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Diene Polymerizations with the Lanthanide Coordination Catalysts IV. Quantochemical Studies of Active Centre Models

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Abstract

Quantochemical studies have been carried out for the models of active centres of butadiene polymerization on the Nd–Al catalytic system. The *syn*-isomeric forms of active centres have been found energetically preferable over the *anti*-isomeric forms; Nd 4f orbitals have been observed as relatively inactive participants in the formation of Nd–C bonds. On the whole, the obtained results provide support to the mechanism of kinetic stereocontrol of the polymer microstructure upon diene polymerizations on lanthanide catalytic systems.

Introduction

Since the discovery of Ziegler-Natta catalysts, much research has been concerned with the structure of active centres (AC) to get insight into the detailed mechanism which governs stereoselectivity. However, the problem turns out rather intricate and ambiguous owing to the complexity and unstability of those catalysts which are sensitive to many factors as well as to the low concentration and preciously high reactivity of AC. As a result, the number of existing models and hypotheses for the stereoregulation mechanism far exceeds the number of catalytic systems in which the AC structure is known. Difficulties arising from direct spectroscopic methods (IR and electronic spectra, X-ray, ESR, ESCA, etc.) used to study AC structures have stimulated the development of quantochemical approaches for investigating the mechanism of stereoregulation from many aspects. This approach is particularly advantageous for elucidating the structures of AC, for investigating AC-to-monomer complexes as well as the possible involvement of various metal or lanthanide orbitals into bonding, and for estimating the reaction route.

Our previous papers of the title series [1, 2] reported on the main regularities of piperylene polymerization and molecular characteristics of polybutadiene with respect to the polymerization conditions employed. The mechanism of kinetic stereocontrol of the polybutadiene microstructure was considered in ref. 3.

This paper is concerned with the investigation results obtained for electronic structures of different AC models of butadiene polymerization on a Nd–Al catalytic system similar to that reported in ref. 3.

Calculation Technique

All calculations were carried out in accordance with the program in ref. 4 realizing the extended Hückel method (EHM). The parameter values are given in Table 1. Conventional values were selected for H and C atoms [5]. Diagonal matrix elements of the effective one-electron Hamiltonian $\mathcal{H}_{ii}$ were taken from ref. 6 for Al and those for Cl and Nd were assumed equal to the values of orbital energies estimated from the relativistic calculations of atoms [7] (the $\mathcal{H}_{ii}$ (5d) value was taken from ref. 8). Upon transformation of relativistic values into quasi-relativistic ones, the weighted average of each multiplet was used. To account for the effect of the energetic positions of 4f and 5d orbitals upon the AC electronic structure, the latter was calculated with the modified values of $\mathcal{H}_{ii}$ for its orbitals (given in parentheses in Table 1). The values of orbital exponents were adopted from refs. 6 and 8.

Results and Discussion

To make the discussion more convenient, one should assume that the active section of the growing polymer chain is arranged in two components: $\sim\sim\sim NdCl_kR_{3-k}$ + $m AlCl_nR'_{3-n}$, where $\sim\sim\sim$ = polymer chain, R and R′ = organic fragments of the starting (or modified) organoaluminium component of the catalyst. The values of *n*, *m* and *k* have not been precisely estimated. The presence of electron-donor, monomer and solvent molecules in the lanthanide coordination sphere is quite possible.

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TABLE 1. Atomic parameters used for extended Hückel calculations

Atoms	Orbital	$\mathcal{H}_{ii}$ (eV)	Exponents[a]
H	1s	−13.0	1.3
C	2s	−21.40	1.625
	2p	−11.40	1.625
O	2s	−32.30	2.275
	2p	−14.80	2.275
Cl	3s	−29.40	1.698(0.252) + 2.525(0.773)
	3p	−13.77	1.386(0.356) + 2.228(0.686)
Al	3s	−11.32	1.372
	3p	−6.0	1.355
Nd	5p	−29.32	2.403(0.633) + 4.94(0.519)
	4f	−9.82(−11.0)	3.208(0.739) + 8.621(0.464)
	5d	−6.36(−8.82; −10.8)	1.304(0.377) + 2.777(0.768)
	6s	−4.74	1.043(0.609) + 1.969(0.535)

[a] The numbers in parentheses are contraction coefficients used in the double expansion.

