3TiI$ is a highly effective catalyst of the synthesis of *cis*-polybutadiene. The polymerisation proceeds with an appreciable induction period due to the slow initiation stage—the insertion of butadiene in the titanium–benzyl bond. The induction period disappears completely following the addition of organoaluminium compounds (R_3Al and R_2AlCl; Al/Ti = 1 mol mol^{-1}) to R_2TiI. It has been shown for the $(C_6H_5CH_2)_2$. .TiI + R_2AlCl system[74] that the exchange reaction results in the immediate substitution of the benzyl groups by isobutyl groups, to which butadiene adds in a broad front:

$$(C_6H_5CH_2)_2TiI + (iso\text{-}C_4H_9)_2AlCl \rightarrow (iso\text{-}C_4H_9)_2TiI + (C_6H_5CH_2)_2AlCl .$$

At the end of the polymerisation process, after the decomposition of reaction mixture with an aqueous solution of acid, all the benzyl groups of the initial dibenzyltitanium iodide can be detected quantitatively in the form of toluene (Fig. 1).[74] It follows from the results that the true active centre in the Ziegler "titanium" system used under industrial conditions to synthesise *cis*-polybutadiene is apparently the compound R_2TiI.

Tri-π-allylniobium leads to the formation of amorphous 1,2-polybutadiene and the substitution of even only one of its allyl groups by chlorine leads to *cis*-stereoregulation. Among all the polyallyl derivatives of transition metals, only the rhodium compounds lead to *trans*- and not 1,2(3,4)-units.[47]

Tetra-allyl derivatives of molybdenum and tungsten do not themselves induce the polymerisation of dienes; polymerisation catalysts based on them are formed after the substitution of one allyl group by a halogen atom or other anionic species[43,45,46]. Two allyl groups in the resulting active centres are linked to the Mo(W) atom by a π-allyl bond and are not involved in polymerisation; one allyl group is linked to the metal by a σ bond and polymerisation proceeds via the latter. The organometallic active centres indicated are extremely stereospecific for the formation of amorphous and crystalline 1,2-polybutadiene. The syndiotactic arrangement of units predominates in the chain[44].

Like $(\pi\text{-}C_3H_5)_3Rh$, tribenzylneodymium leads to *trans*-structures in the polymerisation of butadiene and isoprene[48].

Triphenylmethylneodymium dichloride, containing 3–4 THF molecules in the coordination sphere, becomes an effective *cis*-regulating catalyst of the dimerisation of isoprene and butadiene after the introduction of tri-isobutylaluminium (Al/Nd = 3–5 mol mol^{-}).[49] The role of AlR_3 is still obscure—it is not clear whether it is involved only in complex formation with THF or whether it plays the role of an electron acceptor, forming complexes with $R'NdCl_2$. One cannot rule out the possibility that, as in the $(C_6H_5CH_2)_2TiI$ + R_2AlCl system examined above, the rate-limiting stage in this instance is the addition of the first diene molecule to the Nd–C bond, while the organoaluminium compound eliminates the induction period by replacing the triphenylmethyl group by the isobutyl group in the $(C_6H_5)_3CNdCl_2$ molecule.

The *trans*-isomer and not the *cis*-isomer is involved in the polymerisation of piperylene under the influence of transition metal compounds and RLi in hydrocarbon media in the vast majority of cases. This is correlated with the fact that *trans*-piperylene is capable of bidentate coordination to the metal. For the same reason, only the *trans*-isomer enters into the Diels–Alder reaction with maleic anhydride.

The polymerisation of cyclohexadiene can lead to two types of structure with the *cis*-conformation of units:



1,4-unit 1,2-unit

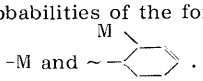
An amorphous polymer with approximately equal contents of the 1,4- and 1,2-units is formed under the influence of RLi in hydrocarbon and solvating media and systems of the Ziegler type ($R_3Al + TiCl_4$, $R_3Al + VCl_3$, etc.). The equal contents of the 1,4- and 1,2-units are apparently correlated with the equal probabilities of the formation of the active centres  . Blocks of 1,2-units cannot arise in the chain owing to steric hindrance. A crystalline polymer with a melting point of the crystalline phase of ~270 °C is formed under the influence of complexes of π-allylnickel halides with electron acceptors (chloral etc.). The polymer contains more than 90% of 1,4-units and its glass point is ~120 °C.[75]

Table 4. Kinetics of the polymerisation of dienes under the influence of organometallic compounds of transition metals.

