Lanthanide Complexes with Different Ligands Used to Catalyze Diene Polymerizations*

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Lanthanide coordination compounds have been widely employed for catalyzing certain processes in organic and high-molecular-weight chemistry. We have implemented profound studies into the synthesis of different ligand complexes with lanthanides and their reactivities when combined with organoaluminium compounds as a catalytic system for the stereoregular polymerization of dienes (isoprene, butadiene, piperylene, etc). Coordinative compounds of lanthanides with different ligands were synthesized as LnX_3L_3 (Ln = lanthanide ion; X = chlorine, bromine, iodine anion; L = organic ligand with an N/O donor atom) and were identified with IR, NMR, ESP and Raman spectroscopy methods. The coordinative compounds were synthesized with respect to the changes in the energetic and steric parameters of Ln–X couplings with varied electronegativity and electron density on O and N donor atoms in the organic ligand. The catalytic activity of the two-component system $NdCl_3 \cdot 3L–R_3Al$ was found to depend on the lanthanide number, the type of halogen anion, the organic ligand and the solvent for the polymerization, as well as on the organoaluminium compound structure. The kinetic parameters of polymerizations were investigated. The stereospecific properties of diene polymerizations and copolymerizations are discussed and the structures of the active centres suggested. The most advantageous and promising catalytic systems are described and proposed for further production of highly stereoregular polymers.

We have studied in various catalytic systems the effects of the nature of all the components in the Ln system and the conditions of the process, catalytic activity, the kinetic parameters, the stereospecificities in 1,3-diene polymerizations and copolymerization, and some properties of 1,4-*cis*-polydienes. The results are reported in Tables I–VIII.

The activity of Ln catalysts depends on their composition and, for the most part, on the Ln type. The type of lanthanide has a much greater effect on the chain propagation constant than on the number of active centres (Table II). With an increase in the lanthanide ordinal number, a tendency of the active centre concentration to decrease has been observed; this is conditioned by the increase in the stability of the lanthanide halide complex as the lanthanide ionic radii decrease. Both the k_p value and the activity of the whole system vary in a complex way in the lanthanide series. Catalysts containing Nd possess the highest activity for different diene polymerizations. The catalyst systems based on high lanthanides have shown extremely low activity. The reason for this is that the reactivity of the active centres changes (k_p decreases), while a reduction in the number of active centres is certainly of secondary value.

In the contents of the earth's crust, the lanthanides occur in the following order: Ce > Nd > La > Gd > Pr > Sm, etc. A comparison of this series with other data shows that lanthanides with strongly pronounced catalytic activity (Ce, Pr, Nd, Gd) are related to the most widespread f-elements.

Although the chain propagation constant k_p depends on the type of lanthanide, the observed catalytic stereoregulating activity remains stable in the polymerization of the most ordinary diene, *i.e.*, butadiene.

TABLE I. The Effect of the AlR_3 Structure on the Chain Transfer Constants in Butadiene *cis*-Polymerization with Nd and Ti Catalysts (toluene, 25 °C)

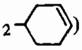
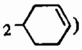
Metal	AlR_3	$\frac{k_t^m}{k} \times 10^4$	k_t^m (1/mol min)	$\frac{k_t^{Al}}{k_p}$	k_t^{Al} (1/mol min)
Nd	$Al(i\text{-}C_4H_9)_3$	1.0	0.014	0.050	7.0
	$Al(CH_2CH_2$$)_3$	1.0	0.013	0.025	3.2
Ti	$Al(i\text{-}C_4H_9)_3$	0.09	0.07	0.46	3.4×10^3
	$Al(CH_2CH_2$$)_3$	0.04	0.03	0.20	1.5×10^3

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TABLE II. The Effect of the Type of Lanthanide on k_p and the Number of Active Centres in Butadiene Polymerization in Toluene with Ln Catalysts at 25 ℃

Lanthanide	k_p (l/mol min)	$\frac{C_{a.c.}}{C_{Ln}} \times 100$ (%)
La	10	12
Ce	40	9
Pr	60	8
Nd	140	7
Gd	130	5
Dy	30	5

TABLE III. The Effect of the Type of Lanthanide on the Polydiene Microstructure (toluene, 25 ℃)

Lanthanide	1,4-*cis* unit content (%)		
	Polybutadiene	Polyisoprene	Polypiperylene
La	95.4		
Ce	94.7	94.7	57
Pr	95.1	94.7	62
Nd	94.6	95.0	64
Gd	95.2	95.9	70
Tb	95.0	96.0	69
Dy	93.7	96.0	66
Ho	92.2		
Er	93.0		

TABLE IV. The Dependence of k_p and the Number of Active Centres on the Solvent in Diene Polymerization with Ln Catalysts at 25 ℃

Monomer	Lanthanide	Solvent	k_p (l/mol min)	$\frac{C_{a.c.}}{C_{Ln}} \times 100$ (%)
Butadiene	Ce	toluene	40	9
		heptane	150	7
	Nd	toluene	140	7
		heptane	470	6
Piperylene	Nd	toluene	14	9
		heptane	70	6

TABLE V. The Effect of the Solvent on the Diene Reactivity Ratios with a Nd Catalyst at 25 ℃