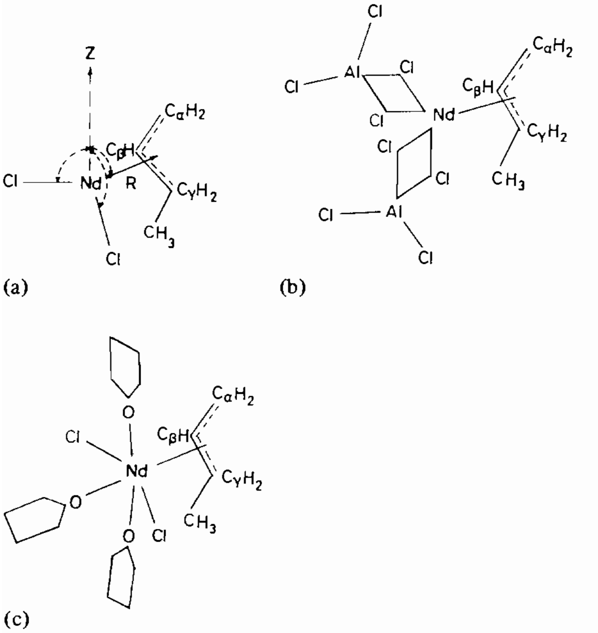

Fig. 1. Schematic layout for AC models: (a) *syn*-$C_4H_7NdCl_2$; (b) *syn*-$C_4H_7Nd(AlCl_4)_2$; (c) *syn*-$C_4H_7NdCl_2 \cdot 3THF$. R = distance from the site crossing C_α–C_β–C_γ atoms of the crotyl group to Nd atom.

Due to the complicated nature of the system under consideration, the electronic structure and geometry of the AC lanthanide component ($m = 0$, $k = 2$) was studied first. Compound $C_4H_7NdCl_2$ was chosen as that (Fig. 1a) providing due regard to the main isomeric π (*anti-*,*syn-*) and σ (*trans-*, *cis-*) forms of AC. Since the literature gives no data of the geometries of Nd allylic compounds, bond lengths and geometries of AC models were estimated from the X-ray structural data obtained for $NdCl_3 \cdot 4THF$ [9] and cyclopentadienyl derivatives of Nd such as $(\eta^5\text{-}C_5H_5)NdCl_2 \cdot THF$ [9], $(\eta^5\text{-}C_5H_5)NdCl_2 \cdot 3THF$ [10], $(\eta^5\text{-}(CH_3)_5C_5)_2NdCH[Si(CH_3)_3]_2$ [11] and $(\eta^5\text{-}C_5H_5)_3Nd \cdot (pyridine)$ [12] as well as for a multinuclear bimetallic complex Nd–Al [13], the latter being active for butadiene polymerization. Analysis of the above data shows the bond lengths of the Nd–C (ring) are in the narrow range of 2.76–2.83 Å, while the σ bond length of Nd–C varies within the range 2.52–2.83 Å; the average distance from Nd to the ring site $R = 2.54$ Å is nearly the same as the shortest length of the σ bond (2.52 Å).

Proceeding from that, the π- and σ-geometries of $C_4H_7NdCl_2$ were considered. Two structures were investigated: those positioned at distance R = 2.4 and 2.0 Å from the site of C_4H_7 to neodymium with bond lengths of Nd–C_i ($i = \alpha, \beta, \gamma$) equal to 2.78 and 2.45 Å, respectively; angle $\theta = 90°$ in each case (Fig. 1(a)). Accordingly, σ-structures with Nd–C bond lengths of 2.4 and 2.0 Å were analyzed. AC *anti-* and *syn*-structures were calculated with optimized angular variables which determine the special position of the CH_3 group.