Catalytic system	Solvent	Reaction order w.r.t. monomer	Reaction order w.r.t. catalyst	E_a^{eff}, kcal mol^{-1}	Refs.
	Butadiene				
$(\pi\text{-RNiI})_2$	benzene	1	0.5	15.5	[57]
π-RNiI; [Ni] = 1·10^{-3}—1·10^{-5}	benzene		1		[76]
$(\pi\text{-}C_4H_7NiCl)_2\cdot 2Ni(OCOCCl_3)_2$	toluene	1	1	6.4	[77]
$(\pi\text{-}C_5H_9NiCl)_2\cdot 2Ni(OCOCCl_3)_2$	toluene, chlorobenzene	1.4—1.6	1	10	[78]
$(\pi\text{-}C_5H_9NiCl)_2\cdot 2Zn(OCOCCl_3)_2$	toluene, hexane	1.6—1.35	1	10	[78]
$(\pi\text{-}C_4H_7NiCl)_2$.chloranil	toluene	1	1	6.2	[79]
$(\pi\text{-}C_4H_7NiCl)_2\cdot 2CCl_3COOH$	toluene	2	1	12.1	[80]
$(\pi\text{-}C_5H_5NiCl)_2TiCl_4$	heptane	0—1*	1	14.6	[81]
π-RNiOCOCCl$_3$	toluene	1.5	1	11	[27]
π-R$_3$Cr	toluene	0	2	19	[31]
R$_3$TiI	toluene	1	0.5	8	[33]
R$_4$Mo + C_3H_5I	toluene	0	1	12	[46]
R$_4$Mo + CCl$_3$COOH	toluene	1	1	13	[47]
	Isoprene				
π-RNiI	toluene	0—1*	0.6	19	[65]
π-RNiOCOCF$_3$	toluene	1	1	19	[82]
π-R$_3$Cr	toluene	0—1*	1	17	[29]
π-R$_2$CrOSi|SiO$_2$	toluene	1	1	10	[30]

*At low monomer concentrations the rate of polymerisation increases with increasing concentration, while at higher concentrations (2–4 M and above) the rate is independent of the monomer concentration. The lower the catalyst concentration[29,65] and temperature[81], the lower the monomer concentration at which the zero order of the reaction with respect to the monomer is observed.

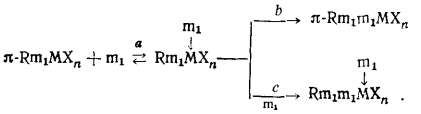
III. KINETICS OF THE POLYMERISATION OF DIENES UNDER THE INFLUENCE OF ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS

The kinetics of the polymerisation of butadiene and isoprene, in particular the reaction orders with respect to the monomer and the catalyst and the effective activation energy have been studied for a series of systems characterised by different stereospecificities of their action. In certain cases the concentration of the effective active centres for the

chain transfer reaction were determined experimentally. The results of these investigations are summarised in Table 4.

The effective activation energies E_a^{eff} for various systems vary from 6 to 19 kcal mol^{-1}. The π-RNiCl.chloranil, π-RNiCl.Ni$(OCOCCl_3)_2$, and tribenzyltitanium iodide systems are characterised by very low activation energies (6 to 8 kcal mol^{-1}). In most cases the rate of polymerisation of dienes is proportional to the concentration of the organometallic compound. In polymerisation under the influence of di-π-allylnickel iodide the order of the reaction at the catalyst concentration normally employed, i.e. $[Ni] > 10^{-3}$ M, is 0.5–0.6. Hence it follows that, like the initial π-allylnickel iodide, oligodienylnickel iodides exist in a dimeric form and the polymerisation reaction involves the monomeric form π-RNiI. The reaction order of 0.6 for the polymerisation of isoprene indicates a somewhat greater tendency of oligoisoprenylnickel iodide towards dissociation. At very low π-RNiI concentrations (10^{-5}–10^{-6} M) the reaction is first order with respect to the catalyst in the polymerisation of butadiene[76], which suggests that at such concentrations the monomeric form π-RNiI predominates.

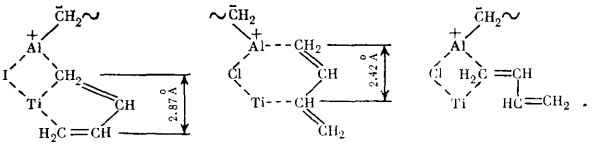
The order of reaction with respect to the monomer varies from 1 to 2, which reflects the influence of the stage in which the monomer is coordinated to the active centre. The mechanism of the incorporation of the monomer into the polymer chain presupposes an equilibrium stage involving the coordination of the monomer to the active centre and the stage in which it is inserted in the chain via a unimolecular or bimolecular mechanism:



Pathway *b* presupposes a unimolecular mechanism of the insertion of the coordinated monomer in the polymer chain via the C–M bond, while pathway *c* presupposes a bimolecular mechanism involving the displacement of a coordinated monomer by another monomer molecule (from the solution). There is a possibility that both reaction pathways operate simultaneously and the order with respect to the monomer can vary from 1 to 2 depending on which of the above stages limits the overall rate of the process.

IV. THE MECHANISM OF STEREOREGULATION IN THE COORDINATION POLYMERISATION OF DIENES

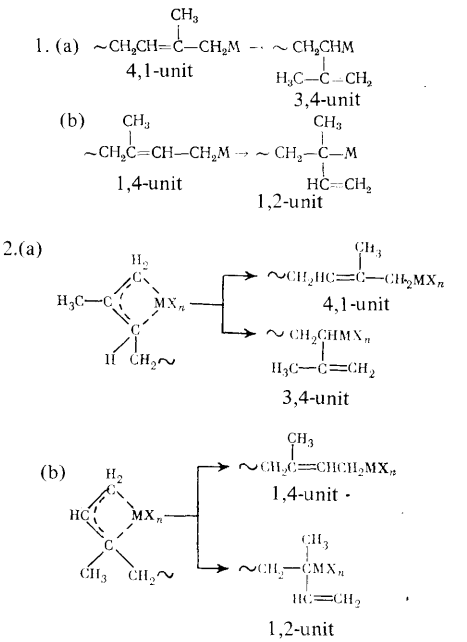
In the majority of studies on the polymerisation of dienes under the influence of Ziegler systems published previously the nature of the active centres and the polymerisation mechanisms were regarded from the same standpoint as in the consideration of the polymerisation of olefins. The structure of a bimetallic complex with bridge bonds was attributed to the active centre. In the first investigations it was assumed that chain propagation proceeds via the C–Al bond of the organoaluminium compound bound in a complex with a transition metal salt. Later schemes presuppose that the transition metal plays a decisive role in this complex and that the monomer is inserted not only in the Al–C bond but also in the carbon–transition metal bond. Furukawa[83] assumed that the structure of the units formed is determined by the length of the C–M bond which is correlated with the electronegativity of the metal. With decrease of the distance between two neighbouring sites, the structure becomes more favourable for coordination in the sequence *cis*-addition, *trans*-addition, and 1,2-addition, in which suitable distances are 2.87, 2.42, and less than 2.42 Å respectively:



