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# Polymerizations of vinyl-cyclohexane in the presence of $C_2$, $C_{2v}$, and $C_s$ zirconocene-based catalysts

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## Abstract

Polymerizations of vinyl-cyclohexane (VCH) in the presence of catalytic systems based on zirconocenes belonging to $C_2$, $C_{2v}$ or $C_s$ symmetry group were performed. All polymers were analyzed by $^{13}$C NMR spectroscopy and show isotactic microstructure. A steric control mechanism, involving a like 1,3-asymmetric induction of the chiral carbon of the last inserted unit on the chirality of the incoming monomer coordination, is proposed. This would be the only stereocontrol mechanism in the presence of a $C_{2v}$-symmetry catalyst, and it would enforce or overcome site control in case of active species with $C_2$ and $C_s$-symmetry, respectively.

*Keywords:* Ziegler–Natta polymerization; γ-Branched-α-olefins; NMR

## 1. Introduction

Polymerization of α-olefins performed in the presence of group 4 metallocene-based catalysts, generally gives rise to products with microstructures strictly related to the symmetry properties of catalytic precursor. For instance, polymerization of propene performed in the presence of $C_2$, $C_s$ or $C_{2v}$ symmetric metallocenes produces isotactic, syndiotactic or atactic polypropylene, respectively [1,2]. As for primary propene insertion, the stereospecificity is due to the enantioselectivity of each monomer insertion step, related to the non-bonded energy interactions of the methyl group of the chirally coordinated monomer with the growing chain chirally oriented by the catalytic site [3]. According to this growing chain chiral orientation mechanism, the enantioselectivity of this reaction is not due to direct interactions of the π-ligands with the monomer, but to interactions of the π-ligands with the growing chain, determining its chiral orientation which, in turn, discriminates between the two prochiral faces of the monomer.

The importance of the role played by the growing chain was confirmed by observing the stereospecificity of the first step of the polymerization [4].

For a given catalytic model, the enantioselectivity of each insertion step does not assure its stereospecificity. In fact, the possible presence, as well as the kind, of stereospecificity depends on possible differences between stereostructures of transition states of two successive insertion steps. The main polymerization mechanism generally accepted implies that, at the end of each insertion step, the growing chain occupies the coordination site previously occupied by the alkene monomer (chain migratory insertion mechanism) [5]. In this framework, the stereospecific behavior of the model sites depends on the relationship between the two intermediates obtained by exchanging the relative positions of the growing chain and of the incoming monomer. Depending on the local symmetry of the coordinated bridged π-ligand, these two intermediates are identical for metallocenes with $C_2$ π-ligands, and enantiomeric for metallocenes with $C_s$ symmetric π-ligands. Consequently, if the insertion step is enantioselective, the catalysts result isospecific and syndiospecific, respectively [1,2].

The clear relationship between polymer microstructure and symmetry properties of metallocene is absent when the hydrocarbon monomer is a γ-branched-α-olefin. In fact, a $C_2$-symmetric metallocene having stereorigid ligands, like ethylene-bis-(1-indenyl), as well as a $C_s$-symmetric stereorigid ligands, like diphenylmethylidene-(cyclopentadienyl)(9-fluorenyl), polymerize 3-methyl-1-butene and 3-methyl-1-pentene to isotactic polymers [6,7].

Thus, in the presence of a $C_s$-symmetric catalyst, the origin of the isotactic placements may arise from a chain-end control mechanism [1a,4a,8–11] or from a back-skip of the chain after every monomer insertion [1e–g,12].

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As for chain-end control, the polyinsertion stereochemistry is controlled, step by step, by the absolute configuration of the chain methine carbon of the last inserted monomer unit. This kind of control is classified, according to Ref. [9], as 1,3-asymmetric induction and the insertion may be either ‘like’ or ‘unlike’. A lot of examples of like as well as unlike induction are present in the literature [1a,4a,8–11]. It is worth noting that, in the case of isotactic propagation in the presence of $C_s$ symmetric catalysts, the site control would always induce the insertion of alternate olefin prochiral face at each insertion step, while the chain end control could induce a like insertion all over the polymerization. Evidently, in order to obtain isotactic polymer, the chain end control should overcome the site control mechanism.

