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Active centers in propylene polymerization catalysts of the fourth generation

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ABSTRACT

Isospecific centers in propylene polymerization catalysts of the 4th generation [combinations of solid catalysts of the $TiCl_4$/aromatic diester/$MgCl_2$ composition and binary cocatalysts containing $Al(C_2H_5)_3$ and methoxysilanes $R_nSi(OCH_3)_{4-n}$] contain several populations of active centers, which differ in kinetic parameters and in the level of stereospecificity control. The differences in the kinetic parameters between the active centers translate into large differences in the average polymerization degree of the polymer material the centers produce, from 500–800 to 8000–17,000. Differences in the stereospecificity level between the active centers result in large differences in melting points of the polymer components. Methoxysilanes $R_nSi(OCH_3)_{4-n}$ directly affect each type of the polymerization center; both the kinetic parameters of the centers and their level of stereocontrol are influenced by the nature of the alkyl groups *R*.

1. Introduction

All heterogeneous transition metal-based catalysts exhibit some degree of active center nonuniformity; they all produce certain amounts of undesirable byproducts. Two different types of active center nonuniformity can be envisaged (Scheme 1):

1. Structural nonuniformity (multi-center catalysts): a situation when several types of active centers co-exist in a catalyst (at a limit, centers A and B in the first example in Scheme 1). Dominant centers A convert a given substrate into a desirable product Pr_A but the catalyst also contains active centers B of a different type (or several different types), which convert the same substrate into different byproducts Pr_B. Selectivity of such catalysts can be controlled by selective poisoning of undesirable centers B.
2. Kinetic nonuniformity of single-center catalysts (the second example in Scheme 1): a situation when a single center A usually converts substrate molecules into molecules of the desirable product Pr_A but, on occasion, the same center converts the same substrate molecule into a molecule Pr_B of a different type.
3. In real situations of nonselective multi-center catalysts, both types of active center nonuniformity can be expected.

The existence of kinetic nonuniformity is difficult to prove in catalytic reactions yielding low molecular weight products. However, transition metal-based catalysts of alkene polymerization provide a unique opportunity to demonstrate the existence of kinetic nonuniformity because all the products in these reactions, monomer units formed one after another from substrate molecules (monomers), remain linked together in polymer chains and the polymer science developed numerous specialized techniques for the structural analysis of linking between such consecutively positioned monomer units in polymer chains.

Isospecific soluble catalysts for propylene polymerization based on racemic bridged bis-indenyl complexes of zirconium with C_2 symmetry were described by Brintzinger, Kaminsky, Ewen and Rytter [1–4]. Their studies clearly showed that when these catalysts are used under optimum conditions, they are structurally uniform but kinetically nonuniform (the third example in Scheme 1). All the centers in these catalysts have the same structure (metallocenium cations) and each center produces predominantly isotactic polypropylene molecules. Formally, in terms of Scheme 1, the generation of a perfectly isotactic polymer chain with such catalysts would correspond to the formation of a string of M′ monomer units, -M′-M′-M′-M′-, or, defining a link

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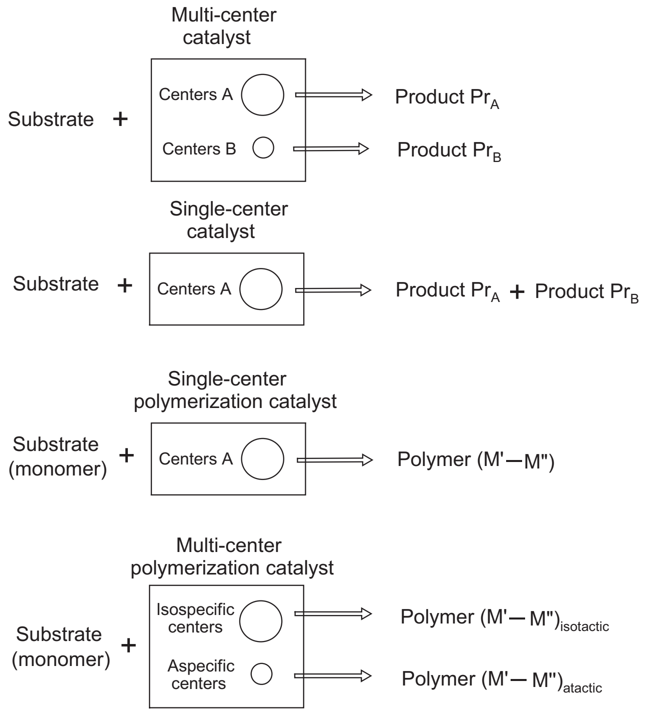

Scheme 1. Different types of center nonuniformity in heterogeneous catalysis.