In Ziegler catalysis stereoregulation is achieved by a complex catalyst having two coordination centres. The idea that a second, non-transition metal (aluminium) etc. must be present in the complex proved invalid after the possibility of the stereospecific catalysis under the influence of individual organometallic compounds of transition metals had been established. The first stage of the polymerisation reaction is coordination of the monomer to the transition metal.

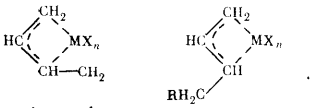
1. The Mechanism of the Formation of 1,4-*cis*- and *trans*-Units

In considering the question of the stereoregulation mechanism, we begin with the assumption that the structure of the units formed on polymerisation is determined by the structure of the terminal unit in the active centre and not the configuration of the monomer in solution[84–86]. This means that the *cis*- and *trans*-units are not genetically linked to the cisoid or transoid state of the monomer. The microstructure of the polymer chain already yields some information about the nature of the active centres. Thus in the organometallic σ-compounds of transition metals and lithium and in the π-allyl complexes the contents of 1,2- and 3,4-units also reflect a definite conformation of the active centre, for example:



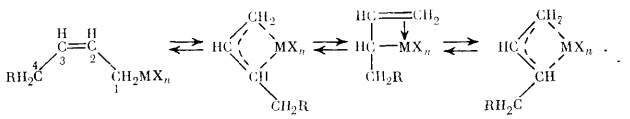
The formation of 1,2- and 3,4-units is genetically linked to a specific concentration of the terminal σ- or π-allyl active centre. The simultaneous presence of 1,2- and 3,4-units in polyisoprene therefore indicates the inhomogeneity of the chain structure in terms of the "head to tail" arrangement (the 1,4–1,4, 1,4–4,1, and 4,1–1,4 structures).

Examples of organometallic σ-compounds of transition metals initiating polymerisation are provided by titanium(IV) compounds as well as the organomolybdenum compounds R
|
π-R_2MoX, in which only the allyl group linked to molybdenum by a σ bond participates in chain propagation. The organometallic derivatives of alkali and alkaline earth metals and apparently the majority of organolanthanide compounds belong to a similar type. The alkenyl derivatives of transition metals, particularly those containing the metal in a reduced state, are formed as the stable compounds of the π-allyl type with two possible configurations (*anti*- and *syn*-), for example, for the crotyl derivatives, we have

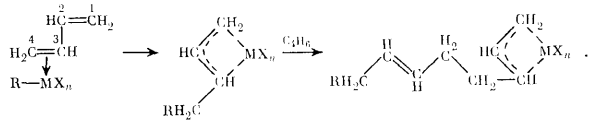


anti-complex *syn*-complex

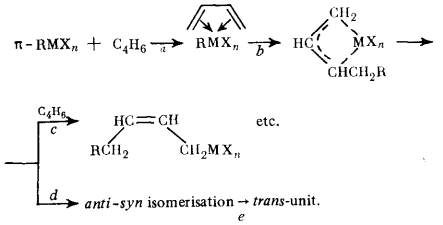
The *anti*-complex can be regarded as a seed giving rise to a *cis*-unit, while the *syn*-complex is a similar seed for a *trans*-unit. Tolman established for the first time that, when butadiene adds to HNi^+L_4 (L = phosphate ligand), an *anti*-complex is formed initially and isomerises subsequently to the *syn*-complex[87]. The *anti–syn* isomerisation can be represented only as a process proceeding via an intermediate σ-state, in which the metal is bound to a third carbon atom, because direct *cis–trans* transitions are energetically difficult:



The isomerisation takes place as a result of the migration of the "counterion" in the allyl conjugation system. The equilibrium amount of the σ-forms in the π-allyl complexes depends on the nature of the metal and the surrounding ligand. Naturally the electron-donating compounds forming complexes with the transition metal, which include also the monomer undergoing polymerisation, displace the equilibrium towards the σ-forms. If there is one vacancy (for coordination) at the transition metal, the diene can be coordinated via only one double bond, assuming a transoid conformation in the coordination sphere of the metal. The primary insertion of the monomer in the chain can then lead to a *trans*-unit:[85]

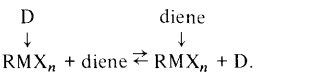


However, in the vast majority of cases the conjugated diene plays the role of a bidentate ligand, which assumes a cisoid conformation on the metal. This entails the transition from the π-allyl structure of the active centre to the σ-state:



The bidentate coordination of the conjugated diene is most likely for the monomeric form of the organometallic compound, characterised by the greatest number of vacancies for coordination.

