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Living and non-living Ziegler–Natta catalysts: electronic properties of active site

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Abstract

Most of polymerization reactions with Ziegler catalysts operate through the 'non-living' mechanism, whereas lanthanide catalysts show a living-mechanism character. The degree of 'livingness' in a polymerization reaction is generally investigated through kinetics and the product analysis rather than by direct analysis of a catalyst. We have developed a new insight for judging the 'livingness' in polymerization reaction in aspect of electronical properties of the active chain ends of Li, Ni and Nd catalysts for 1,3-butadiene polymerization using the frontier orbital analysis. The frontier orbitals of the Ni catalyst are different from those of the Li and Nd based catalysts. The HOMO of the Ni catalyst has mostly the d-orbital (Ni) character while the LUMO has the p-orbital (C_α and C_γ atoms) as well as the d-orbital (Ni) character. The π-butenyl coordination at the Ni catalyst is η^1-type but those of the Nd and Li catalysts are η^3. The atomic charge ($+0.003$) on the Ni atom and the atomic charge (-0.14) on C_α of the Ni catalyst are much lower than those of the Nd catalyst (Nd $+1.09$, C_α -0.56).

Keywords: Frontier orbitals; Ziegler–Natta catalyst; Butadiene

1. Introduction

1,3-Butadiene is a unique monomer; it can participate in 'non-living' and 'living' polymerization with transition- and lanthanide-metal catalysts, respectively [1]. 'Non-living' polymerization reactions take place with typical Ziegler–Natta catalysts, such as Ti-, Co-, Ni-based catalysts, in which irreversible chain-termination reactions are prominent and molecular weight distribution are broad. With these catalysts, chain-end modification or formation of block copolymers is not possible [1,2]. Lanthanide catalysts afford 'living' polymerization reactions with a possibility of chain-end modification or formation of block copolymers. They produce functional polybutadiene with high stereoregularity [1,3]. These polymerization mechanisms, however, are incompletely understood because most of the catalysts have serious limitations: they lack crystallinity, have low stability and operate at low concentration, and thus, direct investigation of the active catalysts is difficult [4–6]. The most common approach to judging their 'livingness' is on the basis of the product analysis or the reaction kinetics [4,7].

The 'livingness' of the Ni and Nd active sites was spectroscopically analyzed by our group using X-ray absorption and UV–visible spectroscopies [8,9]. Here, a new insight for judging the 'livingness' is developed based on electron densities of the active chain-ends using theoretical methods.

2. Results and discussion

Frontier orbital analysis with highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) was carried out to investigate the living nature of the active sites of the Ni, Nd, Li catalysts by calculating the orbital density and the atomic charge (Fig. 1). As models of the polymerization catalysts, the following models of active sites were chosen on the basis of the spectroscopic results [8,9].

Model 1 (Ni): $[\mathrm{MeCOO{-}Ni(F)(\pi\text{-}butenyl)}]^{-1}$
Model 2 (Nd): $[\mathrm{MeCOO{-}Nd(Cl)(\pi\text{-}butenyl)}]$
Model 3 (Li): $[\mathrm{Li(\pi\text{-}butenyl)}]$

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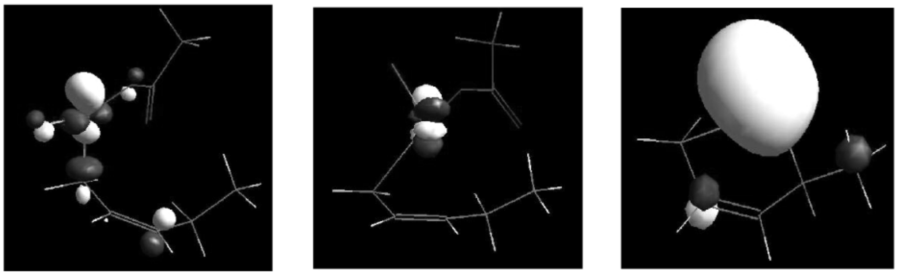
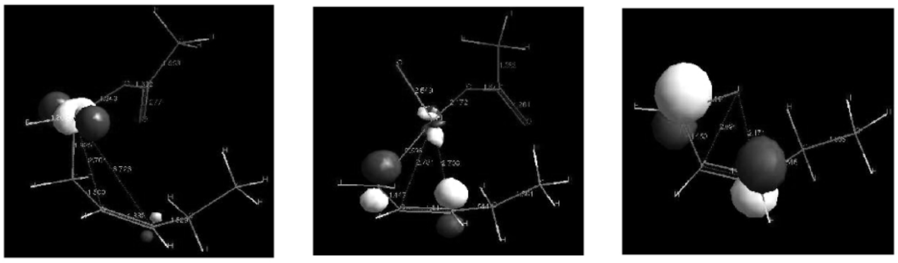