The crotyl group C_4H_7 has three π-orbitals which are similar to those of the allyl group C_3H_5 by the symmetry: π-bonding, n-non-bonding, and π^*-antibonding. With the initially chosen values $\mathcal{H}_{ii}(4f) = -9.82$ eV and $\mathcal{H}_{ii}(5d) = -6.36$ eV, 4f and 5d orbitals of Nd interact mainly with the n orbital of C_4H_7, though the interaction is rather weak. Thus, even with $R = 2.0$ Å the computed Nd–C_α and Nd–C_γ overlap population of the Mulliken type (P) appears below 0.01 indicating their very weak covalency.

Since the contribution of different orbitals into chemical bonding can be crucially dependent on their energetic level, calculations were carried out with different $\mathcal{H}_{ii}$ values for 4f and 5d orbitals. The following

TABLE 2. Calculated overlap populations (*P*) and atomic charges (q_i) for *anti*- and *syn*-isomers of $C_4H_7NdCl_2$ [a]

$\mathcal{H}_{ii}$(4f) (eV)	$\mathcal{H}_{ii}$(5d) (eV)	Isomeric form	*R* (Å)	ΔE (eV)	q_{C_α}	q_{C_γ}	q_{Nd}	*P*(Nd–C_α)	*P*(Nd–C_γ)
−9.82	−8.82	*anti*	2.4	0.11	−0.48	−0.33	1.95	0.07(5)	0.08(3)
		syn			−0.45	−0.34	1.93	0.06(5)	0.10(3)
−11.0	−10.8	*anti*	2.4	0.16	−0.25	−0.10	0.93	0.12(5)	0.14(4)
		syn			−0.23	−0.11	0.91	0.12(3)	0.16(3)
−9.82	−8.82	*anti*	2.0	0.22	−0.37	−0.22	1.74	0.11(14)	0.13(13)
		syn			−0.35	−0.24	1.73	0.11(14)	0.16(8)
−11.0	−10.8	*anti*	2.0	0.24	−0.11	0.03	0.20	0.19(10)	0.20(10)
		syn			−0.10	0.00	0.23	0.18(10)	0.23(8)

[a] $\Delta E = E_{syn} - E_{anti}$, where E_{syn} (E_{anti}) = total energy of AC *syn* (*anti*)-forms. Contributions of partial Nd(4f)–C_i(2p) overlap population into total Nd–C_i overlap population are given in parentheses (%).

values were chosen for the matrix elements: $\mathcal{H}_{ii}(4f) = -11.0$ eV, $\mathcal{H}_{ii}(5d) = -8.82$ eV, −10.8 eV. It should be noted, that with d transition metals 3d orbitals keep to the range of −11 to −14 eV [14].

The results obtained for the electronic structures are given in Table 2, which show the covalency of the Nd–C bond is appreciably dependent on the *R* and $\mathcal{H}_{ii}$ values. Thus, the Nd–C_α overlap population varies from 0.07 (at $R = 2.4$ Å, $\mathcal{H}_{ii}(4f) = -9.82$ eV, $\mathcal{H}_{ii}(5d) = -8.82$ eV) to 0.19 (at $R = 2.0$ Å, $\mathcal{H}_{ii}(4f) = -11.0$ eV, $\mathcal{H}_{ii}(5d) = -10.8$ eV), whereas the total overlap population $\Sigma P(\text{Nd–C}_i)$ with $i = \alpha, \beta, \gamma$ changes from 0.13 to 0.41. As the contribution of 4f orbitals into covalent bonding is low anyway, the contribution of partial Nd(4f)–C_α(2p) overlap population into the total population *P*(Nd–C_α) is below 14%. According to the analysis made, partial covalency can realize itself mainly due to overlapping of the 5d orbitals of Nd with the π-orbitals of C_4H_7. It should be noted also, that the contribution of 4f orbitals into chemical bonding is strongly affected by the bond length. Thus, with *R* lowered from 2.4 to 2.0 Å, the partial Nd(4f)–C_α(2p) overlap population is increased 3–5 times.