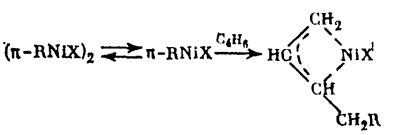
The polymerisation reaction consists of a sequence of stages involving the formation of a π-complex with the diene and its conversion into a π-alkenyl complex after the insertion of the diene in the chain with subsequent transition to the σ-state on coordination with the next monomer molecule (reactions *a–c*). Pathway *d* leads to the *anti–syn* isomerisation of the complex and the formation of *trans*-units. Thus, in polymerisation under the influence of monomeric forms of the organometallic compound, the chain microstructure is determined by the ratio of the rates of growth and isomerisation of the active centre. For systems in which the reaction is of first order with respect to the monomer, one may expect that, at very low monomer concentrations where the "lifetime" of the terminal unit increases, the number of *trans*-units should increase at the expense of the *cis*-units. This has been confirmed experimentally in the case where individual organonickel and Ziegler systems with participation of titanium and cobalt compounds were used[88] (Fig. 2). The results of studies presented in Fig. 2 show that in all cases indicated an appreciable decrease of the content of the *cis*-units and the corresponding increase of the content of *trans*-units are observed at low monomer concentrations (up to 0.4 M). Any factors favouring the "sticking" of the terminal unit in the active centre increase the role of the isomerisation in reaction. Electron-donating compounds (D) (ethers, sulphides, and amines) have a similar effect, being coordinated to the transition metal and displacing the diene:

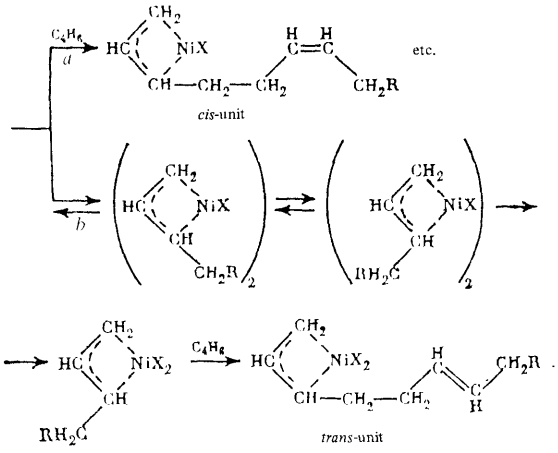


As will be shown below, the second monomer (m_2) has an analogous effect in copolymerisation if the rate of its insertion in the chain is less than the rate of insertion of the first monomer (m_1).

The question of the stereoregulation mechanism in cases where the organometallic active centre is in an associated state and the main true active centre in the chain propagation stage is the monomeric form is of great interest. This applies, for example, to the *trans*-regulating π-alkenylnickel halides, which exist in solution in the form of dimers and for which the reaction order with respect to the catalyst is 0.5,[57] and also to the butadienyl and isoprenyl derivatives of lithium. The latter exist in a hydrocarbon solution in the form of the associated species $(RLi)_4$ and the reaction order with respect to the catalyst is 0.25.[91,93] It follows from the data presented that, in the instances indicated, generally a small number of the monomeric active centres, in equilibrium with the associated species, participate in the polymerisation.

The mechanism of the chain propagation reaction involving π-alkenylnickel halides is[86,89]





In the primary product of the addition of the diene to the monomeric form π-RNiX the unit has the *cis*-conformation. In the associated species formed subsequently the π-alkenyl unit undergoes the *anti–syn* (*cis–trans*) isomerisation, which leads to *trans*-units on subsequent dissociation[89]. Since the fraction of the monomeric forms is very small, the associated species, not involved in the chain propagation steps, play a decisive role in the formation of microstructures. It is essential to note that only *trans*-β-butene is formed in the hydrogenolysis of π-crotylnickel chloride with complete absence of *cis*-butene[90]. This shows that the equilibrium concentration of the *syn*-form of π-crotylnickel halides is close to 100%.

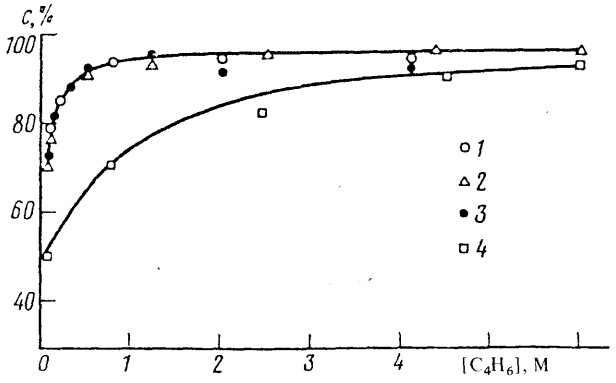
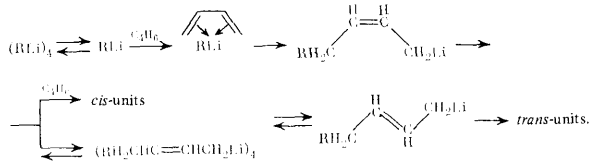


Figure 2. The influence of the monomer concentration on the microstructure of polybutadiene[88] (*c* = content of *cis*-units): *1*) π-C_5H_9NiCl–$Ni(OCOCCl_3)_2$; *2*) π-$C_3H_5NiOCOCF_3$; 3) $CoCl_2$–R_2AlCl; 4) TiI_2Cl_2–R_3Al; *1*), *3*), and 4) 20 °C; *2*) 40 °C; *1*), *3*), and 4) solvent–toluene; *2*) solvent–heptane.

