Control of Ultrahigh Molecular Weight Polypropene Microstructures via Asymmetric "Dual-Side" Catalysts

*C. Cobzaru, B. Rieger**

Summary: Asymmetric *ansa*-metallocene catalysts based on fluorenyl and specifically substituted indenyl ligands allow a continuous change of the properties of isotactic polypropene and thus generate a new portfolio of polypropene materials, ranging from excellent thermoplastic elastic to stiff plastomers. Controlling the length of the crystallizable, isotactic segments by means of isolated stereoerrors introduced into the isotactic enchainment made this possible. The combination of synthetic, structural and polymerization studies of a series of *ansa*-asymmetric catalysts has provided much insight into the effectiveness of the substitution patterns on tailoring the polymer microstructures. Ligand substitution, temperature and concentration of the propene monomer in the reaction medium can influence stereoerrors distribution, and therefore the crystallinity of the materials. Ultrahigh molecular weight polypropenes with tacticities varying in a broad range (20% < [mmmm] < 80%) are available via (Ind-Flu)-based asymmetric hafnocenes.

Keywords: catalysis; elastomers; microstructures; plastomers; poly(propene)

Introduction

Chien et al.[1] succeeded in the early 90s in the production of the first uniform elastomeric polypropene using an asymmetric titanium catalyst ([MeHC(Me_4Cp)(Ind)]-$TiCl_2$). The elastic properties were assumed to arise from the two different coordination sides leading to a polymer microstructure of atactic and isotactic blocks forming a physically crosslinked network. Despite its good elastic properties Chien's polypropenes lacked high enough molecular weights to be interesting for industrial applications. In order to remedy this insufficiency, we[2] developed a new catalysts family which is based on a fluorenyl and indenyl unit. However, first experiments using *rac*-[1-(9-η^5-fluorenyl)-2-(η^5-indenyl)ethane]zirconium dichlorides revealed, similarly to the results of Chien, a strong tendency toward lower molecular weights. Newly, our group successfully managed by introducing a cyclopentyl substituent into the indenyl fragment the production of the first high molecular weight, isotactic polypropene which evidenced to own excellent elastomeric properties[3]. To determine the origin of the enhanced polymerization performance of (*rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta- 2-methyl-1-η^5-indenyl)ethane]-zirconium dichloride) (**1**, Figure 1) great attention was paid in the present work to elucidate the role of the substituents on the indenyl ligand.

The preparation of a series of asymmetric zirconocenes bearing various substituents but similar bridging units and their use in standard polymerization experiments intend to acquire more detailed information how the divergent substitution patterns influence the polymerization behavior of the catalysts. Therewith it is expected to

Inorganic Chemistry II, Department of Material Science and Catalysis, University of Ulm, D-89069, Germany
Phone: +49-731-502-3038; fax: +49-731-502-3039
E-mail: bernhard.rieger@uni-ulm.de

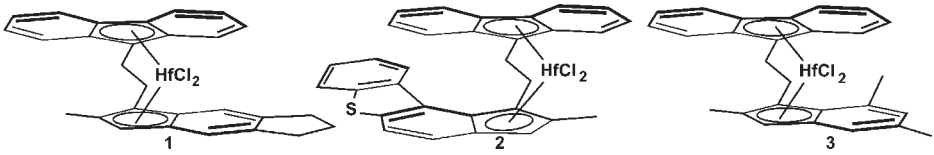

Figure 1.
Hafnium *ansa*-metallocene catalysts 1-3.

develop a construction kit that possibly enables to anticipate different fields of polypropene material properties, especially for the new ultrahigh molecular weight species. The finding that the *5,6*-cyclopentyl group represents a key success for the production of high molecular weight, elastomeric polypropene directed our further interest to a *6,7*-substitution bearing sulphur atoms in the indenyl moiety[4] (**2**, Fig. 2). An optimum study of the different substitution patterns of the ligand framework could be completed with the [1-(9-η^5-fluorenyl)-2-(2,5,7-trimethyl-indenyl)ethane]-hafnium dichloride[5] (**3**, Figure 3) which combines the positions of the ligand substitutions from both previously mentioned catalysts, **1** and **2**.

