

Butadiene polymerization with lanthanide catalysts: activity and X-ray diffraction study of neodymium bromide complexes with basic ligands

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This paper reports on the study of five neodymium bromide complexes of general formula $\text{NdBr}_3 \cdot n\text{L}$ prepared according to the scheme $\text{NdBr}_3 \cdot 6\text{H}_2\text{O} + 6\text{HC}(\text{OCH}_3)_3 \rightarrow \text{NdBr}_3 \cdot n\text{CH}_3\text{OH} + 6\text{HCO}(\text{OCH}_3) + (12 - n)\text{CH}_3\text{OH}$, followed by ligand exchange, leading to neodymium tribromide complexes $\text{NdBr}_3 \cdot n\text{L}$ with $n\text{L} = 4i\text{PrOH}$ (I), 4THF (II), 4Py (III), 2THF (IV) and 2*i*PrOH (V) where *i*Pr = isopropyl, THF = tetrahydrofuran and Py = pyridine. The catalytic activity of all the above complexes in the polymerization of butadiene is very high and it increases from I to III. The diffraction study of I and II shows that both molecules are monomeric (coordination number 7), indicates that the nature of the Nd-Br bonds is influenced by ligand substitution, and reveals that the covalent contribution is more important in II than in I. The correlation of these findings with the results obtained from the study on the activity is discussed.

(Keywords: polybutadiene; neodymium catalysts; ligand basicity; activity; diffraction)

INTRODUCTION

One of the first lanthanide catalysts reported for diolefin polymerization was a binary system consisting of a rare-earth chloride and trialkylaluminium¹; however, because of its low activity it was not extensively studied. Other catalysts based on ternary systems consisting of lanthanide salts, alkylaluminium halides and trialkylaluminium were later developed. Studies on the formation of the active species in these systems showed that the aluminium alkylhalide acts exclusively as a halogen-supplying component to give LnCl_3 (containing some Al), eventually alkylated by AlR_3 .

Investigations on well characterized neodymium complexes^{2,3} also showed that the presence of at least one halogen atom in the catalyst is relevant to the stereospecificity, activity and molecular weight of the polymer. Moreover, the activity of the catalyst is a function of the halogen content and decreases remarkably as the Cl/Nd ratio changes from 3 to 1, although the catalyst becomes homogeneous⁴ at low ratios.

Thereafter, systems based on a lanthanide trihalide received greater attention and a good number of catalysts consisting of AlR_3 and NdCl_3 coordinating electron-donor organic ligands such as alcohols⁵⁻⁸, phosphates⁹, amines^{10,11}, tetrahydrofuran (THF)¹², dimethyl sulphoxide (DMSO)¹³, etc., were developed. Their activity, however, is not as high as that of the previous three-component systems. Indeed, the number of active centres determined for $\text{NdCl}_3 \cdot \text{EtOH} - \text{Al}(\text{iBu})_3$ (0.7×10^{-2} (ref. 14) and $(0.5-2.8) \times 10^{-2}$ mol/mol Nd^{15}) is lower than that determined for $\text{Nd}(\text{naphthenate})_3 -$

$\text{Al}(\text{iBu})_2\text{Cl} - \text{Al}(\text{iBu})_3$ (3.9×10^{-2} mol/mol Nd)¹⁴, while the polymerization constant K_p is practically the same for the two systems. The state of dispersion of these heterogeneous catalysts greatly affects their activity; indeed, this factor should be taken into account when considering the higher activity of the three-component systems, in which the Nd active species precipitates from the initial solution as a very fine powder.

However, this does not seem to be a sufficient explanation for the difference in activity; more reasonably, other factors are to be taken into consideration, such as the number of available coordination sites on the metal and/or the electronic modifications of the metal-halogen bond. The latter factor could affect the alkylation step, which is surely crucial for the formation of active centres, as proved by the fact that very high Al/Nd ratios are usually needed (Al/Nd ratios of 30-60).

EXPERIMENTAL

Products

Butadiene (SIO 99.95%) was condensed at -80°C and added to a few millilitres of $\text{Al}(\text{iBu})_3$ with stirring; the temperature was allowed to rise to -5°C . Then butadiene was distilled through alumina drying columns into a cold vessel.

Solutions of butadiene in heptane (1.8 M) were used for the polymerizations.