In the case of organolithium compounds the chain microstructure depends greatly on the RLi concentration in solution, which is illustrated by the data in Table 5. With decrease of the RLi concentration, the content of the *cis*-units in polyisoprene and polybutadiene increases. Presumably at vanishingly low concentrations of organolithium compounds only the *cis*-units are formed. The higher content of the *cis*-units in polyisoprene compared with polybutadiene for the same RLi concentration is consistent with the higher rate of chain propagation. It has been shown[93] that the rate of homopolymerisation of isoprene is significantly higher than that of butadiene. The mechanism of stereoregulation in the polymerisation of dienes under the influence of organolithium compounds must be represented by the same general scheme as for π-allylnickel halides:



The *cis–trans* isomerisation in the associated species apparently proceeds as a result of the transfer of the counterion (Li^+) to neighbouring molecules in the associated species and not via a unimolecular mechanism, because direct *cis–trans* transitions require a high activation energy.

Table 5. The influence of the catalyst concentration on the microstructure of the polymers obtained under the influence of organolithium compounds (20 °C, solvent—heptane).

[RLi], M	Contents of units, %				Refs.	[RLi], M	Contents of units, %				Refs.
	1,4-*cis*	1,4-*trans*	1,2-	3,4-			1,4-*cis*	1,4-*trans*	1,2-	3,4-	
	Butadiene						Isoprene				
0.073	30	46	24	—	[91]	0.061	74	18	0	8	[91]
0.0124	44	46	10	—	[91]	0.001	78	17	0	5	[91]
0.0003	47	45	8	—	[91]	0.0001	84	11	0	5	[91]
0.000054	70	28	2	—	[91]	0.000008	97	0	0	3	[91]
0.00001	86	10	4	—	[92]						

Polyakov et al.[94] showed for the first time that polymerisation on crystalline ethyl-lithium with supply of the diene from the gas phase takes place very slowly and leads to the preferential formation of 1,2(3,4)- and *trans*-units. Such a structure is characteristic of polymerisation involving the more polarised C–Li bond in the associated species.

The structure of such associated species depends greatly on their composition, which is indicated by the different compositions of the butenes formed on decomposition of the homoassociated crotyl-lithium species or mixed associated species incorporating crotyl-lithium and lithium alkyl by water or acid. In the former case β-butenes are formed preferentially, while in the latter α-butene is the preferred product[95].

The differences between the microstructures of polyisoprene and polybutadiene at the same RLi concentration can also be explained by the different rates of the *cis–trans* isomerisation in the associated species.

It was shown above that, depending on the nature of the ligands, either *trans*- or *cis*-units are formed in the presence of the same transition metal. It might have been expected that the rate of propagation in a *cis*-regulating system (v_a) would be significantly higher than in a *trans*-regulating system (v_b). Table 6 presents data illustrating the decrease of the rate of chain propagation (v_a/v_b) in the

presence of the same metal (Ni, Cr, and Ti) when the stereospecificity of the catalytic action is reversed from *cis*-stereoregulating to *trans*-stereoregulating.

Table 6. Comparison of the rates of chain propagation in the *cis*- and *trans*-stereoregulating systems[96].

No.	Catalytic system	Contents of units, %				v_a/v_b
		cis-	*trans*-	1,2-	3,4-	
	Isoprene					
1a	π-RCr(OAl)(OAl)|Al_2O_3	95	0	0	5	10^3
1b	R(R)Cr—O—Si|SiO_2	0	95	0	5	
	Butadiene					
2a	π-RNiCl·Ni$(OCOCCl_3)_2$	97	0	3		$7.8\cdot10^2$
2b	$(\pi\text{-RNiI})_2$	0	95	5		
3a	$(C_6H_5CH_2)_3TiI$	95	2	3		$7.4\cdot10^3$
3b	$(C_6H_5CH_2)_4Ti$	20	20	60		

Table 7. The relative reactivities of butadiene (m_1) and styrene (m_2) in coordination copolymerisation (solvent—toluene).

Catalytic system	Contents of units in butadiene chain component, %			r_1	r_2	Refs.
	cis-	*trans*-	1,2-			
RLi*	0	9	91	0.2	8.0	[97]
RLi**	43	50	7	10	0.035	[98]
$(C_3H_5)_3MoOCOCCl_3$	8	2	90	30.5	0.02	[99]
$(C_3H_5)_4W+C_3H_5Cl$	0	9	91	10.1	0.12	[99]
$(C_3H_5)_4Zr$	61	4	35	34	0.02	[99]
$(C_6H_5CH_2)_4Ti$	15	25	60	27.5	0.02	[99]
π-RNiCl.chloranil	96	2	2	4.6	0.13	[100]
π-RNiCl·CCl_3C(H)(O)	93	6	1	4.6	0.13	[100]

*Solvent—THF.
**Solvent—benzene.

