The Particularities of Isospecific Polypropylene Synthesis in Bulk with Ansa-metalloocene Catalysts

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Abstract. Hiral ansa-metalloccenes with indenyl ligands are useful as catalysts for producing isotactic polypropylene (iso-PP). In this work the kinetics of propylene polymerization in bulk with ansa-zirconocenes C2 symmetry at 30-80°C with using of different cocatalysts, mainly the polymethylaluminoxane, have been investigated. The following aspects were in focus of our interest: the nature of the bridge, the presence of substituents in the bridge and on the indenyl ligands; conditions of the pre-activation stage and the polymerization process and the study of relations between these parameters and PP properties. Using the Me2Si(4-Ph-2-Et-Indenyl)2ZrCl2 (rac : meso = 1 : 2)/MAO the high molecular iso-PP was produced. The activity during iso-PP synthesis reaches 900 kgPP/gcat.h. Influence of hydrogen on activity and molecular weight characteristics also were studied. We compared properties of metallocene iso-PP with the same of PP produced with heterogeneous catalytic systems on the base of high effective Ti/Mg catalysts.

Introduction

Metallocene catalysts have created new impulses in the investigation of stereospecific polymerization and copolymerization of α-olefins [1-5]. New catalysts have allowed to control microstructure, molecular weight characteristics and the tailoring of polyolefins properties. The metallocene catalysts (MC) allow to synthesize almost all kinds of stereoregular polymers. These catalytic systems posses high activity and in contrast to the heterogeneous metallocomplex catalysts have a single active centers (AC). MC allow the rational design of multi-site catalysts by mixture of different metalloccenes. This leads to production of PP with mono-, bi- and polymodal molecular mass distributions and this broadens the PP applications areas on a base of homo and propylene copolymers [6].

Activity, molecular weight and stereoregularity of polymers produced on metallocene catalysts, in contrast to the heterogeneous catalysts, are very sensitive to the polymerization conditions: polymerization temperature, monomer and catalyst concentrations, nature of solvent, ratio of Al/Zr etc. PP with the higher
molecular weight and higher yield one can produce at polymerization with high concentration of propylene, namely in a medium of a liquid monomer. High concentration of propylene at polymerization in bulk promotes increasing of the degree of PP regularity also [7-9].

In the present work during study of iso-PP synthesis in medium liquid propylene with ansa-metallocene catalyst the following aspects were in focus of our interest: the nature of the bridge, the presence of substituents in the bridge and in the indenyl ligands; the influence of conditions of the pre-activation stage and the polymerization process (temperature, ratio Al to Zr, concentration of metallocene and hydrogen) on the kinetic characteristics, catalytic systems activity and PP properties.

We studied propylene polymerization in bulk with the next ansa-metallocenes: rac-(CH₃)₄Ind₂ZrCl₂ (MC-1), rac-Me₂C(Ind)₂ZrCl₂ (MC-2), Me(c-C₅H₄)C(Ind)₂ZrCl₂ (MC-3), rac-(CH₂-C₆H₅-CH₂)(Ind)₂ZrCl₂ (MC-4) rac-Me₂Si(Ind)₂ZrCl₂ (MC-5) and Me₂Si(4-Ph-2-Et-Ind)₂ZrCl₂ (rac: meso=1:2) - (MC-6).

A comparison with some property of iso-PP produced with heterogeneous Ti/Mg catalyst also was done.

**Experimental**

Propylene of polymerization-grade without additional purification was used. Content of admixtures - CO, CO₂, H₂O was less than 5 ppm.

Polymethylaluminoxane (MAO) from Witco (10 % w solution in toluene) was used without further treatment.

Rac-(CH₃)₄Ind₂ZrCl₂ - ethylenebis(1-indenyl)zirconium dichloride; rac-Me₂C(Ind)₂ZrCl₂ - dimethylcarboniumbis(1-indenyl)zirconium dichloride; Me(cyclo-C₅H₄)C(Ind)₂ZrCl₂ - methylcyclopropylcarboniumbis(1-indenyl)zirconium dichloride; rac-(CH₂-C₆H₅-CH₂)Ind₂ZrCl₂ - o-xylilidenbisindenylzirconium dichloride; rac-Me₂SiInd₂ZrCl₂ - dimethylsilyl-bis(indenyl) zirconium dichloride and Me₂Si(4-Ph-2-Et-Ind)₂ZrCl₂ (rac: meso=1:2) - dimethylsilyl(4-phenyl-2-ethyl-indenyl) zirconium dichloride were prepared as described in [10-12].

Modified Ti/Mg catalyst containing 2,3% Ti in combination with AlEt₃ was used. Dibutylphthalate and propyltrimethoxisilane (PrTMS) were used as internal and external donors [13].

Propylene was polymerized in a liquid monomer medium at a pressure exceeding that of the propylene saturated vapor pressure by original method described in [11, 14]. PP characterization was described in [11, 13].

**Results and discussion**

All complexes studied for iso-PP synthesis were chiral ansa-metallocenes with C₂ symmetry having indenyl ligands. This type of symmetry is favorable for the isospecific polymerization of propylene. However exists the high difference in propylene polymerization behavior between metallocenes with unsubstituted (MC-1-MC-5) and substituted ligands (MC-6).