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POLYMERIZATION OF 1,3-DIENES WITH NEODYMIUM CATALYSTS

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Abstract: Neodymium catalysts are typical for the cis polymerization of 1,3-dienes. The systems prepared from a neodymium-carboxylate, a chlorine donor and $Al(i\text{-}C_4H_9)_3$ are characterized by a low efficiency, only ca. 6% of the neodymium being active in the catalysis. Much more active systems are obtained using allyl derivatives of neodymium in combination with aluminoxanes, in particular with methylaluminoxane (MAO). These systems have the characteristics of a single site catalyst. Evidence suggesting an ionic structure for the catalytic species is reported. Terminally substituted butadienes give polymers with a cis-1,4 isotactic structure, with the exception of (E,E)-2,4-hexadiene, which gives trans-1,4 polymers. An interpretation is reported.

INTRODUCTION

Catalysts based on neodymium have several advantages over other catalysts used for the cis polymerization of butadiene, e.g. those based on titanium, cobalt and nickel (Ref. 1). They are more active in aliphatic than in aromatic solvents (Ref. 2), are free of cationic activity and give essentially linear polymers with a high cis content. The cis polybutadiene obtained with these catalysts has excellent elastomeric properties and is particularly suitable for use in tires. Neodymium catalysts also give predominantly cis polymers from various substituted butadienes, such as isoprene, (E)-1,3-pentadiene and (E)-2-methyl-1,3-pentadiene. Much work has been done during the last few years on neodymium catalysts, which has led to the identification of much more efficient catalyst systems. The present paper reports on the most significant results of this work.

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RESULTS AND DISCUSSION

Catalysts from $NdCl_3$

The first generation catalysts are usually prepared in two steps. In the first step a solution of neodymium carboxylate, $Nd(OCOR)_3$, in an aliphatic solvent is reacted with a chlorine donor ($Al(C_2H_5)_2Cl$, $Al_2(C_2H_5)_3Cl_3$) to form a precipitate of $NdCl_3$ or $NdCl_2(OCOR)$, depending on the Cl/Nd mole ratio. Then $Al(i\text{-}C_4H_9)_3$ is added to the suspension, in a Al/Nd mole ratio 20-30. Other aluminum-alkyls ($Al(CH_3)_3$, $Al(C_2H_5)_3$) are less efficient than $Al(i\text{-}C_4H_9)_3$ (Ref. 3). The use of complexes $NdCl_3{\cdot}nD$ ($D = C_2H_5OH$, amine, ether) has been reported (Refs 1, 4, 5), but gives less active systems.

The catalysts based on $Nd(OCOR)_3$ are now used, with minor variants, for the industrial scale polymerization of butadiene to cis polymer. The percentage of the Nd active in these catalysts has been found to be rather low, about 6-7% (Ref. 6). This low value is likely attributable to two factors: a) the reaction between $Al(i\text{-}C_4H_9)_3$ and the insoluble Nd compound is slow, mainly because it takes place only at the surface of the neodymium compound; b) the neodymium-carbon bonds formed in the reaction between $Al(i\text{-}C_4H_9)_3$ and $NdCl_3$ are rather unstable at room temperature and decompose to give inactive species. It may be recalled that $Nd(benzyl)_3$ is stable only below -15°C (Ref. 7). That these two factors are mainly responsible for the low number of active centers is shown by results obtained with catalysts prepared and aged respectively at +20°C, 0°C and -20°C (Refs. 3, 8). The activity of the catalyst prepared and aged at -20°C increases slowly with the aging time. Catalyst suspensions kept in the refrigerator at -20°C were found to be still very active even after 2-3 years. These results show that, although the reaction between $Al(i\text{-}C_4H_9)_3$ and $NdCl_3$ is slow at -20°C, the Nd-C bonds that are formed are stable at that temperature, thus producing an increase in the number of active centers. It is well known that transition metal-allyl bonds are more stable than transition metal-carbon bonds of σ type; this is the reason why the polymerization of dienes with neodymium catalysts can be carried out at room temperature or even at 70-80°C. With this in mind we have tried to use, as catalyst component, allyl derivatives of neodymium. If the low efficiency of neodymium catalysts actually depends on the fact that the alkylation of $NdCl_3$ by $Al(i\text{-}C_4H_9)_3$ gives only a few neodymium-carbon bonds, catalysts prepared from neodymium compounds containing preformed neodymium-allyl bonds should show a much higher activity than the conventional ones.