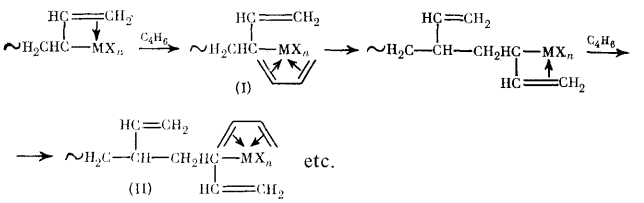
The positive role of electron-accepting components forming complexes with the organometallic active centre consists in a decrease of the probability of the formation of the associated species and in an increase of the rate of chain propagation. It is noteworthy that mainly *trans*-structures (95–98% of *trans*-units) are produced in systems involving vanadium compounds characterised by very high rates of chain propagation (indicated by the formation of isoprene and butadiene polymers with very high molecular weights). When account is taken of the considerations described above concerning the stereoregulation mechanism, this can be due by the very high rate of the *cis*–*trans* isomerisation or monodentate coordination of the diene.

2. The Mechanism of the Formation of 1,2(3,4)-Structures

The preferential formation of 1,2(3,4)-units in the polymerisation of dienes under the influence of RLi in solvating media or under the influence of RK(RNa) is always associated with an increase of the polarity of the C–M bond. As in all the anionic systems, leading to the preferential formation of 1,2(3,4)-structures, in the copolymerisation of butadiene (m_1) with styrene (m_2) in systems of this kind, styrene is much more reactive than butadiene ($r_2 \gg r_1$). On the other hand, in coordination systems dienes are appreciably more reactive than styrene regardless of the nature of the stereoregulation, which is illustrated by the data in Table 7.

The results presented show that the formation of 1,2(3,4)-units in the systems considered is associated with the coordination mechanism of the catalytic action and not with the polarisation of the C–M bond. As mentioned above, the preferential formation of 1,2(3,4)-units is characteristic of organometallic compounds of the type MR_n ($M = Ti^{3+}$, Ti^{4+}, Cr^{3+}, or Cr^{2+}), R_3MoX, R_3WX, etc. and the formation of a crystalline or amorphous polymer with a syndiotactic arrangement of units (for R_3MoX and R_3WX) is characteristic of the polymerisation of butadiene. Many of the systems indicated in Table 7 are also active in olefin polymerisation processes, which indicates the stability of the organometallic σ-compounds. The stability of the C–M σ-bond increases in the polymerisation of dienes as a result of its conjugation with the double bond.

Although the mechanism of the formation of 1,2-units in coordination systems has not so far been studied experimentally, one may put forward certain considerations concerning the most probable pathway leading to the formation of syndiotactic structures under the influence of organomolybdenum, organotungsten, and organocobalt compounds, as well as organic derivatives of certain other metals[101]:

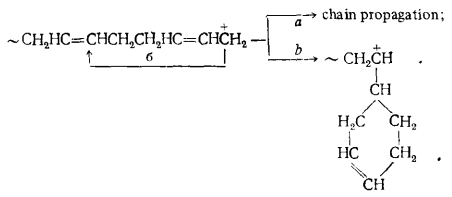


Complexes (I) and (II), formed alternatively in the course of chain propagation, differ sterically by the positions of the π-coordinating double bonds in the terminal unit of the polymer chain and the monomer. This chain propagation mechanism leads to a syndiotactic arrangement of units.

V. THE COPOLYMERISATION OF DIENES IN COORDINATION SYSTEMS

There is an antiparallel variation of the relative activities of dienes in cationic and anionic systems: chloroprene, butadiene, isoprene, *trans*-piperylene, cyclohexadiene, and 2,3-dimethylbutadiene. The reactivities increase in the above sequence when the active centres are cationic and decrease in polymerisation under the influence of anionic systems[97]. The above diene reactivity series in cationic systems is well illustrated by the increase of r_2 in the copolymerisation of isobutene (m_1) with dienes (m_2). The similarity of the copolymerisation constants r_1 and r_2 in the cationic copolymerisation of dienes with the corresponding olefins, for example, in the copolymerisation of butadiene with β-butene,[102] favours the development of cyclisation processes in the polymerisation and copolymerisation of

dienes:



In view of its high steric probability, reaction *b* takes place very vigorously even for low degrees of polymerisation and leads to cyclisation and loss of unsaturation.

In anionic copolymerisation, for example, under the influence of organometallic derivatives of alkali metals, the values of r_1 and r_2, reflecting the reactivity of the monomers, are consistent with the above sequence.

Table 8. The relative reactivities of the monomers (m) in coordination copolymerisation.