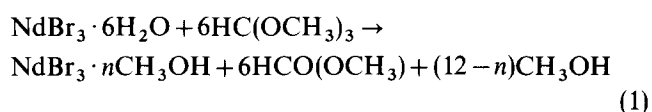
Aluminium trialkyls (Schuchardt), neodymium oxide (Merck) and trimethyl- or triethylorthoformate (Fluka)

were used as received. $\text{NdBr}_3 \cdot 6\text{H}_2\text{O}$ and $\text{NdBr}_3 \cdot \text{H}_2\text{O}$ were prepared from Nd_2O_3 and HBr according to the literature. The solvents used were refluxed and distilled under argon over Na–K alloy or potassium benzophenone ketyl and kept on A_3 molecular sieves after two or three freeze–thaw degassing cycles. Particular care was taken in the case of THF, which had to be freshly distilled from potassium ketyl just before use; non-fresh distillate causes the neodymium salts solutions to turn yellow. All operations were performed by a syringe–septum technique in purified argon atmosphere.

$\text{NdBr}_3 \cdot 4i\text{PrOH}$, $\text{NdBr}_3 \cdot 4\text{THF}$ and $\text{NdBr}_3 \cdot 4\text{Py}$ were prepared by a method developed for NdCl_3 complexes¹⁶, modified as described below.

Preparation of $\text{NdBr}_3 \cdot 4i\text{PrOH}$ (I)

$\text{NdBr}_3 \cdot 6\text{H}_2\text{O}$ or $\text{NdBr}_3 \cdot \text{H}_2\text{O}$ was caused to react with 6 or 1 mol, respectively, of trimethyl- or triethylorthoformate. Methyl- or ethylformate and most of the corresponding alcohol (CH_3OH or $\text{C}_2\text{H}_5\text{OH}$) formed according to equation (1) were distilled out and the resulting syrup was evaporated *in vacuo* to crystallization or dryness:



When ethylorthoformate was used, a better crystalline complex was obtained ($\text{NdBr}_3 \cdot n\text{EtOH}$); however, methylorthoformate proved to be preferable when the number of water molecules of the starting NdBr_3 was not correctly determined, methylorthoformate in excess being easily removable *in vacuo*.

The solid obtained was crystallized two or three times from isopropyl alcohol by dissolution at room temperature and by cooling the solution to -15°C . The solvent was partially evaporated in the first crystallization to remove all the CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ previously bonded. The complex obtained was very soluble in *iPrOH* and the resulting saturated solutions were very viscous. Sometimes it was convenient to initiate the crystallization with a few previously prepared crystals.

Crystals were separated from the mother liquor, rapidly washed twice with pentane and dried *in vacuo* just for the time necessary to eliminate pentane, since protracted drying gives products with an *iPrOH* content varying from 4 to 2 mol per 1 mol of NdBr_3 . Mother liquors were reutilized or concentrated to give a second portion of crystals; yields were nearly quantitative.

Preparation of $\text{NdBr}_3 \cdot 4\text{THF}$ (II)

The complex can be obtained from $\text{NdBr}_3 \cdot n\text{CH}_3\text{OH}$ prepared as above or from $\text{NdBr}_3 \cdot 4i\text{PrOH}$ by dissolving the starting compound in freshly distilled boiling THF and by cooling to room temperature. The complex is only slightly soluble in THF. Crystals were separated, washed with pentane, and dried as described above. The complex is indefinitely stable in the presence of THF; it is therefore preferable to store crystals under solvent and separate them at the moment of use.

In the solid state and in suspension the complex slowly loses THF, as shown by gas chromatographic (g.c.) quantitative determination of THF in a $\text{NdBr}_3 \cdot 4\text{THF}$ suspension in heptane using a weighed amount of toluene as an internal standard. Referring to the 4 mol initially

bonded to Nd complex, 0.8 mol were found in solution after 90 min, 2 mol after 270 min and still 2 mol after 28 h. G.c. conditions: isotherm 60°C ; column—Carbowax 20M on Chromosorb W AW DMCS, 4 m, 20%, 1/8 inch steel.

Preparation of $\text{NdBr}_3 \cdot 4\text{Py}$ (III)

The complex was prepared by dissolving $\text{NdBr}_3 \cdot 4\text{THF}$ in pyridine at room temperature. The solution was concentrated until the complex began to precipitate, then left at room temperature. The complex is rather soluble in pyridine and a second crop of crystals could be obtained by addition of pentane to the mother liquor.