Catalysts from allyl neodymium compounds

At the beginning of our work on this problem (Refs. 9,10), only one allyl neodymium-compound was known, $Li[Nd(allyl)_4]$ (Ref. 11). With the aim of obtaining a simple allyl derivative of neodymium we have examined the reaction between $NdCl_3$ and Mg(allyl)Cl in tetrahydrofuran. Operating at -20°C, at a Mg/Nd mole ratio between 2 and 3, we obtained, after evaporation of the solvent, a green air-sensitive powder **(I)**. Recrystallization of this powder from tetrahydrofuran gave only crystals of $MgCl_2 \cdot 2THF$. It was clear that **(I)** contained an allyl derivative of neodymium by the fact that $MgCl_2$ was formed and that **(I)** gave propene on reaction with alcohols. We used **(I)** as catalyst component, in combination with various aluminum-alkyls.

Tab. 1. Polymerization of butadiene (B) and isoprene (I) with different Nd-catalysts[a]

Catalyst[b]	Monomer	Polymerization Time in min.	Conv. in %	N[c] in h^{-1}	[η][d] in $dL \cdot g^{-1}$
$Nd(OCOC_7H_{15})_3$-$Al(C_2H_5)_2Cl$-$Al(i\text{-}C_4H_9)_3$	B	15	23.5	4858	> 10
	I	60	36.6	1506	4.6
$Nd(OCOC_7H_{15})_3$-$Al(C_2H_5)_2Cl$-$Al(CH_3)_3$	B	120	<2	-	
(I)-$Al(i\text{-}C_4H_9)_3$	B	10	65.2	20300	9.0
	I	60	35.1	1444	3.9
(I)-$Al(CH_3)_3$	B	10	69.6	21644	7.7
	I	90	43.7	1200	3.2
(I)-TIBAO	B	3	57.8	60000	6.0
(I)-MAO	B	1.5	72.3	150000	6.2
	I	15	65.2	10743	2.8

[a] Polymerization conditions: heptane, 10 mL; monomer, 2 mL; Nd, $5 \cdot 10^{-6}$ mol; 0°C.

[b] $Nd(OCOC_7H_{15})_3$-$Al(C_2H_5)_2Cl$-AlR_3 (mole ratio 1:3:30) preformed and aged at room temperature for ca. 24 h, as reported in Ref. 8. **(I)** is the product of the reaction between $NdCl_3 \cdot 2THF$ and $(C_3H_5)MgCl$; **(I)**-based catalysts were prepared and aged at -20°C for 24 h; TIBAO: tetraisobutylaluminoxane, MAO: methylaluminoxane.

[c] Moles of monomer polymerized per mol of Nd per hour.

[d] Determined in toluene at 25°C.

The results, Tab. 1, can be summarized as follows:

1) **(I)**-$Al(i\text{-}C_4H_9)_3$ was found to be more active than $Nd(OCOC_7H_{15})_3$-$Al(C_2H_5)_2Cl$-$Al(i\text{-}C_4H_9)_3$ by a factor of at least 3.

2) **(I)** gives active catalysts also with $Al(CH_3)_3$ or $Al(C_2H_5)_3$. These aluminum-alkyls give poor catalysts in combination with $NdCl_3$, presumably because of their low alkylating power towards $NdCl_3$ (Ref. 3).

3) Aluminoxanes give, in combination with **(I)**, catalysts much more active than those obtained with $Al(i\text{-}C_4H_9)_3$. The system **(I)**-MAO was found to be more active than $Nd(OCOC_7H_{15})_3$-$Al(C_2H_5)_2Cl$-$Al(i\text{-}C_4H_9)_3$ by a factor of ca. 30. The enhancement of activity seems to depend

not only on an increase of the number of active centers, but also on an increase of the kinetic constant of the propagation reaction. The formation of the catalytic species from **(I)** and MAO or other aluminum-alkyls is not immediate. We have found that some aging time is necessary to reach maximum catalytic activity; in our runs we have aged the catalyst for ca. 24 hours at -20°C, but it is possible that a shorter time is sufficient.