m_2	Catalytic system	Solvent	r_1	r_2	Refs.
		m_1—Butadiene			
Isoprene	$TiCl_4$ + (iso-C_4H_9)$_3$Al	benzene	1.00	1.00	[103, 104]
	TiI_4 + (iso-C_4H_9)$_3$Al	benzene	1.88	0.55	[105]
	$CoCl_2 \cdot C_2H_5OH$ + (iso-C_4H_9)$_2$AlCl	benzene	2.30	1.15	[103]
	$NiCl_2 \cdot Py$ + (C_2H_5)$_2$AlCl	benzene	1.15	0.59	[106]
	π-RNiCl + $TiCl_4$	toluene	6.20	1.15	[104, 107, 108]
	(π-RNiI)$_2$	toluene	0.30	2.35	[66, 109]
	π-R_2CrOSi|SiO_2	toluene	1.06	0.80	[62, 110]
	chromium oxide catalyst	toluene	1.04	0.76	[62, 110, 111]
	RLi	hexane	3.38	0.47	[105]
Cyclohexadiene	(π-RNiI)$_2$	toluene	0.80	1.10	[112]
	π-RNiCl·Ni(OCOCCl$_3$)$_2$	toluene	0.47	0.93	[113]
	π-RNiCl·A*	toluene	0.23—0.50	0.6—1.0	[113]
trans-Piperylene	(π-RNiI)$_2$	toluene	1.20	0.32	[82, 109]
	TiI_4 + R_3Al	toluene	3.60	0.50	[104, 107]
	$CoCl_2$ + R_2AlCl	toluene	1.20	0.30	[104, 107]
2,3-Dimethylbutadiene	TiI_4 + R_3Al	toluene	6.30	0.15	[104, 107]
	$TiCl_4$ + R_3Al	toluene	2.16	0.33	[114]
	π-RNiCl.chloranil	toluene	2.80	0.18	[115]
	$CoCl_2$ + R_2AlCl	toluene	2.70	1.13	[114]
Styrene	π-RNiCl·A*	toluene	4.60	0.13	[100]
	RLi	benzene	10.00	0.035	[116]
	RCaI	benzene	10.00	0.04	[117]
		m_1—Isoprene			
Cyclohexadiene	(π-RNiI)$_2$	benzene	0.50	1.64	[118]
	$TiCl_4$ + LiR (1 : 1)	toluene heptane	0.30	0.80	[119]
	RLi	benzene	0.80	0.40	[119]
Piperylene	RLi	hexane	17±5	0.06	[120]
	$Ti(OR)_4$ + (C_2H_5)$_3$Al	benzene	0.30	0.30	[121, 122]
2,3-Dimethylbutadiene	RLi	hexane	17.00	0.06	[120]

*A = acceptor.

The most important characteristic feature of the copolymerisation in coordination systems, particularly under the influence of organometallic compounds of transition metals, is the role of the coordination stage in the reactivity of the monomers. The probability of the incorporation of the monomer in the chain is determined both by the equilibrium in the coordination stage

$$RMX_n \overset{m_1}{\rightleftarrows} RMX_n + m_1; \quad RMX_n \overset{m_2}{\rightleftarrows} RMX_n + m_2$$

and by the rate of incorporation of the coordinated monomer in the chain. Since the "lifetime" of the terminal chain in the active centre depends on the rate of incorporation of the coordinated monomer (m_1 and m_2) in the chain, the rate of the *cis–trans* isomerisation of this unit should also vary in the copolymerisation process. The structure of the copolymers can therefore differ extremely significantly from that of homopolymers. Table 8 presents data for the relative reactivities of dienes in copolymerisation under the influence of various Ziegler systems and organonickel and organolithium compounds. It is seen from these results that the values of r_1 and r_2 depend greatly on the nature of the organometallic active centre. The copolymerisation in hydrocarbon media under the influence of RLi, where characteristics most typical for anionic systems are manifested, can serve as a comparison standard. Whereas the reactivity of butadiene (r_1) is much higher than those of isoprene, piperylene, and 2,3-dimethylbutadiene (r_2) in anionic systems, in systems of the Ziegler type the reactivities of the same pairs of monomers greatly approach one another, in some cases become identical, and in a few instances, for example in the copolymerisation of butadiene with isoprene or cyclohexadiene under the influence of π-RNiI, r_2 is much higher than r_1.

Table 9. The relative reactivities of the monomers (m) and the microstructure of the copolymers (m_1-butadiene, degree of conversion ~10%).

Catalytic system	m_2	[m_2], mole fraction	Contents of units in butadiene chain component, %			r_1; r_2	Refs.
			cis-	*trans*-	1,2-		
TiI_4 + R_3Al	isoprene	0	90	6	4	$r_1 = 2.8 \pm 0.2$; $r_2 = 0.53 \pm 0.05$	[104, 107, 108]
		0.30	49	37	12		
		0.66	41	40	19		
TiI_4 + R_3Al	2,3-dimethylbutadiene	0.35	76	19	5	$r_1 = 6.3 \pm 0.2$; $r_2 = 0.15 \pm 0.06$	[104, 107, 108]
π-C_4H_7NiCl + $TiCl_4$	isoprene	0	90	8	2	$r_1 = 6.2 \pm 0.4$; $r_2 = 1.15 \pm 0.08$	[104, 107, 108]
		0.10	77	19	4		
		0.26	71	24	5		
		0.38	50	39	11		
π-C_4H_7NiCl + chloranil	2,3-dimethylbutadiene	0	96.5	1.5	2	$r_1 = 2.8 \pm 0.3$; $r_2 = 0.18 \pm 0.05$	[115]
		0.14	87	7	6		
		0.28	78	13	9		
		0.51	64	20	16		
		0.72	40.5	37.5	21		

*Content of m_2 in the copolymer.

A second distinctive feature of the copolymerisation under the influence of coordination systems with participation of transition metals is the mutual influence of the monomers on the chain microstructure. The structure of the copolymers differs in most cases from that of the homopolymers obtained in the presence of the same catalysts. Under the influence of the second monomer (isoprene, piperylene, 2,3-dimethylbutadiene), participating in the copolymerisation, the *cis*-butadiene units in the copolymer are converted into the *trans*-units whose number is approximately equal to the content of the second monomer in the chain. This indicates a direct genetic relation between the conversion of the *cis*-butadiene unit into the *trans*-unit and the incorporation of

Table 10. The relative reactivities of the monomers (m) and the microstructure of the copolymers (m_1—butadiene).