Preparation of $\text{NdBr}_3 \cdot 2\text{THF}$ (IV)

One gram of $\text{NdBr}_3 \cdot 4\text{THF}$ was dissolved in 20 ml of anisole. This operation was facilitated if the starting complex was wetted with THF mother liquor or, alternatively, if the anisole contained 2% (w/w) of THF. Solutions left at room temperature gave a crystalline precipitate of $\text{NdBr}_3 \cdot 2\text{THF}$ in a few hours. Rapid dissolution of the starting material was essential in preventing the new complex from precipitating on the starting $\text{NdBr}_3 \cdot 4\text{THF}$. After separation of the crystals, the amount of THF bonded to Nd was determined by gas chromatography after displacement with 95% ethanol. G.c. conditions: column—OV 17, 10%, 2 m, 1/8 inch; 3 min isotherm 60°C , then $10^\circ\text{C min}^{-1}$ to 230°C ; toluene was used as an internal standard. No anisole was detected.

Preparation of $\text{NdBr}_3 \cdot 2i\text{PrOH}$ (V)

$\text{NdBr}_3 \cdot 4i\text{PrOH}$ was dissolved in the minimum amount of ethyl ether. Solutions left at room temperature gave crystals of $\text{NdBr}_3 \cdot 2i\text{PrOH}$.

Analysis

All the complexes were characterized by elemental analysis. The bonded ligand was determined by g.c. as stated above and by n.m.r. in D_2O with addition of a weighed amount of methanol as an internal standard.

Single-crystal X-ray diffraction of I and II

The crystals of both compounds are unstable in air and, under X-ray exposure, decompose within a few days even if sealed under argon in glass capillaries. In both cases intensity data were measured (MoK α radiation on a CAD-4 Nonius four-circle diffractometer) following the decay of three standard reflections for monitoring the decomposition process and empirically correcting the errors due to absorption. Information about the measured intensities and the crystal data is given in Table 1.

The two structures were solved by Patterson and Fourier methods and refined by least squares to the values given in Table 1 for the conventional *R* factor. Tables showing the observed and calculated structure factors can be obtained from the authors (see note in the following section).

Catalyst preparation

The neodymium complex (1 mmol) was ground in an argon atmosphere with a magnetic stirrer for 20 h; then 42.5 ml of heptane and 17.5 ml (30 mmol) of aluminium

Table 1 Crystal data of NdBr₃·4iPrOH (complex I) and NdBr₃·4THF (complex II)

	Complex I	Complex II
Number of measured intensities	5569	2089
Number of observed (> 3σ) intensities	2367	714
Space group	Pbca	P $\bar{1}$
Z (number of molecules in the unit cell)	8	2
Unit-cell parameters ^a (standard deviations × 10 ³ are given in parentheses)	13.110(3), 19.029(7), 16.814(4)	8.323(3), 9.389(4), 15.841(8), 79.95(4), 87.51(3), 74.76(4)
Final value of conventional R factor (for the observed intensities)	0.047	0.068

^a Parameters are, in order, *a*, *b* and *c* (Å), and α , β and γ (deg)

triisobutyl were added with vigorous stirring. After 30 min, the catalyst was ready for use. The final neodymium concentration was $1 \times 10^{-2} \text{ mol l}^{-1}$.

Polymerization

All polymerization runs were performed in unstirred glass reactors equipped with a septum cap and a side arm connected to a vacuum/argon system. A thermostatically controlled oil bath was used for high-temperature polymerizations.

In a typical polymerization run, 40 ml of the butadiene solution in heptane (1.79 mol l^{-1}) were introduced into the reactor and brought to the selected temperature for 10–15 min; then 0.2 ml of the catalyst suspension was added with a syringe. The polymerization was terminated with methanol, and the polymer was precipitated with CH₃OH containing an antioxidant and repeatedly washed with fresh CH₃OH; then it was dried *in vacuo* at room temperature.

Molecular weights were calculated from the intrinsic viscosity (measured in toluene at 30°C) using the following values: $K = 3.24 \times 10^{-4}$ and $\alpha = 0.7$. Polymer microstructures (*cis*, *trans* and 1,2 contents) were calculated from i.r. spectra as indicated in the literature.