between two adjacent M' monomer units as the *meso*-link (*m*), a perfectly isotactic polymer chain is an $\cdots mmmm\cdots$-linked chain. However, these active centers are not perfect; periodically, each center makes a steric error and forms a racemic (*r*) link between two adjacent monomer units, $\cdots mmmr$. Formally, such an error can be viewed as introducing an M'' unit in the chain, $-M'-M'-M'-M''$. The active center usually corrects itself in the next reaction step, i.e., it forms a string $-M'-M'-M'-M''-M'-M'-M'$, thus producing an isolated *rr* steric error in monomer linking, $\cdots mmmrrmmm\cdots$. Because all the centers in such catalysts are the same, the probability of the *rr* error cannot be controlled by selective poisoning but the frequency of this error can be affected by placing various substituents into each of the indenyl ligands in the metallocene complex [5]. For example, the probability of meso-linking between two connected propylene units (p_{iso}) in a polymer prepared with a catalyst derived from *rac*-$Me_2Si(Ind)_2ZrCl_2$ at 70 °C is ~0.966 (the probability of the steric error, 1-p_{iso}, is ~3.4%) but the p_{iso} value increases to 0.978 when the metallocene complex is *rac*-$Me_2Si(4\text{-}Ph\text{-}Ind)_2ZrCl_2$ and to 0.996 when the complex is *rac*-$Me_2Si(2\text{-}Me,4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (from experimental data in [6]).

At the present time, most of isotactic polypropylene is produced commercially using heterogeneous Ti-based Ziegler–Natta catalysts of the 4th generation. These catalysts consist of two components, a solid particulate material of the general formula $TiCl_4$/aromatic diester/$MgCl_2$ and a binary cocatalyst containing $Al(C_2H_5)_3$ and an organic modifier (often called "an external donor"), a methoxysilane of the general formula $R_nSi(OCH_3)_{4-n}$, where *R* is a branched alkyl group and $n = 2$ or 1. Although the methoxysilane is used in a small quantity (the [Si]/[Al] molar ratio usually ranges from 0.03 to 0.1), it exerts crucial influence on the performance of the catalysts. In the absence of an alkoxysilane, the catalysts produce a mixture of crystalline isotactic and amorphous atactic polymers in a ~1:1 to 2:1 ratio but addition of a "high-efficiency" organic modifier leads to a desirable increase in the content of the isotactic material, up to 99%.

The behavior of these catalysts can be very formally represented by the last example in Scheme 1. The catalysts, in a general sense, have two types of active centers, isospecific and aspecific. The isospecific centers produce highly crystalline isotactic polypropylene (formally, chains of linked M' and M'' monomer units with a large predominance of M' units), whereas the aspecific centers produce amorphous atactic polypropylene, which chains contain M' and M'' units in comparable quantities.

A number of earlier publications have described detailed correlations between the number and size of alkyl groups *R* in $R_nSi(OCH_3)_{4-n}$ on one hand and the catalyst productivity and the content of the crystalline polypropylene fraction on the other hand [7–15]. This research clearly showed that all the catalysts are structurally nonuniform, each contains two groups of active centers (some distinguish three groups [8]). Within this approach, the organic modifiers are usually viewed as selective poisons; they suppress reactivity of the aspecific centers and, additionally, may convert the aspecific centers into the isospecific ones.

The present research is devoted to a different subject, analysis of kinetic nonuniformity in the performance of the isospecific centers. We attempted to investigate the frequency of the *rr* linking error in molecules of crystalline isotactic polymers prepared with different methoxysilanes. To this goal, we compared the "quality" of isospecific centers formed in the presence of five different organic modifiers $R_nSi(OCH_3)_{4-n}$ by analyzing distributive characteristics of propylene polymers prepared with the respective catalyst systems.

2. Materials and methods

2.1. Catalyst systems

A single supported Ziegler–Natta catalyst of the 4th generation, $TiCl_4$/aromatic diester/$MgCl_2$, was used to catalyze all the polymerization reactions. The catalyst (trade name SAL) was provided by Sinopec Catalyst Company. This is a high-productivity catalyst designed for gas-phase propylene polymerization reactions [16]. It is prepared with diisobutyl phthalate (an "internal donor" in the parlance of the polymerization catalysis) as a means of the formation of microcrystalline $MgCl_2$ particles, which serve as a support for Ti-bearing active centers. Synthetic procedures for 4th generation propylene polymerization catalysts are described in Chapter 4 in Ref. [5]. The catalyst composition and its principal physical parameters are as follows: [Ti] 3.4 wt.%, [Mg] 18.4 wt.%, [diisobutyl phthalate] ~15 wt.%, the average diameter of spherical particles 25 μm, the specific surface area ~140 m^2/g, the pore volume 0.15 cm^3/g.

The catalyst was activated with combinations of $Al(C_2H_5)_3$ and five different methoxysilanes $R_nSi(OCH_3)_{4-n}$, which were used at an [Al]:[Si] molar ratio of 30. Synthesis of the methoxysilanes was described previously [15].

2.2. Propylene polymerization

Propylene polymerization reactions were carried out in the liquid monomer medium in a one-liter stainless steel autoclave equipped with a mechanical stirrer; the stirring speed was 300 rpm. The standard composition of the reaction mixture was as follows: liquid propylene 800 g; $Al(C_2H_5)_3$ 12 mmol (used as 0.88 M solution in heptane); methoxysilane 0.39 mmol; catalyst 20 mg. Hydrogen was used to control the molecular weight of the polymers. The hydrogen partial pressure was the same in all the experiments, 0.3 MPa; the H_2/propylene molar ratio was $2.6 \cdot 10^{-3}$. All the polymerization reactions were carried out at 70 °C for 60 min.