Catalytic system	m_2	$[m_2]$, mole fraction*	Contents of units in butadiene component, %			r_1; r_2	Refs.
			cis-	*trans*-	1,2-		
π-RNiCl·A	cyclohexadiene	0 0.175 0.355 0.565	96 95.5 94.5 94.0	2 2 2.5 3.0	2 2.5 3.0 —	r_1=0.4—0.5; r_2=0.8—1.0	[113]
π-C_3H_5NiI	isoprene	0 0.50 0.83	0 0 0	95 96 91	5 4 9	r_1=0.30±0.04; r_2=2.35±0.15	[82, 109]
π-C_3H_5NiI	*trans*-piperylene	0.20 0.40 0.75	0 0 0	94 95 96	6 5 4	r_1=1.12±0.13; r_2=0.32±0.08	[82, 109]
π-$R_2CrOSi\|SiO_2$	isoprene	0.45 0.70 0.83	0 0 0	97 97 97	3 3 3	r_1=1.06; r_2=0.8	[62, 111]

*Content of m_2 in the copolymer.

the second monomer in the chain. Table 9 presents data for the copolymerisation of butadiene with other monomers under the influence of the *cis*-regulating TiI_4–R_3Al and π-RNiCl.A systems. Together with the increase of the content of the *trans*-butadiene units, a change in the microstructure of the isoprene and 2,3-dimethylbutadiene units incorporated in the chain towards an increase of the content of the *cis*-units is observed. In all the instances discussed, electron-donating additives (ethers, sulphides, and amines) exert the same influence on the butadiene homopolymer structure as the second comonomer in copolymerisation.

It is noteworthy that the rate of chain propagation decreases on passing from homopolymerisation to copolymerisation and, in the homopolymerisation of butadiene, also under the influence of added electron-donating compounds. In the copolymerisation of butadiene (m_1) with cyclohexadiene (m_2) under the influence of the complexes π-RNiX.A we have $r_2 > r_1$ and the *cis*-configuration of the butadiene units is fully retained in the copolymer[113]. The *trans*-configuration of the units is fully retained in the copolymers in the copolymerisation of butadiene with isoprene and of butadiene with piperylene under the influence of *trans*-regulating systems (π-RNiI, π-$R_2CrOSi|SiO_2$).[111] These postulates are illustrated by the data in Table 10.

In the copolymerisation of butadiene with other dienes in the presence of Ziegler systems containing active centres involving cobalt compounds, an inversion of stereoregulation is also observed under the influence of the second monomer, but it involves a change to 1,2-units and not *trans*-units, the number of the former corresponding approximately to the molar content of the second monomer in the chain. This is illustrated by the data in Table 11. Evidently, for approximately equal values of r_1 and r_2, isoprene and 2,3-dimethylbutadiene induce a sharp increase in the content of buta-1,2-diene units in the copolymer chain. Bearing in mind that the system based on cobalt compounds is used under certain conditions to synthesise crystalline 1,2-polybutadiene, presumably, on coordination of the second, more electron-donating monomer, the terminal butadiene unit passes to the σ-state, as in the mechanism proposed above for molybdenum and tungsten compounds. Electron-donating additives (ethers, sulphides, and amides), leading to an increase of the number of 1,2-units, exert a completely analogous influence on the microstructure of the butadiene homopolymer.

Table 11. The relative reactivities of the monomers (m) and the chain microstructure in copolymerisation under the influence of the $CoCl_2.C_2H_5OH$ + $(iso\text{-}C_4H_9)_2AlCl$ (m_1—butadiene) catalytic system[104,107,108].

m_2	$[m_2]$, mole fraction	Contents of units in butadiene component, %			r_1; r_2
		cis-	*trans*-	1,2-	
Isoprene	0 0.32 0.53	94 75 58	3 7 3	3 18 39	r_1=1.0±0.1; r_2=0.9±0.1
2,3-Dimethylbutadiene	0.27 0.41	44 26	7 6	49 68	r_1=0.74±0.02; r_2=0.67±0.05
trans-Piperylene	0.21 0.41 0.57	95** 80** 50**		5 20 50	

*Content of m_2 in the copolymer.
**Overall content of the *cis*- and *trans*-units.

It is noteworthy that in butadiene–isoprene copolymers the 3,4-units, whose content in the copolymer obtained in the presence of the "cobalt" system reaches 31%, have disappeared from the isoprene component of the copolymer chain. This means that only 1,4-isoprene units adjoin the butadiene units in the chain. In the butadiene–2,3-dimethylbutadiene copolymers the conversion of the *trans*-units of 2,3-dimethylbutadiene, adjoining the butadiene units, into the *cis*-units is observed. In the joint presence of the second monomer and an electron donor, a still more marked increase of the content of buta-1,2-diene units in the copolymer is observed. The rate of the process decreases

significantly in the presence of the second monomer or an electron-donating additive[104,107,108].

Studies in individual fields have been surveyed and published in other reviews[60,86,101,123–125].

VI. CONCLUSION

The investigations carried out have shown that the true active centres for the stereospecific polymerisation of dienes are individual organometallic compounds of transition metals. Chain propagation takes place as a result of the insertion of the monomer in the carbon–transition metal bond. The stereospecificity of the catalytic action is determined by the nature of the metal and the ligands surrounding it.

Experimentally supported hypotheses concerning the stereoregulation mechanism, according to which the structure of the polymer chain units is determined by that of the terminal unit in the active centre in the chain propagation stage, have been put forward. The specific features of coordination copolymerisation, distinguishing it from ionic and radical copolymerisation, have been determined.

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