Experimental Section

General Procedure

The synthesis of the C_1-symmetric catalysts, **1**, **2** and **3** were reported previously [3–5].

Polymerization reactions in liquid propene were performed in a 500 ml Büchi autoclave at constant temperature. Propene was condensed at −10 °C up to the desired volume in the autoclave. Subsequently, at the desired polymerization temperature, the catalyst and cocatalyst solutions were injected into the autoclave via a pressure buret. The polymerization reactions were quenched with MeOH, and the polymer product was dissolved in toluene and then precipitated by pouring it into an excess of MeOH. The product was filtered off, washed with methanol and dried in vacuum at 60 °C overnight.

Polymer Analysis

^{13}C NMR spectra were recorded on a Bruker AMX 500 spectrometer ($C_2D_2Cl_4$, 90 °C) and analysed by the known methods. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (Waters, alliance GPC 2000, 145 °C in 1,2,4-trichlorobenzene) universal to polystyrene and relative to polypropene standards.

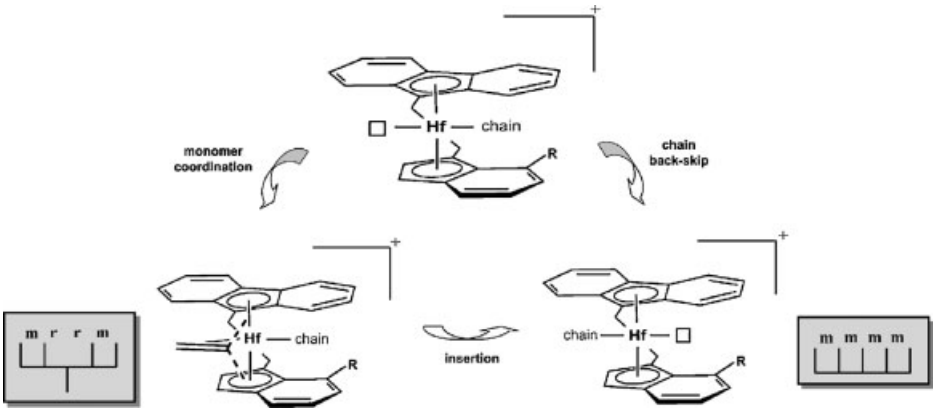

Figure 2.
Monomer coordination and chain back skip during the polymer chain growth.

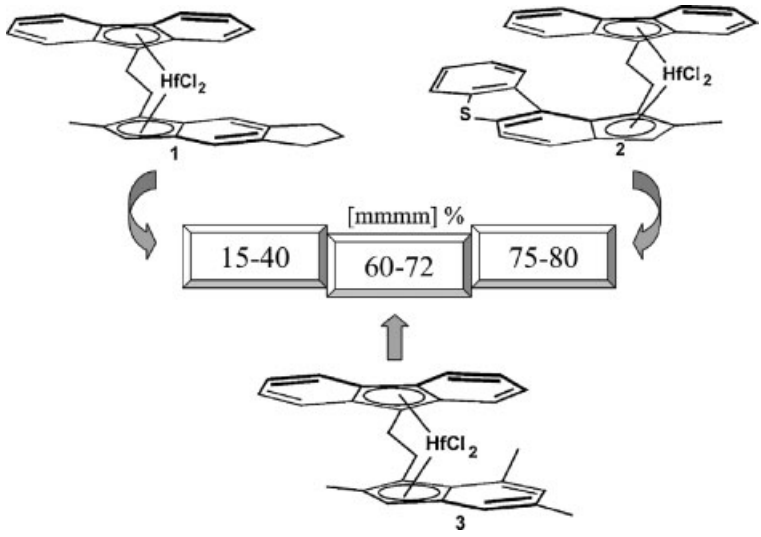

Figure 3.
Tacticity ranges of the polypropenes obtained with different indenyl substitutions.

