

Review

“Dual-side” catalysts for high and ultrahigh molecular weight homopolypropylene elastomers and plastomers

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Received 30 December 2004; accepted 9 June 2005

Available online 10 August 2005

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Abstract

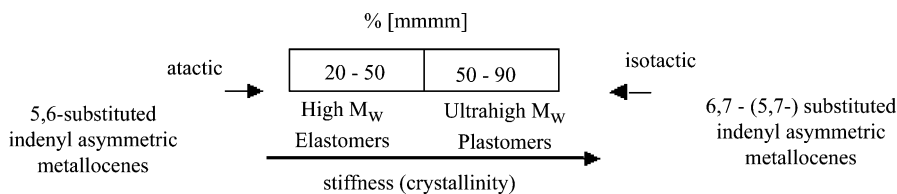
Classical Ziegler–Natta catalysts are capable of producing homopolypropylenes with high isotacticities. New trends are focussed on obtaining polypropylenes with different properties through control of the polymer microstructure. Metallocene catalysts with variable structures revealed a great potential toward this challenge.

The flexibility of the indenyl ligand substitution proved to be the key in controlling the stereoerror formation. Error type and error distribution have major implications on the mean isotactic sequence length, and therefore also on the mechanical properties of the polymer products.

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This review focuses on the synthesis of asymmetric *ansa*-metallocene catalysts, their polymerization mechanism and chain transfer reactions. The impact of the presented asymmetric *ansa*-metallocene extends beyond simple propylene polymerization disclosing a way to materials that fill the gap between “soft” thermoplastic elastomers and stiff polypropylene materials.

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Keywords: Asymmetric metallocenes; Homogeneous catalysis; Polypropylenes; Thermoplastic elastomers; Plastomers

1. From elastomers to plastomers by homogeneous catalysis

1.1. Transition metal-based catalysts for propylene polymerizations

1.1.1. Metallocenes

The discovery that organic and organometallic tools can be applied for a rational catalyst design laid the foundation of worldwide activities at academia as well as in industry, leading to several types of metallocenes with precise correlation to the corresponding polymer microstructures (Fig. 1). These catalysts enable not only the synthesis of highly isotactic or more or less atactic polypropylenes but also syndiotactic, hemiisotactic and different kinds of stereoblock polymer structures, providing a portfolio of tailor-made microstructures for different industrial applications [1].

Isospecific by virtue of their symmetry [2,3], C_2 -symmetric *ansa*-zirconocene catalysts produce isotactic polypropylene by enantiomorphic control. The same mechanism can be employed as a tool toward producing polymers with a wide range of isotacticities and molecular weights. Kaminsky et al. [4] designed the basic structure of the C_2 -symmetric catalysts (ethylene-bridged bis(tetrahydroindenyl) zirconium complex; Fig. 1). In time, many variations of this catalyst have been realised by changing the substitutions on the cyclopentadienyl rings.

By introducing a bulkier moiety, e.g. fluorenyl in the bis(cyclopentadienyl)-based structures, a new class of catalysts was developed, known as C_s -symmetric metallocenes [5]. Due to the enantiotopic nature of their coordination positions, the chain-end control is present as the only stereo-control mechanism leading to syndiotactic polypropenes. Highly syndiotactic polypropene [5,6] was first obtained by Ewen with C_s -symmetric catalyst $Me_2C(Cp)(9-Flu)-ZrCl_2$ [7] (Fig. 1).

Lacking any symmetry element by introducing one or more substituents in different positions of the cyclopentadienyl moiety, C_1 -symmetric metallocenes possess two diastereotopic coordination sites. Thus, the stereochemistry of the polymerization reaction can be converted from the production of syndiotactic polypropene to a hemiisotactic form and even to a highly isotactic material [3]. Chien [8] reported first the synthesis of C_1 -symmetric species [1-(η^5 -indenyl)-1-(η^5 -tetramethylcyclopentadienyl)ethane] $TiCl_2$ providing elastic polypropylenes with narrow molecular weight distribution and of fairly uniform composition. Modification of the system introduced by Chien toward dimethylsilane bridged indenyl–cyclopentadienyl zirconium or hafnium complexes by Collins et al. [9,10] (1, Fig. 2) afforded an improved activity and higher molecular weights ($M_w \sim 49\,000$ g/mol with hafnium complex). In analogy to the work of Chien, the elastic properties of these new materials were attributed to blocklike structures composed of isotactic and atactic sequences.

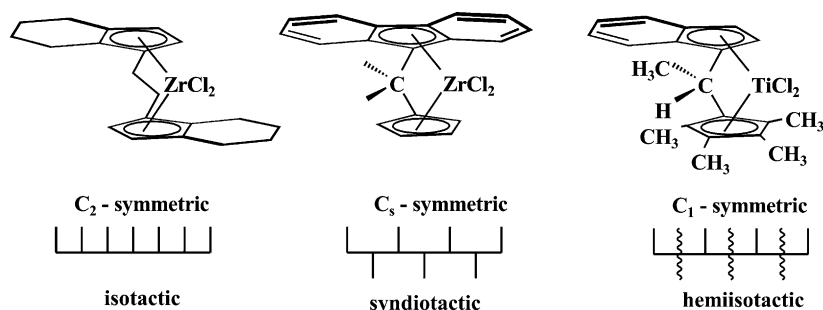


Fig. 1. Correlation of the polymer microstructure with the catalyst symmetry.

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