4) Polymer molecular weights are lower than those obtained with conventional systems.

In 1991 the reaction between $NdCl_3$ and Mg(allyl)Cl was examined by Wu et al., who succeeded in isolating single crystals of an allyl neodymium-compound by adding tetramethylethylenediamine (tmed) to the tetrahydrofuran reaction solution. The molecular structure of this complex, which had the formula $Nd(allyl)_2Cl\cdot 2MgCl_2\cdot 2tmed$, was determined by X-Ray analysis (Ref. 12). After Wu's paper appeared, we reexamined the composition of **(I)** and have found it to consist essentially of the complex $Nd(allyl)_2Cl\cdot 2MgCl_2\cdot 4THF$ when obtained at Mg/Nd mole ratio ca. 2.

More recently, Taube et al. have isolated and characterized, starting from the known complex $Li[Nd(allyl)_4]$, the following allyl derivatives of neodymium: $Nd(allyl)_3\cdot 1.5$ Dioxan, $Nd(allyl)_2Cl\cdot THF$ (Refs. 13-15). Each of these complexes was used, in combination with various aluminum-alkyls, as catalyst for the polymerization of butadiene. The most active system was found to be $Nd(allyl)_2Cl\cdot THF$-MAO. As mentioned above, $Nd(allyl)_2Cl$ is contained in product **(I)**, obtained from Mg(allyl)Cl and $NdCl_3$.

Nature of the catalytic species

At present little is known about the structure of the catalytic species in neodymium catalysts. We have examined the polymerization of butadiene with $Nd(OCOR)_3$-$Al(C_2H_5)_2Cl$-$Al(i\text{-}C_4H_9)_3$ in methylene chloride as solvent and have found that the activity is higher in this solvent than in heptane by a factor of ca. 3 (Ref. 16). The same phenomenon has been observed in the polymerization of propene with zirconocene/MAO catalysts and has been attributed to the ionic nature of these systems (Ref. 17). We believe that the same interpretation holds for neodymium catalysts. Other data which suggest an ionic nature for the neodymium catalysts concern the polymerization of butadiene with unaged **(I)**-$Al(CH_3)_3$, at Al/Nd mole ratio ca. 30. The activity of this catalyst combination is enhanced 3.5 fold on addition of $B(C_6F_5)_3$, B/Nd mole ratio ca. 1.5 (Ref. 18). This enhancement in activity on addition of the strong Lewis acid $B(C_6F_5)_3$ speaks in favor of an ionic structure of the neodymium-catalyst.

Polymerization of substituted butadienes

Various substituted butadienes have been polymerized with the system $Nd(OCOR)_3$-$Al(C_2H_5)_2Cl$-$Al(i\text{-}C_4H_9)_3$ (Refs. 3, 19-24). Tab. 2 reports some data concerning the polymerization of the following monomers: (E)-1,3-pentadiene, P; 2-ethyl-1,3-butadiene, 2EB; (E)-1,3-hexadiene, H; 2,3-dimethylbutadiene, DMB; (E)-2-methyl-1,3-pentadiene, 2MP; (E)-3-methyl-1,3-pentadiene, 3MP; (E,E)-2,4-hexadiene, 2,4-H. Some data concerning the polymerization of isoprene have been reported in Tab. 1.