Mechanical Testing

To test the mechanical properties of the samples stretching experiments have been performed on a commercial stretching device (Zwick 1445). Samples with a thickness of 1 mm were punched using a dog-bone puncher with nominal dimensions of 20 mm in length and 5 mm in width. The thickness of the samples was estimated using a micrometer screw. The initial length of the sample has been measured by the optical detection system of the used stretching device. Stretching experiments were performed with a stretching rate of 4 mm/min until the samples failed.

Results and Discussion

Temperature dependency of the different catalysts was investigated in propene polymerizations, after *in situ* activation with trityl tetrakis pentafluorotetraphenyl borate ($[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$), in order to obtain polypropenes with tailored isotacticities (Table 1).

Large differences were observed in the polymerization behavior of the examined catalysts. The highest polymer activities could be obtained with the ethylene bridged metallocenes **3**/borate (at $T_p = 40\,^{\circ}C$ up to 3.2×10^5 kg of PP (mol cat $\times$ h)$^{-1}$). Moreover, it was found that the rate of catalyst activation for this type of asymmetric zirconocenes raises with increasing temperature. Although containing a heteroatom, catalyst **2** shows activities nearly comparable to the ones of the catalyst **1**. Obviously, the sulphur function does not deactivate the catalytically active species via an intramolecular mechanism. Instead it might take part in intermolecular coordination processes that influence chain growth. This hypothesis could explain the difference between the activities (up to 20 times higher) achieved with **2** and **3**.

The [mmmm]-pentad concentration of the polymers, produced with different C_1-symmetric metallocene catalysts, varies over a broad range (17% to 78%, Table 1). With *5,6*-cyclopentyl substitution of the indenyl fragment, as well with the *6,7* —and *5,7* —substitutions, an increase of the isotacticity is observed at higher polymerization temperatures. This effect can be explained by a favored back-skip of the growing polymer chain [3,6] before a new monomer coordinates to the aspecific side of the complexes induced by the additional steric hindrance of the substituents (Fig. 2).

Table 1.
Polymerization results of propene with asymmetric complexes 1-3/borate

Entry	Catalyst	T_p (°C)	Activity kg PP(mol cat.)$^{-1}$h^{-1}	[mmmm] (%)	M_w (g/mol)
1	**1**	0	6000	17	4900000
2	**1**	20	23000	24	1600000
3	**1**	50	50000	34	700000
4	**2**	0	5300	75	1500000
5	**2**	30	15900	78	250000
6	**3**	10	39000	63	960000
7	**3**	40	320000	72	300000

Remarkably, the catalyst **3**, which bears on the indenyl ligand (*5,7*-position) a combination of the other two substitutions (*5,6*- and *6,7*-positions), leads to polymers with tacticities that fill the gap between the tacticities obtained with the catalysts **1** and **2** (Fig. 3). Thus, a controlled stereoerror formation along the polymer chain via indenyl substitutions is made possible with these catalysts frameworks. Varying the catalyst architecture results in a continuous change of the polymer crystallinity and thus of the material mechanical properties from elastomeric low isotactic to plastomeric isotactic polypropenes (Fig. 4).

Apart high catalytic activity and a wide range of polymer tacticity, notable is the strong tendency toward high and ultra-high molecular weight of the polymers obtained with each of the substituted catalysts (Table 1). Major contributions in this regard belong to the hafnium metal center, known for increased molecular weigths in comparison to its zirconium analog[7], as well as to the positions of the substituents on the indenyl ligand of (Ind-Flu)-type dual-side asymmetric catalysts. These substitutions effectively suppress the chain end epimerization process [8] (source of stereo-errors in C_2 — symmetric catalysts) and hinder at the same time a subsequent chain termination reaction, leading to higher molecular weight products.