RESULTS AND DISCUSSION

For the purpose of elucidating the influence of the number of coordination sites or electronic effects on the activity of the catalysts based on NdX₃ in dienes polymerization complexes of general formula NdX₃·*n*L (where *n* should be as high as possible) with ligands L of different basicity but similar steric hindrance were prepared.

The bromide ion was chosen as a halogen residue on the basis of the hypothesis that it might give complexes with a higher coordination number, greater solubility and better crystallizability. It was also chosen because the catalytic activity of systems containing chloride or bromide were found to be very similar, whenever the halogen influence has been examined^{3,17}, although the results so far reported for isoprene polymerization have been contradictory^{18,19}. The complexes prepared are: NdBr₃·4iPrOH (I), NdBr₃·4THF (II), NdBr₃·4Py (III), NdBr₃·2THF (IV) and NdBr₃·2iPrOH (V).

All the complexes were characterized by elemental analysis; furthermore the amount of the ligand bound to NdBr₃ was determined by gas chromatographic, n.m.r. and thermogravimetric techniques. An X-ray single-crystal determination was performed for complexes I and II.

The main result of the diffraction experiments* is that, in the crystals of I and II, the structure is based on the packing of discrete molecules of NdBr₃·4iPrOH and NdBr₃·4THF, respectively, with a coordination number of 7†. The coordination polyhedron is a distorted monocapped trigonal prism with molecular symmetry C₁ in I, and a distorted pentagonal bipyramid with approximate molecular symmetry C_{2v} in II (see Figure 1). For the 'parameter of crowding' SAS²² we essentially found the same low value for both molecules (0.74 for I and 0.73 for II). Recently^{23,24} this parameter has been used as a stability criterion in comparable actinide complexes. In the present case, consideration of this parameter leads to the result that in these molecules no structural detail can be attributed to overcrowding and that their coordination sphere is far from being saturated. The latter feature is in agreement with the well known fact that the coordination number of trivalent lanthanide ions is usually higher than 7—e.g. [Nd(H₂O)₉]³⁺—and may constitute a possible factor in the determination of the high catalytic activity of these compounds (see later).

Selected interatomic distances are given in Table 2. In complex II, the difference between the Nd–Br(1) distance and the average (2.867 Å) of the other two Nd–Br distances is probably significant; while in structure I this difference is highly significant. In complex II the average of the three Nd–Br distances (2.857(6) Å) is very significantly shorter than the average (2.903(2) Å) of the two longer Nd–Br distances in I and definitely shorter than the sum (2.945 Å) of the ionic radii of Nd³⁺ and Br[−]. This fact indicates that in the complex with THF the covalent contribution to the Nd–Br bond is more important than in the complex with isopropyl alcohol, which implies that the nature of this bond can be influenced by ligand substitution. This would be no novelty in the case of transition-metal complexes; however, we have no record of such mutual influence by ligands in the case of inorganic coordination compounds of rare earths.

Owing to the ease of obtaining a pure crystalline compound in good yield, NdBr₃·4THF represents, among the complexes prepared (I–III), the best starting material for reactions with a large variety of ligands, such as dimethyl sulphoxide, dipyridyl, anisole, amines, etc. The stability of the complexes depends on the ligand; all of them, however, lose part of the ligand more or less easily on heating to room temperature *in vacuo* or, sometimes, by simple dissolution in a solvent or even by suspension. NdBr₃·4iPrOH and NdBr₃·4THF, when dissolved in ethyl ether or anisole, respectively, give the corresponding crystalline complexes with only 2 mol of ligand (NdBr₃·2iPrOH and NdBr₃·2THF), and no trace of ethyl ether or anisole was detected in the new complexes. However, it cannot be excluded that

* A full account of these experiments and of all the structural details will be given elsewhere

† Preliminary reports of these two structures were given at recent meetings^{20,21}