Calculations made for $C_4H_7NdCl_2$ σ-structures confirm the above conclusion on the low involvement of 4f orbitals into Nd–C bonding. Thus, the value of the Nd–C overlap population has been found within 0.35–0.41 with respect to $\mathcal{H}_{ii}$ chosen for Nd. However, despite a considerably high covalency of the Nd–C bond, the partial contribution of Nd 4f orbitals is below 5%, reaching 13–14% at $R = 2.0$ Å.

Another peculiarity in the electronic structure of AC models is that the excessive charge of the C_α atom surpasses that of the C_γ atom in both *anti*- and *syn*-isomeric forms of $C_4H_7NdCl_2$. Apparently, it entails the monomer attachment to the C_α atom of the centre resulting in 1,4-units rather than to the C_γ atom, which would lead to vinyl 1,2-units being formed. The positive charge on Nd in both isomeric forms of AC is approximately the same.

The *syn*-structure of AC is somewhat more preferable to the *anti*-structure by its energy with related $\Delta E = 0.11$–0.24 eV (Table 2), being in good agreement with the reported data obtained from kinetic studies [3]. The latter demonstrate the close thermodynamic equivalence of AC *anti*- and *syn*-structures (*syn*-structure is slightly more preferable than the *anti*-structure, constant of *anti*–*syn*-isomerization $K = 0.9$).

To confirm the results obtained, AC structures were calculated with the optimized values of angle θ (Fig. 1(a)). The qualitative pattern of the electronic environment remains unchanged. It should be noted though, that the total energy minimum is attained at $\theta = 110°$ for π-structures and at $\theta = 120°$ for σ-structures. The total energy ΔE gains 0.11–0.17 eV (depending on $\mathcal{H}_{ii}$(4f) and $\mathcal{H}_{ii}$(5d) values) for π-structures and 0.35–0.52 eV for σ-structures.

Compound $C_4H_7Nd(AlCl_4)_2$ has been chosen as a simple model of bimetallic AC with its two Al atoms coupled to Nd by chlorine bridges (Fig. 1(b)). The presence of aluminium chloride in the Nd coordination sphere results in a decreased contribution of 5d orbitals into Nd–C bonding. As a consequence, the Nd–C bond covalency is entirely lost because its overlap population acquires a value of 0.01–0.05 (Table 3), the negative charge of C_α and C_γ atoms is slightly more and the positive charge on Nd is thus decreased. The *syn*-structure remains somewhat preferable over the *anti*-structure ($\Delta E = 0.05$ eV).

Compound $C_4H_7NdCl_2 \cdot 3THF$ was used to investigate the role of electron-donor molecules which can exist in the lanthanide coordination sphere (Fig. 1(c)). The bond lengths and valency angles (excepting the C_4H_7 group position) were selected on the basis of X-ray structural data obtained for (η^5-C_5H_5)-$NdCl_2 \cdot 3THF$ [10]. Analysis of the results given in

TABLE 3. Calculated overlap populations (P) and atomic charges (q_i) for *anti*- and *syn*-isomers of AC models[a]

$\mathcal{H}_{ii}$(4f)	$\mathcal{H}_{ii}$(5d)	Isomeric form	R (Å)	ΔE (eV)	q_{C_α}	q_{C_γ}	q_{Nd}	P(Nd–C$_\alpha$)	P(Nd–C$_\gamma$)
$C_4H_7Nd(AlCl_4)_2$									
−9.82	−8.82	*anti*	2.4	0.05	−0.55	−0.38	1.88	0.01	0.03
		syn			−0.52	−0.40	1.85	0.01	0.05
$C_4H_7NdCl_2 \cdot 3THF$									
−9.82	−8.82	*anti*	2.4	0.10	−0.51	−0.36	1.87	0.04	0.06
		syn			−0.48	−0.37	1.84	0.04	0.07

[a] $\Delta E = E_{syn} - E_{anti}$, where E_{syn} (E_{anti}) = total energy of AC *syn* (*anti*)-form.