Tab.2. Polymerization of 1,3-dienes with $Nd(OCOC_7H_{15})_3$ - $Al(C_2H_5)_2Cl$ - $Al(i\text{-}C_4H_9)_3$ a)

Monomer	Polymerization		Polymer Microstructure b)		$[\eta]$ c)	m.p. d)	i.p. e)
	Time in h	Conv. in %	cis-1,4 in %	trans-1,4 in %	in $dl \cdot g^{-1}$	in °C	in Å
B	0.25	53	98-99		> 10		
I	1	75.8	91.8		4.6		
2EB	5	31.4	93		2.9		
DMB	23	7.5	100			194.7	
2MP	30	10.2	100			161	7.9
P	6	30	87		5.2	45	8.15
H	5	17.7	85		1.3	85.6	8.0
3MP	5	28.2	79.4		2.0	68.9	8.02
2,4-H	100	8.3		100		91.1	

a) Polymerization conditions: monomer, 2mL; heptane, 10 mL; Nd, $1 \cdot 10^{-5}$ mol; 0°C.

b) Determined by NMR analysis; the remaining units are 1,2 (3,4 in the case of I and 2EB).

c) Determined in toluene at 25°C.

d) Determined by DSC analysis.

e) Identity period

The most notable trends in these results are as follows:

1) All the monomers give predominantly cis polymers, with the exception of 2,4-H, which gives polymers with a predominantly trans structure. The cis content, however, varies significantly from polymer to polymer. DMB and 2MP give polymers consisting almost exclusively of cis units (> 99%), in the temperature range between +20 and -20°C. P and H give, instead, polymers that are 85-88% cis at +20°C and ca. 93% cis at -20°C. I and 2EB have a similar behavior, giving polymers ca. 94% cis at +20°C. In all the above polymers, with the exception of 2,4-H, trans-1,4 units are practically absent, the non-cis units being only 1,2 or 3,4. It is well known that formation of a cis-1,4 vs a 1,2 unit depends on whether the incoming monomer reacts at C1 or at C3 of the last polymerized unit (Refs. 1, 25, 26). The different content of cis units in the polymers obtained from substituted butadienes likely depends on the

different reactivity of C1 and C3 of the allylic units derived from the various monomers, because of the presence of substituents on these carbon atoms.

The case of 2,4-H has been examined in previous papers (Refs. 19, 27). The formation of polymers with a trans structure depends on the fact that this monomer polymerizes much more slowly than other dienes, because of steric factors due to the two methyl groups in 1 and 4 position. During the polymerization, the last polymerized unit has time to isomerize from an *anti* to a *syn* structure before the insertion of the new monomer, thus giving a trans unit. This interpretation is supported by the finding that in butadiene/2,4-hexadiene copolymers the hexadiene units that are isolated between two butadiene units have a cis structure (Ref. 27).

2) The molecular weight of the polymers from substituted butadienes is lower than that of the polybutadiene obtained under the same conditions. This presumably depends on the fact that the polymerization rate of substituted butadienes is generally slower than that of butadiene, for steric reasons. The MW depends on the ratio between the kinetic constants of the propagation reaction (k_p) and of the reactions that bring above the termination of a growing chain (k_t). In the case of the polymerization with neodymium catalysts the main termination reaction is the transfer between the growing chain and AlR_3. Both k_p and k_t depend on the monomer, but in the case of butadienes, k_p probably decreases more rapidly than k_t with increasing substitution.

3) Monomers CH_2=CH-CH=CHR give cis polymers with an isotactic structure. Fig.1 shows the X-ray spectra of some polymers. Schemes for the formation of polymers with a cis-1,4

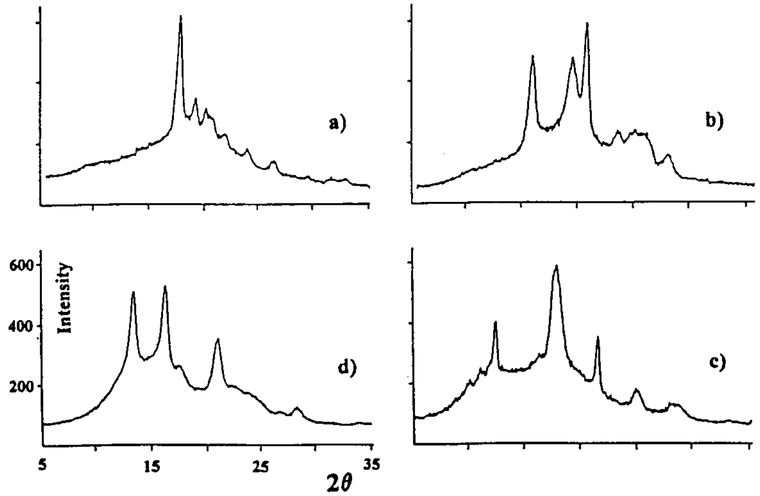

Fig. 1. X-ray powder spectra of **a)** cis-1,4 isotactic poly(1,3-pentadiene); **b)** cis-1,4 isotactic poly (1,3-hexadiene); **c)** cis-1,4 isotactic poly(3-methyl-1,3-pentadiene); **d)** cis-1,4 isotactic poly(2-methyl-1,3-pentadiene).