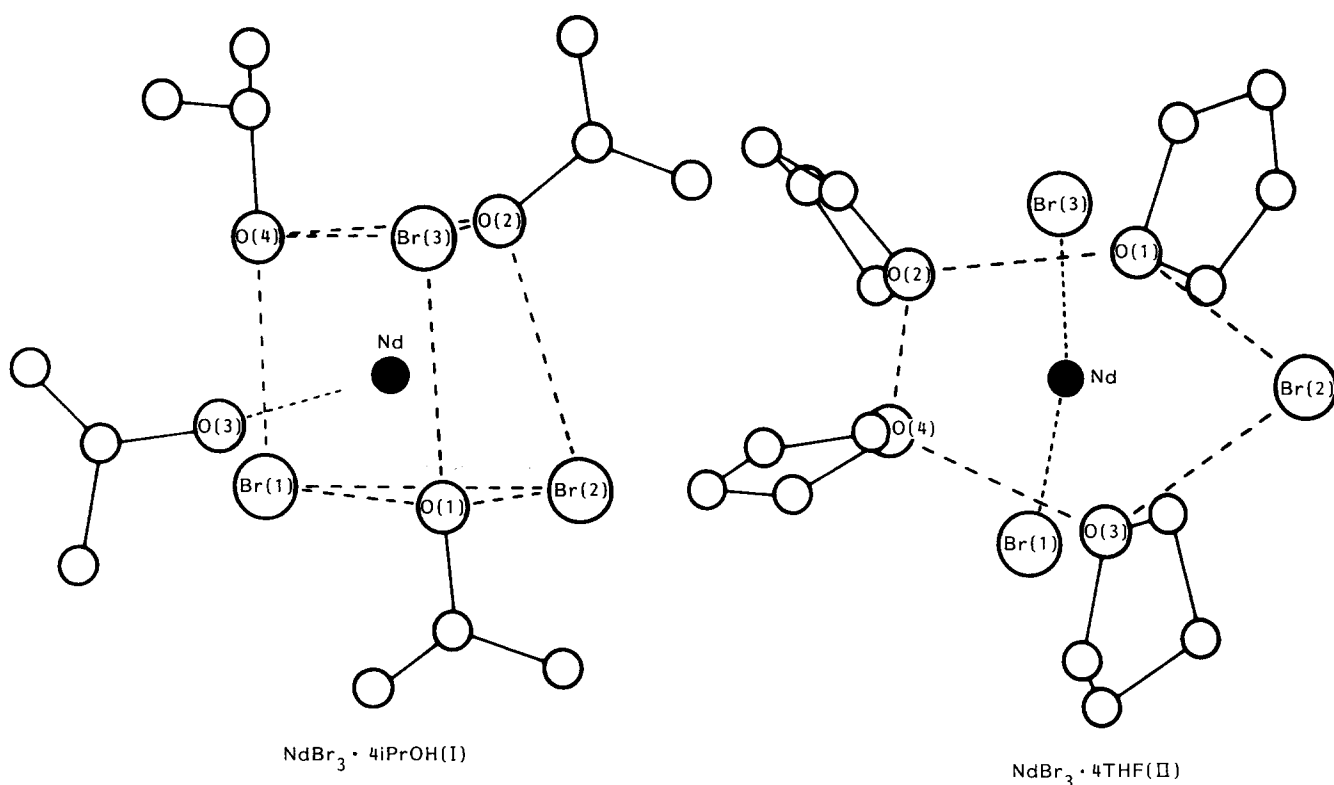


Figure 1 Coordination geometry of NdBr₃ · 4iPrOH and NdBr₃ · 4THF. Atoms Br(1) and Br(3) of II are on opposite sides of the average plane defined by atoms O(1), O(2), O(3), O(4) and Br(2)

Table 2 Nd–X coordination bond distances in complexes I and II (standard deviations × 10³ are given in parentheses)

X	I	II
Br(1)	2.872(1)	2.837(6)
Br(2)	2.902(1)	2.863(4)
Br(3)	2.904(1)	2.871(6)
O(1)	2.462(6)	2.524(24)
O(2)	2.470(6)	2.529(20)
O(3)	2.471(6)	2.443(25)
O(4)	2.455(6)	2.514(20)
O(average)	2.465(5)	2.503(20)

Table 3 Comparison of the catalytic activities^a of neodymium tribromide complexes with different ligands

Neodymium complex	Conversion (%)	<i>cis</i> (%)	<i>trans</i> (%)	1,2 (%)	[η] (g dl ⁻¹)
NdBr ₃ · 4Py	64	98.82	—	1.17	8
NdBr ₃ · 4THF	60	98.9	—	1.1	4.5
NdBr ₃ · 2THF	53	98.8	0.1	1.1	7
NdBr ₃ · 4iPrOH	52	98.6	0.1	1.3	5.5

^a Catalyst: [Nd] = 2 × 10⁻² mol l⁻¹; Al(iBu)₃/Nd = 30 mol/mol; solvent = heptane. Polymerization: [Nd] = 1 × 10⁻⁴ mol l⁻¹; [C₄H₆] = 1.79 mol l⁻¹; solvent = heptane; T = 50°C; polymerization time = 30 min

protracted treatment may induce a substitution of ligands.