As expected, the molecular weights of the polypropenes can be significantly increased by lowering the polymerization temperature [9]. This effect indicates the ability of these catalysts in producing various temperature-controlled polymer microstructures, beside the above mentioned control via catalyst framework.

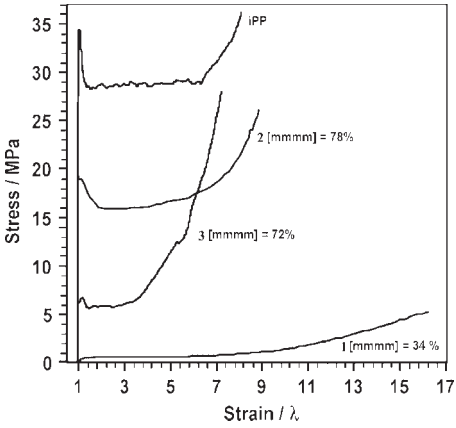

Figure 4.
Stress-strain curves[a] of polypropenes prepared using different catalysts.

[a] $\lambda = (L_f - L_i)/L_i$

Mechanical Behavior

To study the influence of the morphology on the macroscopic mechanical behavior of the polypropenes prepared by different catalysts, melt pressed samples are subjected to uniaxial stretching until they fail. The stress-strain curves of the resulting polypropenes with increasing amount of tacticity are compared with the deformation characteristics of the highly isotactic PP (98% [mmmm], Fig. 4). As long as the [mmmm] content is around 35% (**1**, Fig. 4) the observed stress-strain curves are characteristic for elastomeric materials[10]. Maximum deformation ratios up to 17 times the original length have been detected for this sample. The curves display no yield point, but a broad elastic plateau

with slowly increasing stress up to 5 MPa. This profile results from the formation of a crystalline network, which reinforces the amorphous phase. Yet, due to low tacticity, the sample does not contain sufficient amounts of long crystallizable sequences which can form stable lamellar super structures, such as spherulites. Therefore this polymer possesses high elasticity.

When the [mmmm] content increases further (**3**, 72% [mmmm], Fig. 4) the stress increases up to 7 MPa pointing out reduced elasticity. The decrease in elasticity is accompanied by a decrease in elongation to fracture. This refers to an increase in crosslinking. No yielding zone characteristic for the deformation of thermoplastic material occurs, but the stress increases with increasing deformation ratio. This indicates a change in deformation behavior from elastomeric to plastomeric.

If the [mmmm] content rises above 75% (**2**, Fig. 4) the maximum elongation drops to values around $\lambda = 9$ and a relative pronounced yield point appears for this sample. Unlike stiff, highly isotactic polypropenes (iPP), these materials combine flexibility with a degree of crystallinity high enough to display mechanical behavior similar to plastomers. Nevertheless, they show different deformation behavior than polymers produced with **3**, leading to more thermoplastic materials, fact also indicated by the higher stress at yield point (up to 3 times). Different deformation behavior found for samples with comparable tacticities (**2** and **3**) can be explained by higher amounts of crystalline aggregates[11], formed within the sample obtained with **3**, which cause differention in the polymer morphologies.

Conclusion

The polymerization behavior of a series of ethylene bridged asymmetric zirconocene dichlorides is compared and information regarding the influence of the ligand substitution pattern on the polypropene characteristics were presented. It is shown that changing the catalyst architecture enables a detailed tailoring of homopolypropene plastomers and elastomers. This directive in metallocene chemistry is attributed to the new family of ''dual-side'' complexes combining an isoselective side with a less selective side leading predominantly to single stereoerrors within one well defined species. Asymmetric metallocenes serve as a precise tool to control the amount of stereoerrors along an isotactic polymer chain allowing to adjust polymers of variable crystallinity with material properties from flexible, semicrystalline to excellent thermoplastic elastic.

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