isotactic structure from terminally substituted butadienes have already been proposed for other catalysts (Refs. 1, 28, 29). These schemes likely also apply to polymerization with neodymium catalysts.

EXPERIMENTAL PART

The ternary system $Nd(OCOC_7H_{15})_3$ - $Al(C_2H_5)_2Cl$ - $Al(i\text{-}C_4H_9)_3$ was prepared as reported in the literature (Ref. 8).

Reaction of $NdCl_3{\cdot}2THF$ with $(C_3H_5)MgCl$

$NdCl_3{\cdot}2THF$ (8.5 g; $2.15{\cdot}10^{-2}$ mol) was suspended in THF (200 mL) and the suspension was cooled to -20°C. A 0.4 M solution of $(C_3H_5)MgCl$ (160 mL; $6.4{\cdot}10^{-2}$ mol) in THF was slowly added in about 2 h, under stirring. The suspension was kept at -20°C under stirring for 24 h., after which the solvent was removed under high vacuum at the same temperature. A green powder, **(I)**, extremely sensitive to air and moisture, pyrophoric, moderately soluble in toluene, was obtained as a residue. The neodymium and chlorine contents of this powder were about 15 and 26 wt.-%, respectively. This powder was used as obtained, in combination with aluminum-compounds for the preparation of the catalyst.
The same results were obtained using $(C_4H_7)MgCl$.

Preparation of the catalyst based on (I)

Complex **(I)** (0.374 g, $5.2{\cdot}10^{-4}$ moles based on Nd) was suspended in toluene (47.6 mL), in which it was partially soluble, the suspension was cooled to -20°, and MAO (3.6 mL; $1.56{\cdot}10^{-2}$ moles of Al) was added. The solution became slightly opalescent and turned from green to a yellow-red color. The catalyst was aged for one day at -20°C and then used in the polymerization runs. Catalysts prepared using different aluminum-compounds (tetraisobutylaluminoxane (TIBAO), $Al(CH_3)_3$ and $Al(i\text{-}C_4H_9)_3$) instead of MAO were obtained following the same procedure.

Polymerization

Butadiene (2 mL) was condensed in a glass reactor at -20°C. Heptane (10 mL) was then added, and the solution thus obtained was brought to the desired polymerization temperature. The catalyst ($5{\cdot}10^{-6}$ moles of Nd, 0.25 mL of the suspension described above) was introduced into the monomer/solvent mixture. The polymerization was terminated with methanol, the polymer was coagulated and repeatedly washed with methanol, then dried in vacuo at room temperature. Polymerization of other 1,3-dienes of this work were carried out in a similar way.

CONCLUSIONS

Neodymium catalysts have a set of properties that make them preferable to other systems for the preparation of cis polybutadiene for tires. Only a small percentage (less than 10%) of the neodymium was active in the first generation catalysts. Much more active catalysts are obtained using allyl derivatives of neodymium, in combination with MAO. These can be considered single site catalysts.

Little is known about the nature of the catalytic species in neodymium catalysts, but the fact that they are more active in methylene chloride than in heptane suggests that they have an ionic structure. This conclusion is confirmed by the fact that active catalysts are obtained using perfluorophenylboron as cocatalyst in combination with allyl derivatives of neodymium.

Neodymium catalysts also give cis polymers with substituted butadienes, the polymers from terminally substituted monomers having an isotactic structure. Most of the work with substituted butadienes has been carried out with the first generation catalysts. It is not known at present whether the sites in the more active catalysts based on neodymium allyl species are equivalent to those of the first generation $NdCl_3$ based catalysts.

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