Comonomers	Solvent	r_1	r_2
Butadiene–isoprene	toluene	1.69	0.54
	heptane	1.0	1.0
Butadiene–piperylene	toluene	4.60	0.26
	heptane	3.20	0.39

TABLE VI. The Effect of AlR_3 Radical Structure on the Butadiene Polymerization Parameters with Nd Catalyst (toluene, 25 ℃)

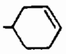
R	1,4-*cis* unit content (%)	k_p (l/mol min)	$\frac{C_{a.c.}}{C_{Nd}} \times 100$ (%)
i-C_4H_9	94.6	140	7.0
-CH_2CH_2	94.4	130	3.5

TABLE VII. The Effect of the Monomer Structure on Nd Catalyst Stereospecificities in Polymerization (toluene, 25 ℃)

Monomer	Unit content in polymer (%)	
	1,4-	1,2-
Butadiene	99.5	0.5
Isoprene	95	5.0[a]
Pentadiene-1,3	76	24.0
Octatriene-1,3,6	63	37
5-Methylheptatriene-1,3,6	33	67

[a] 3,4-units

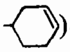
TABLE VIII. The Reactivity Ratios of Butadiene (r_1) and Other Compounds (r_2) with Nd Catalysts (toluene, 25 ℃)

Comonomer	r_1	r_2
Isoprene	1.69	0.54
1,3-Pentadiene	4.6	0.26
2-Cyclopropylbutadiene	0.51	2.18
5-Methyl-1,3,6-heptatriene	6.8	0.09

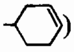
With piperylene polymerization, the Ln catalyst stereospecificity depends noticeably on the type of lanthanide; a more stereoregular polypiperylene is formed with a Gd catalyst. The absence of an effect of the halide ligand on stereoregulating properties in butadiene polymerization is considered a peculiarity of lanthanide catalysts; it has not been observed in the use of the already known catalysts based on d-elements.

The presence of toluene in the ligand environment of the lanthanide means that both the activity and the stereospecificity of the catalysts are determined by the solvent. Butadiene and isoprene polymerizations at 25 ℃ lead to the formation of polydienes, the microstructures of which are irrespective of the solvent used. Under the same conditions the solvent influences the catalyst specificities of piperylene polymerization: the contents of 1,4- and *cis*-structure units in polypiperylene are higher with the use of an aliphatic solvent.

Non-identical lanthanide active centres in toluene and heptane have been confirmed by diene copolymerization data. Copolymerization constants depend on the solvent; the values of the relative activities of comonomers are approximately the same in heptane. The data obtained show that the temperature range depends on the lanthanide; for example, polypiperylene microstructures are the same in toluene and heptane with a gadolinium catalyst at 0 ℃.

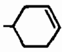
Since the modern ideas of the structures of the active centres in Ziegler-type catalysts imply that trialkylaluminium is a transition metal ligand, the effect of the AlR_3 structure on diene polymerizations with Ln catalysts should be considered. The catalytic activity of lanthanide catalysts has revealed strong dependence on the trialkylaluminium structures, the stereoregulating property remaining unchanged. The use of $Al(i\text{-}C_4H_9)_3$ and $Al(CH_2CH_2$-$)_3$ has established that the differences in catalytic activity with AlR_3 variations are conditioned by changes in the concentrations of the active centres, the reactivities (k_p and stereospecificity) being stable. The changes in polymerization temperatures are followed by changing a series that corresponds to polydiene yields with these organoaluminium compounds, all other conditions being equal.

Polymerization temperature 25 ℃:

$Al(i\text{-}C_4H_9)_3 > Al(CH_2CH_2$-$)_3 > Al(n\text{-}C_{10}H_{21}) >$

$Al(n\text{-}C_6H_{13})_3 > Al(C_2H_5)_3 > Al(i\text{-}C_4H_9)_2H$

Polymerization temperature 80 ℃:

$Al(CH_2CH_2$-$)_3 > Al(i\text{-}C_4H_9)_2H > Al(C_2H_5)_3 >$

$Al(n\text{-}C_6H_{13})_3 > Al(n\text{-}C_{10}H_{21})_3 > Al(i\text{-}C_4H_9)_3$

The diene monomer effect on the π-alkenyl centre isomerization is seen in the higher sensitivity of the polypiperylene microstructure towards all these variations as compared with polybutadiene. Nevertheless, at 25 ℃ almost all the units of 1,4-addition in a polypiperylene chain have a *cis*-configuration with a neodymium catalyst. An analogous phenomenon is observed in polymerization of more complicated monomers with a diene grouping. However, Ln catalysts become less stereospecific, with complications in monomer structure diminishing the number of units of 1,4-addition in a polymer (Table III).

Thus, the main properties of lanthanide catalysts of diene *cis*-copolymerizations correspond to those of ion-coordinating catalysts. Their active centres are of the π-allyl type. The main peculiarities of the catalyst, *i.e.* the low sensitivity of the stereoregulating activity to variations in the ligand environment of a transition metal and to the polymerization conditions, the extremely high temporal and thermal stabilities of active centres in the π-allyl form, and the formation of the diene homo- and copolymers with high contents of *cis*-chains – all these have been conditioned by the feeble realization of the ***anti–syn*** isomerization of the π-allyl end unit and by its true strength of bonding with a transition metal at moderate polymerization temperatures.