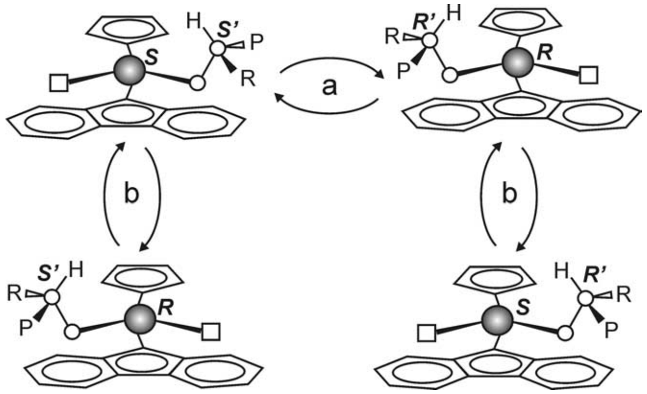
Alternatively a back skip of the chain may occur after every monomer insertion [1e–g,12]. In Scheme 1, the configuration of the metal of the active species (according to the rules of Cahn–Ingold–Prelog [13] extended to chiral metallocenes as proposed by Schögl [14]) and that of the last unit of the chain end (this latter configuration is primed) are reported.

Pathway **a** leads to syndiotactic polymer, because, after each insertion, the inversion of the absolute configuration of the catalytic site, determining the coordination of incoming monomer alternatively with opposite enantioface, is obtained. Pathways **b**, which represent the back-skip reaction [6], lead to catalyst isomerization without insertion. The ($RR'$, $SS'$) and ($RS'$, $SR'$) species are mirror image pairs with equivalent free energies, whereas the ($RR'$, $SR'$) and ($SS'$, $RS'$) pairs are diastereoisomeric with different free energy. The back skip occurs when the diastereoisomeric intermediate generated by an insertion step is largely unfavored with respect to a monomer free intermediate which presents the terminal growing chain on the opposite site [6].

## 2. Results and discussion

In order to investigate the role of the steric hindrance of the γ substituent of the monomer on the polymerization control, vinyl-cyclohexane (VCH) polymerizations were run by using three zirconocene-based catalysts, having different symmetry properties. In particular, the considered $C_2$, $C_{2v}$, and $C_s$ zirconocene precursors are reported as following:

- *rac*[ethylene-bis-(1-indenyl)]$ZrCl_2$ (**1**)
- [methylene(9-fluorenyl)$_2$]$ZrCl_2$ (**2**)
- [diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)]$ZrCl_2$ (**3**).



Scheme 1.

Table 1
Polymerization of VCH performed in the presence of (**1**), (**2**) and (**3**) activated with MAO

| Run[a] | Catalyst | Symmetry | Activity[b] |
|---|---|---|---|
| 1 | (**1**) | $C_2$ | 2900 |
| 2 | (**2**) | $C_{2v}$ | 6.0 |
| 3 | (**3**) | $C_s$ | 2.3 |

[a] All the polymerizations were carried out in dry toluene using 1 mL of monomer, $1\times10^{-5}$ mol of catalyst and $1\times10^{-2}$ mol of MAO (based on Al) at 20 °C. Reaction time: 20 h.

[b] Activity: $g_{polymer}$/[monomer][catalyst]h.

Table 1 shows the data concerning the polymerization of VCH performed in the presence of (**1**) (sample 1), (**2**) (sample 2) and (**3**) (sample 3) activated with MAO. The structures of the products were determined by $^{13}C$ NMR analysis comparing the chemical shifts of the resonances observed in the spectra with the data reported in the literature [15]. In Fig. 1, the $^{13}C$ NMR spectra of samples 1–3 (Fig. 1(A)–(C)) and, for the sake of comparison, the $^{13}C$ NMR spectrum of a syndiotactic poly(VCH) obtained by hydrogenation of syndiotactic polystyrene [16] (Fig. 1(D)) are reported. The spectra of samples 1–3 present the same sharp resonances associated with carbons 1 and 3 and a strong difference, between the chemical shift resonance of methine carbon 2 and the same methine of syndiotactic poly(VCH), is observed (Fig. 1). This clearly indicates that all polymers are prevailingly isotactic [15]. Moreover, the sharpness of the carbon 3 resonances of the samples 1, 2 indicates that they are more stereoregular than sample 3. Differential scanning calorimetry (DSC) analysis showed that the melting temperatures are enclosed in a sharp range (350–370 °C) for the three samples.