LUMO of Ni catalyst LUMO of Nd catalyst LUMO of Li catalyst



HOMO of Ni catalyst HOMO of Nd catalyst HOMO of Li catalyst

Model 1 (Ni catalyst) Model 2 (Nd catalyst) Model 3 (Li catalyst)

Fig. 1. Active site structures and orbital amplitude plots of the HOMO/LUMO. (a) LUMO/HOMO of Ni catalyst; bond distances Ni–C_α 1.925 Å, Ni–C_β 2.761 Å, Ni–C_γ 3.728 Å (Model 1). (b) LUMO/HOMO of Nd catalyst; Bond distances Nd–C_α 2.593 Å, Nd–C_β 2.731 Å, Nd–C_γ 2.708 Å (Model 2). (c) LUMO/HOMO of Li catalyst; Bond distances Li–C_α 2.114 Å, Li–C_β 2.094 Å, Li–C_γ 2.171 Å (Model 3).

Nickel(II) is coordinated with the acetate anion, the π-butenyl active end and the fluoride anion, and neodymium(III) is coordinated with the acetate, the π-butenyl active end and the chloride anion, respectively. A monomeric model of the Li catalyst with π-butenyl coordination is employed because it is the typical example of living polymerization for dienes, and delivers a very narrow polydispersity, $M_w/M_n = 1.0$ [7,10].

The frontier orbitals of the Ni catalyst are different from those of Li- and Nd-based catalysts. The HOMO of the Ni catalyst mostly has the d-orbital (Ni) character while the LUMO has the p-orbital (C_α and C_γ atoms) as well as the d-orbital (Ni) characters. The π-butenyl coordination in the Ni catalyst is η^1-π-coordination but those in Nd and Li catalysts are η^3. For the butenyl coordination of the Ni catalyst, Cosses and Arlman suggested η^1-σ-coordination and Taube et al. η^3-π-coordination [11]. The difference is probably due to steric and electronic effects of the models of active site. The atomic charge (+0.003) on Ni and the atomic charge (−0.14) on C_α of the Ni catalyst are both much lower than those in the Nd catalyst (Table 1). This result suggests that the Ni-catalyst has a weakly polarizable bond that is covalent, and can be easily reduced. The HOMO electron density of the Nd catalyst is mostly concentrated on the p orbital of the C_α and C_γ atoms, and the electron density of LUMO is concentrated on the 4f and 5d orbitals of the Nd atom. In other words, the C_α atom of the chain end nucleophilically attacks the C_1 atom (LUMO) of 1,3-butadiene resulting in C–C bond formation (Fig. 2(a) and (b)) while the Nd atom electrophilically attacks the C_4 atom (HOMO) of 1,3-butadiene resulting in the Nd–C bond formation (Fig. 2(c) and (d)) [12]. The positive atomic charge (+1.09) on the Nd atom and the negative atomic charge (−0.56) on C_α support the highly ionic character, in good agreement with the spectroscopic results [9]. As for the Li catalyst, the HOMO possessing the p-orbital is located on the C_α and C_γ atoms and the LUMO possessing the s-orbital is located on the Li atom. The positive atomic charge (+0.16) on the Li atom and the negative atomic charge (−0.56) on C_α indicate the highly ionic character. The atomic charges of the three models indicate that Li- and Nd-based catalysts have a strong ionic character on each of the C_α carbon and the metal atom, resulting in living polymerization, while the Ni-based catalyst has not the ionic but the covalent character. This analysis shows that 'livingness' increases in the case of the highly polarizable C–M bond because the highly ionic C–M bond cannot be easily broken via β-hydride elimination, chain-transfer reactions or reduction [13].