Table 3, shows that the qualitative pattern of the AC electronic structure is slightly changed but the energetic relation between the *anti*- and *syn*-isomeric structures of AC remains unchanged.

The fact that there is no energetic preference for the *anti*-structure as opposed to the *syn*-structure in all AC models considered here, serves as reliable proof for the occurrence of *anti–syn*-isomerization as well as to the presence of end-units in the growing polymer chains for both *anti*- and *syn*-forms. Therefore, the high *cis*-regulating ability of the Nd–Al catalytic system cannot be regarded as determined only by the energetic preference of the AC *anti*-structure. This supports the mechanism of microstructure kinetic stereocontrol discussed in ref. 3, that the incorporation of a monomer into the polymer chain is followed by the formation of an end anti-unit, while the relative content of 1,4-*cis*- and 1,4-*trans*-units is determined by the ratio of propagation reaction and AC *anti–syn*-isomerization rates.

To elucidate the role of the monomer-to-AC coordination stage in the stereoregulating mechanism, $C_4H_7NdCl_2 \cdot C_4H_6$ complexes were calculated with their diene molecules positioned at different distances (2.6–2.0 Å) from the Nd atom. As follows from the analysis results, the butadiene *cis*-structure incorporated into that complex has been shown to be energetically preferable over the *trans*-structure for 0.13–0.23 eV. Although the above calculations require further verification (one should account for possible changes of AC and monomer structures upon coordination), the *cis*-structure of butadiene molecules can be assumed to exist as early as at the stage of their coordination to AC.

Conclusions

The results of quantochemical calculations of AC models provide support to the mechanism of kinetic stereocontrol of microstructure, which was described in detail in ref. 3, and give evidence to the relatively low involvement of Nd 4f orbitals into Nd–C bonding. Partial covalency of Nd–C bonds arises mainly due to the participation of Nd 5d orbitals in chemical bonding.

References

1 Yu. B. Monakov, N. G. Marina, R. M. Khairullina, O. I. Kozlova and G. A. Tolstikov, *Inorg. Chim. Acta, 142* (1988) 161.

2 V. G. Kozlov, N. G. Marina, I. G. Savel'eva, Yu. B. Monakov, Yu. I. Murinov and G. A. Tolstikov, *Inorg. Chim. Acta, 154* (1988) 239.

3 Z. M. Sabirov, N. Kh. Minchenkova and Yu. B. Monakov, *Inorg. Chim. Acta,* (1989) in press.

4 V. N. Khleskov, *Zh. Strukt. Khim., 22* (1981) 3.

5 R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc., 101* (1979) 3821.

6 Zhang Xiao-Guang, Xu Yin-Sheng and Guo Xie-Xian, *J. Mol. Catal., 43* (1988) 381.

7 J. P. Desclaux, *Atomic Data and Nuclear Data Tables,* Vol. 12, Academic Press, New York, 4th edn., 1973, pp. 311–406.

8 L. L. Lohr and Y. Q. Jia, *Inorg. Chim. Acta, 119* (1986) 99.

9 W. Chen, Z. Lin and Y. Xing, *Inorg. Chim. Acta, 130* (1987) 125.

10 G. Yang, Y. Fan, Z. Jin, Y. Xing and W. Chen, *J. Organomet. Chem., 322* (1987) 57.

11 G. B. Deacon, B. M. Gatchouse, S. N. Platts and D. L. Wilkinson, *Aust. J. Chem., 40* (1987) 907.

12 G. Jeske, H. Lauke, H. Monermann, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc., 107* (1985) 8091.

13 C. Shan, Y. Lin, J. Ouyang, Y. Fan and G. Yang, *Makromol. Chem., 188* (1987) 629.

14 K. Tatsumi and A. Nakamura, in V. H. Smith, Jr., H. F. Schaefer III and K. Morokuma (eds.), *Applied Quantum Chemistry,* Reidel, Dordrecht, 1986, pp. 299–311.