Complexes I–IV were tested in the polymerization of diolefins. The catalysts were prepared by addition of a trialkylaluminium, in aliphatic or aromatic hydrocarbons, to a finely ground neodymium complex. The use of an aliphatic solvent secured a slightly higher polymerization rate and *cis*-1,4 unit contents in the polymer. No ageing of the catalyst is required but the highest activity was found after 30–60 min. Afterwards it slowly decreases with time; a still good level of activity was, however, found in catalysts aged 2 or 3 months (Table 4, runs 10 and 11).

All the polymerizations were performed with butadiene monomer. Selected results are reported in Table 3. No stirring is required because the catalyst is a cloudy stable system and the polymer grows almost homogeneously. Polymerization data are scattered within a reasonable range as a result of working with high-viscosity unstirred solutions. For this reason, slightly different polymer yields are obtained also by operating with catalysts taken from the same batch. The value reported in Table 3 for each catalytic system is an average of several runs.

During the preparation of the catalysts from the various starting complexes, great care was taken to follow the same procedure, in particular as concerns the grinding time of solid NdBr₃ · *n*L and the conditions of milling. A polymerization time of 30 min was chosen for the purpose of obtaining rather low monomer conversions. As a consequence, solutions of low viscosity were obtained, allowing a more significant comparison between the complexes used. For this comparison Al(iBu)₃ was used, but analogous results were obtained with AlEt₃ and AlH(iBu)₂.

The catalyst activity of complexes I–IV shows a dependence on the Al/Nd ratio similar to all other neodymium catalysts reported so far: it increases markedly until the Al/Nd ratio reaches a value of 50–60. However, a good activity is observed also for ratios of 10–15. Polymer yields increase linearly with time at low conversions with no induction time, while the polymer obtained shows a high viscosity also at very low conversion values (Figure 2).

Table 4 illustrates the dependence of Nd-based catalyst activity on temperature, catalyst concentration and

ageing time for complex II. At very low catalyst concentration, the impurities of the monomer or of the solvent affect the catalyst activity, which is much lower than expected (Table 4, run 3). The polymer *cis* content is always very high (98–99%) and is not influenced by the variables considered.

All the complexes considered show a catalytic activity that is much higher than that of other similar catalysts and even higher than that of some ternary systems. The productivity values of selected binary catalysts and of a few representative ternary systems characterized by very high productivity values are reported in Table 5. The said values were calculated, when pertinent experimental data were available, from polymerization runs with parameters as close as possible to those adopted by us. In some cases, the difference in activity was remarkable and could not be attributed to the presence of bromine instead of chlorine because, as already mentioned, the opposite effect was reported for butadiene polymerization by $\text{NdCl}_3 \cdot \text{C}_2\text{H}_5\text{OH}^{31}$ or $n\text{L}^{17}$. A better explanation might be the higher coordination number found in the bromine complexes obtained by us, which keeps the complex in a monomeric form. Indeed, the results reported by Yang