Table 1
Calculated atomic charges of Ni-, Nd- and Li-catalysts

Atomic charge	Ni catalyst	Nd catalyst	Li catalyst
Metal	+0.003	+1.09	+0.16
C_α	−0.14	−0.56	−0.56
C_β	−0.17	−0.07	−0.09
C_γ	−0.37	−0.34	−0.36

Based on the theoretical calculations on the non-living and living Ziegler catalysts, the following conclusions can

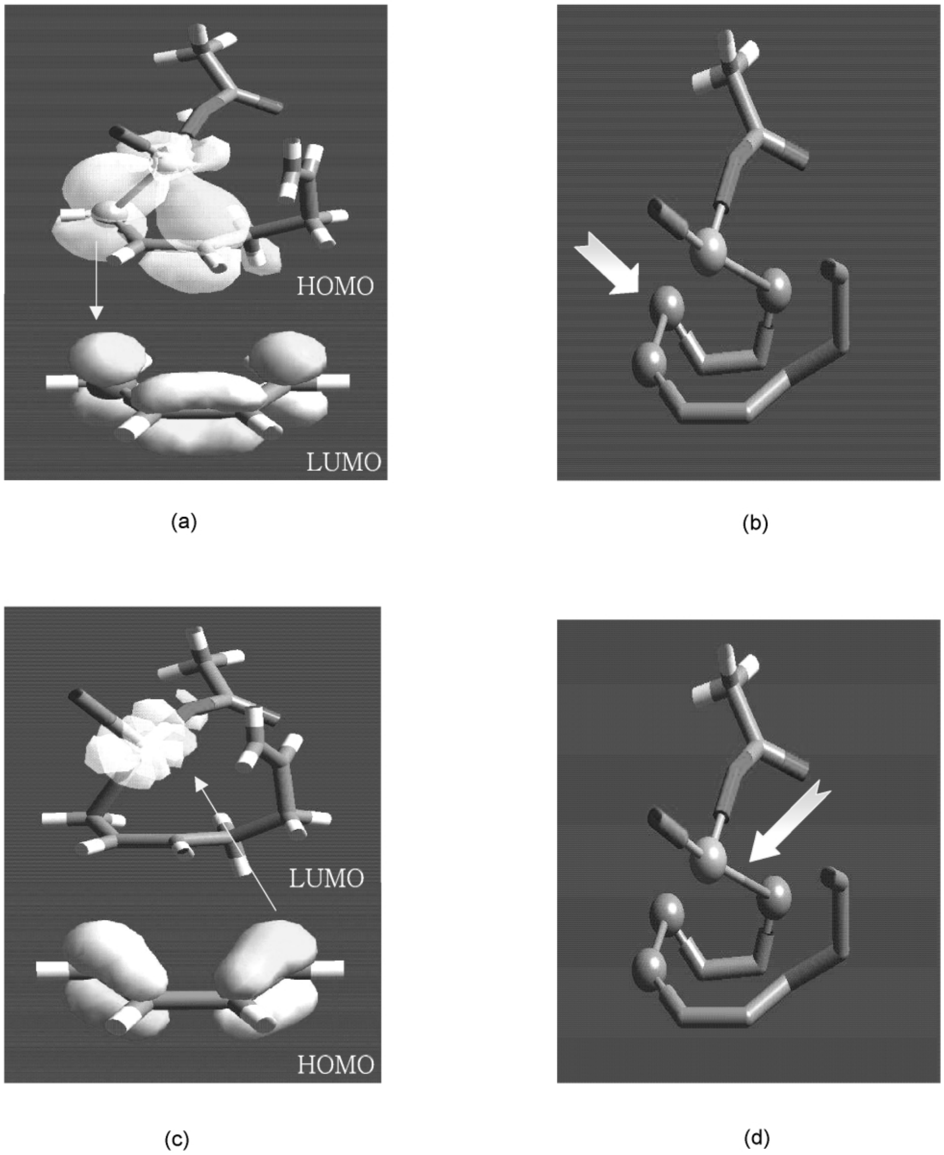


Fig. 2. Mechanism of C–C and Nd–C bond formations in 1,3-butadiene polymerization with Nd catalyst. (a) The orbital overlap of HOMO of Nd catalyst and LUMO of butadiene. (b) C–C bond formation through pathway (a). (c) The orbital overlap of LUMO of Nd-catalyst and HOMO of butadiene. (d) Nd–C Bond formation through pathway (c).

be made: a 'non-living' catalyst would have (1) a covalent character, and (2) it is readily reduced by a cocatalyst (like alkylaluminum), while a 'living' catalyst has (1) a strongly ionic character and (2) a stable oxidation state of the active chain end.

In order to design a 'living' Ziegler catalyst, one has to take into account the following conditions: (1) a highly polarizable active chain end and (2) an active-site metal possessing a stable oxidation state.

3. Experiments

3.1. Calculations

All density functional calculations were performed using the Gaussian98 package with the CEP-31G basis set to obtain the structures and electronic properties of Li, Ni, and Nd catalysts. For graphical representation, the Cerius^2 software was utilized.

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