The results can be rationalized by considering that the stereoregularity of the polymers obtained using (**2**)/MAO arises from a chain end control where the configuration of the chain methine carbon of the last inserted monomer unit gives a like kind of induction.

In fact, the like 1,3-asymmetric induction would:

- reinforce the stereocontrol in polymerizations performed in the presence of $C_2$ (isospecific) catalyst as (**1**)
- be the only stereocontrol in polymerizations performed in the presence of $C_{2v}$ (aspecific) catalyst as (**2**)
- compete, in the polymer stereoregularity determination, in polymerizations performed in the presence of $C_s$ (syndiospecific) catalyst as (**3**).

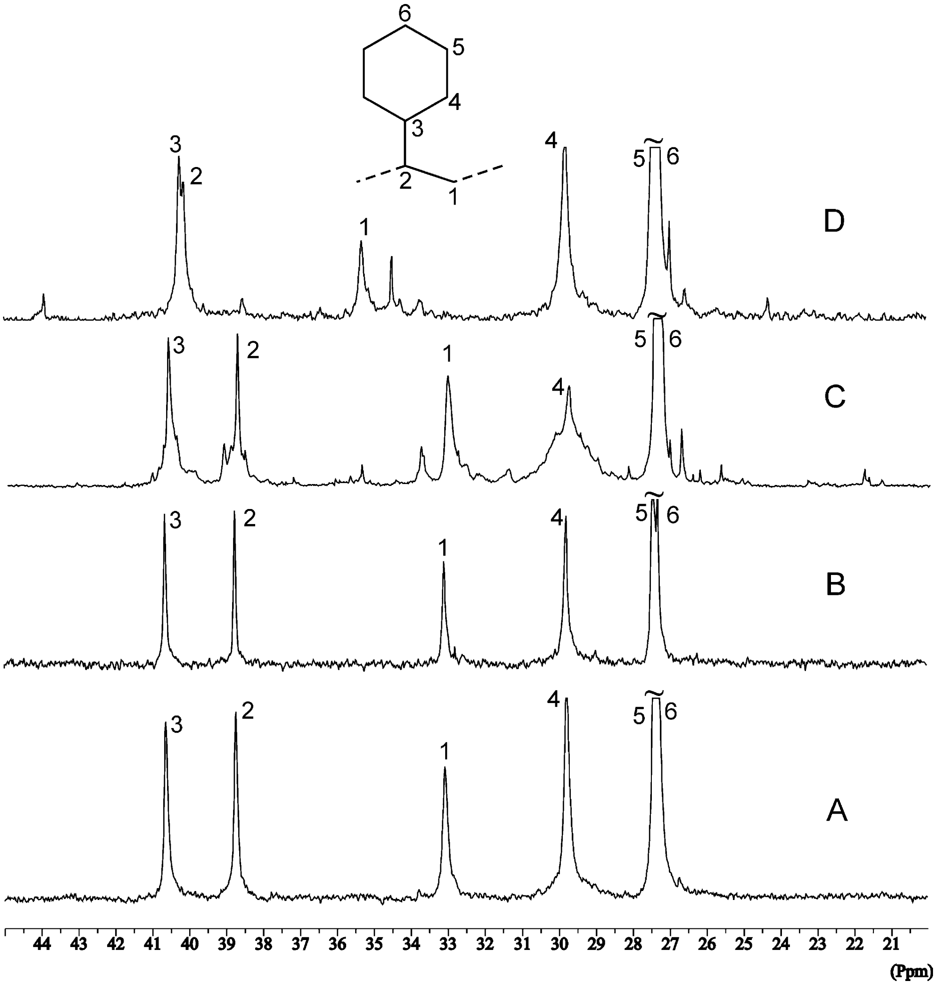
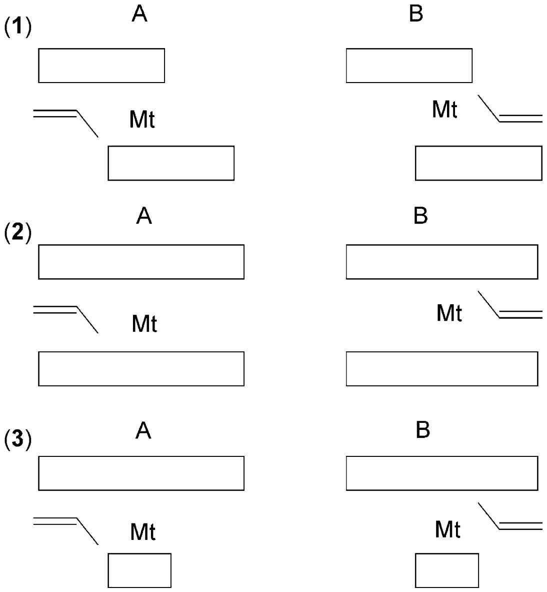