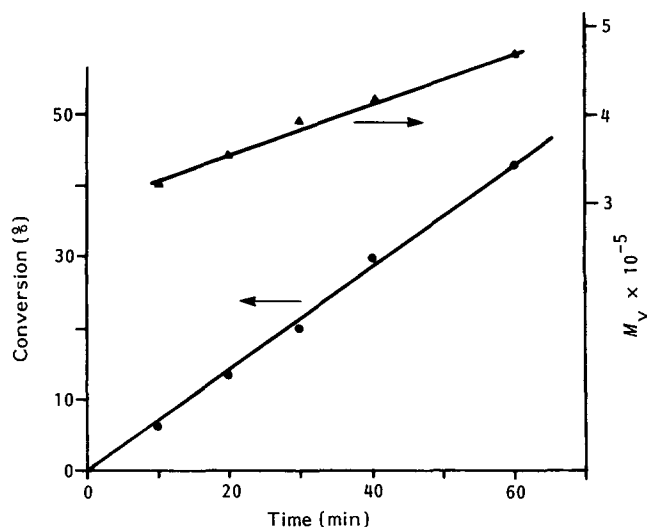


Figure 2 Dependence of molecular weight and conversion on polymerization time. Catalyst = $\text{NdBr}_3 \cdot 4\text{Py} - \text{Al}(\text{iBu})_3$; solvent heptane; $[\text{Nd}] = 1 \times 10^{-4} \text{ mol l}^{-1}$; $[\text{C}_4\text{H}_6] = 1.79 \text{ mol l}^{-1}$; $T = 30^\circ\text{C}$

Jihuo *et al.*⁵ show that a maximum activity is found at an alcohol/Nd ratio of 4, although the authors were unable to isolate a complex with that stoichiometry and the complex isolated ($\text{NdCl}_3 \cdot 3\text{iPrOH}$) is reported to be dimeric³². Indeed, as can be seen from Table 3, complexes with only 2 mol of ligand present a lower activity.

An increase in catalyst activity with the number of THF molecules coordinated is not unusual in rare-earth complexes and has also been reported for $\text{PhONdCl}_2 \cdot \text{THF}^{33}$ and $\text{C}_5\text{H}_5\text{NdCl}_2 \cdot \text{THF}^{34}$.

Further proof of the activity being affected by the coordination number around the Nd and not by the simple presence of electron-donor molecules in solution was obtained from the comparison of catalytic systems prepared from $\text{NdBr}_3 \cdot 4\text{THF}$ by a different procedure. The said procedure was suggested by the observation that $\text{NdBr}_3 \cdot 4\text{THF}$ suspended in heptane loses 2 mol of THF in 4 h (see Experimental), thus being rearranged to $\text{NdBr}_3 \cdot 2\text{THF}$.

In the first system, solid $\text{NdBr}_3 \cdot 4\text{THF}$ was ground for 20 h and then heptane and $\text{Al}(\text{iBu})_3$ were added simultaneously. In the second system $\text{NdBr}_3 \cdot 4\text{THF}$ was suspended in heptane and stirred for 20 h; then $\text{Al}(\text{iBu})_3$ was added. Polymer yields from polymerizations performed with the second system were lower with respect

Table 4 Representative features of catalysts from $\text{NdBr}_3 \cdot 4\text{THF}$. Dependence of the activity on the polymerization temperature, catalyst ageing time and Nd concentration during polymerization^a

	$[\text{Nd}]$ (mol l^{-1})	Ageing time (days)	Polym. temp. ($^\circ\text{C}$)	Polym. time (min)	Conv. (%)
1	2×10^{-4}	11	30	30	36.9
2	2×10^{-4}	11	30	60	74.3
3	5.3×10^{-5}	10	50	35	10
4	1.06×10^{-4}	10	50	35	57
5	2.9×10^{-4}	10	50	35	80
6	2×10^{-4}	6	30	35	43.3
7	3×10^{-4}	6	30	35	54.9
8	1×10^{-4}	8	30	35	25
9	1×10^{-4}	8	50	35	59
10	1×10^{-4}	273	50	35	45
11	1×10^{-4}	450	50	35	33

^a Catalyst: $\text{NdBr}_3 \cdot 4\text{THF} - \text{Al}(\text{iBu})_3$; $\text{Al}/\text{Nd} = 30 \text{ mol/mol}$. Solvent: heptane; $[\text{C}_4\text{H}_6] = 1.79 \text{ mol l}^{-1}$

Table 5 Catalyst efficiency of some neodymium complexes in solution polymerization of butadiene to *cis*-1,4 polymer

Neodymium compound	$[\text{Nd}]$ (mol l^{-1}) $\times 10^{-4}$	$[\text{C}_4\text{H}_6]$ (mol l^{-1})	T ($^\circ\text{C}$)	AlR_3/Nd (mol/mol)	Productivity (g polym/g Nd per hour)	Ref.
<i>Binary systems</i>						
$\text{NdBr}_3 \cdot 4\text{Py}$	1	1.8	50	30	8000	
$\text{NdBr}_3 \cdot 4\text{THF}$	1	1.8	50	30	7300	
$\text{NdBr}_3 \cdot 2\text{THF}$	1	1.8	50	30	6900	
$\text{NdCl}_3 \cdot 3\text{ROH}$	1.2	2.2	50	15	1178	5
$\text{NdCl}_3 \cdot 4\text{THF}$	0.7	1.8	50	30	1544	25
$\text{NdCl}_3 \cdot 2\text{THF}$	3	1.8	50	30	415	12
$\text{NdCl}_3 \cdot \text{PO}(\text{OBu})_3$	5.9	0.6	40	20	50	9
$\text{NdCl}_3 \cdot 6\text{H}_2\text{O} + \text{Py}$	1.4	3.7	60		2350	26
$\text{NdCl}_3 \cdot \text{L}$	0.3	1.8	50	30	1109	17
<i>Ternary systems</i>						
$\text{Nd}(\text{octanoate})_3$	1.8	1.7	40	20	1755	27
$\text{Nd}(\text{2-ethylhexanoate})_3$	1	1.8	60	35	3466	28
$\text{Nd}(\text{OC}_{10}\text{H}_{21})_3$	0.5	1.7	50	30	4738	29
$\text{Nd}[\text{OPO}(\text{OR})_2]_3$	2.3	2.1	65	30	3133	30
$\text{Nd}(\text{naphthenate})_3$	0.8	1.0	50	30	8674	14

to the first and were identical to that obtained with complex IV. In addition, this finding makes circumstantial the polymerization results of Chen²⁵, the complex $\text{NdCl}_3 \cdot 4\text{THF}$ being unstable at room temperature under the conditions of catalyst preparation. The results reported lead to the conclusion that the coordination state of the crystalline complex is important for the activity independently of the number of ligand molecules present in solution.

From the data of Table 3, the polymerization yield and the *MW* appear also to depend upon the nature of the donor ligand.

As already suggested in the introduction, electronic contributions could play a role in the alkylation of $\text{NdBr}_3 \cdot 4\text{L}$ by AlR_3 . Indeed the nature of the bonds in the coordination sphere of neodymium bromide complexes I and II, with its influence on the reactivity of these compounds, is a point of interest in any discussion aimed at finding correlations between activity and the structural features of these catalysts.

The results—see previous section—that the covalent contribution to the Nd–Br bond is more important in complex II than in complex I can be related to the different basicity of the ligands. As a consequence, the electronegativity of Nd in II is higher than in I and may be correlated with the observation (see Table 1) that the polymerization yield obtained with II is higher than with I. Unfortunately, in the case of complex III, we were unable to grow single crystals of X-ray diffraction quality. Indeed the basicity of pyridine is much higher than that of THF and the structural analysis of III could have given us stronger evidence for the proposed correlation.

CONCLUSIONS

The activity of the catalysts studied seems to be related to the following two structural features of the corresponding neodymium bromide complexes with basic ligands.

(i) Molecules I and II are monomeric and show a coordination number of 7, leading to a low value of the 'parameter of crowding' and to the possible availability of 'free' sites on the metal. This circumstance and the presence of easily replaced basic ligands in the coordination sphere make these monomeric complexes ideal species for allowing the alkylation step. From this point of view, one may expect negative consequences on the activity when the number of basic ligands decreases from 4 to 3⁵, which leads to the formation of dimeric species³², and from 4 to 2 as shown in Table 5 for $\text{NdCl}_3 \cdot 4\text{THF}$ ²⁵ and $\text{NdCl}_3 \cdot 2\text{THF}$ ¹² and as indicated by our own results.

(ii) The nature of the Nd–Br bonds is influenced by ligand substitution, which indicates that in complex II (with THF) the covalent contribution is more important than in complex I (with *i*PrOH) and implies that the formation of the active species by reaction with AlR_3 is easier for complex II than for complex I.

This reasoning is in agreement with the suggestion by Wang Fosong *et al.*³⁵ that the 4f orbitals of trivalent rare-earth metals in complexes of this kind participate, to some extent, in bond formation. These authors try to give a qualitative explanation of the differences in catalytic activity in terms of molecular-orbital theory. However, the simplifying assumptions about molecular structure (coordination number of 6) and symmetry (O_h)

formulated by them at the beginning of their theoretical considerations seriously limit the validity of their conclusions. We plan to extend our studies to related complexes of other lanthanides with a view to giving a firmer experimental basis to the theory and possibly to reaching more quantitative conclusions.

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