Fig. 1. Spectra of samples 1 (A), 2 (B) and 3 (C), and spectrum of a syndiotactic poly(VCH) obtained by hydrogenation of syndiotactic polystyrene [16] (D).

Thus, when the substituent of the chiral carbon of the last inserted unit, which in this case is a cyclohexyl group, is sterically more hindered with respect to the polymeryl chain, the asymmetric induction of this carbon can exceed that of the catalytic site, determining isotactic stereoregularity of the polymers also using $C_{2v}$ and $C_s$ symmetric metallocenes.

The three catalysts present a very different activity. In fact, the activity of (**1**) is about three orders of magnitude higher of (**2**) and (**3**). Since, the olefin must insert always with the same prochiral face to give an isotactic polymer, the olefin coordination to catalyst (**1**) could be favored with respect to (**2**) and (**3**) because it does not involve steric interactions with the ancillary ligands (see the two-dimensional drawing of Scheme 2) [17]. In fact, as for (**1**), the coordination sites A and B are homotopic. On the contrary, the coordination to site B of catalyst (**3**), presenting enantiotopic sites, would involve a steric interaction between the olefin and the ancillary ligand. Finally, as for catalyst (**2**) the incoming monomer would interact with the ancillary ligand for both coordinations on site A and B. The decrease of the polymerization rate, due to those



Scheme 2.

interactions, could rationalize the activity decrease (**1**)≫(**3**)≈(**2**).

## 3. Conclusions

The clear cut relationship between the symmetry properties of zirconocene-based catalysts in the polymerization of propene and the stereoregularity of the obtained polymers is lost when the monomers are γ-branched-α-olefins. In fact, in the presence of zirconocene-based catalysts only isotactic polymers, independently from the symmetry of zirconium compound are produced. The catalysts, probably because of the bulky substituent on the γ-carbons of the last inserted olefins in the polymer chain, give rise to chiral carbon able to give an asymmetric induction on the incoming monomer. The like insertion all over the polymerization can exceed that of the catalytic site, determining isotactic stereoregularity of the polymers also using $C_{2v}$ and $C_s$ symmetric metallocenes. Steric interactions of incoming monomer with the ancillary ligands of catalysts having symmetry $C_{2v}$ or $C_s$, would probably influence the activity of these catalysts.

## 4. Experimental part

### 4.1. Polymerization: general procedure

All the operations were performed under nitrogen atmosphere by using conventional Schlenk-line techniques. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. Methylaluminoxane was purchased by Witco and used as a solid after distillation of solvent. The catalytic precursors (**1**), (**2**), and (**3**), were synthesized according to the literature [1g,18,19].

VCH were purchased from Aldrich and purified by distillation in the presence of Al(*i*-Bu)$_3$.

*Runs 1–3*. Polymerizations of VCH were carried out in 50 mL glass flasks equipped with magnetic stirrer by sequentially introducing toluene, MAO and monomer. After thermostating at polymerization temperature (20 °C), reactions were started by injecting 1 mL of toluene solution of catalytic precursor **1**, **2**, **3**, respectively. The amounts of reagents are reported in Table 1.

Polymerizations were stopped by introducing a few milliliters of ethanol. Then, the polymers were coagulated in an excess of acidified ethanol, washed several times with fresh ethanol and dried in vacuo at 60 °C.

### 4.2. Polymer analysis

NMR spectra were recorded on an AX 300 Bruker spectrometer operating at 75 MHz at 373 K. The samples were prepared by dissolving 20 mg of polymer in 0.5 mL of tetrachlorodideuteroethane (TCDE). Hexamethyldisyloxane (HMDS) was used as internal chemical shift reference.

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