

Differences in Activities and Polymer Microstructures by Supporting Metallocene Catalysts¹

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Abstract— C_s -symmetric catalysts of the type $[(RPh)_2C(Cp)(2,7-t-Bu_2Flu)]ZrCl_2$ are investigated in the syndiospecific polymerization of propene under four sets of conditions: in toluene solution, bulk, toluene slurry, and gas phase. Generally, highly syndiotactic polypropene ($rrrr > 99\%$) with high molar masses ($M\eta > 10^6$ g/mol⁻¹) and high melting temperatures (T_m up to 153°C) are produced. The highest activities are obtained in the solution process (11000 kg_{PP}/(mol_{Zr} h mol_{propene}/l)), since physical and kinetic limitations such as diffusion and sorption occur when the heterogeneous systems are applied. Comparisons between relevant polymer properties show that the polymerization performance is only slightly influenced by the support. In gas phase polymerizations, the observed activities are about 20 times lower than in solution. The molar masses of the produced polymers are mainly influenced by the monomer concentration and not by the support.

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Polypropene (PP) is one of the most important plastics nowadays. Its properties depend largely on its microstructure, molecular weight, and molecular weight distribution and can be tuned over a wide range. The most common commercial form of PP is isotactic PP, which features good stiffness, high melting temperature and tensile strength, good chemical resistance, and excellent moisture barrier properties [1]. Polypropene and its copolymers are, for example, used in packaging (films, containers, etc.), domestic appliances, and automotive applications [2, 3]. Syndiotactic polypropene is now also available by metallocene catalysts.

The first suitable sPP catalyst was synthesized by Ewen and Razavi in 1988 [3]. The two coordination sites are enantiotropic, resulting in alternating enantiofacial orientations of the successive olefin insertions. Several modifications of the original catalyst design have been reported in the literature [4]. By modifying the bridge (e.g., Ph_2C), researchers have obtained higher molar masses of the produced polymers [5], whereas the syndiotacticity has been increased by expansion of the fluorenyl ligand framework [6]. A substitution in the 2 and 7 positions with tertbutyl groups has turned out to be very promising [7, 8]. The influence of a modified Ph_2C bridge, which is substituted with electron withdrawing alkyl or alkoxy groups, on syndiotacticity, catalyst activity, and molar mass will be investigated in the present study.

Due to a totally new quality profile with some interesting features such as high transparency, high γ -resistance, high impact resistance, and a silky touch, sPP opens up niche markets, e.g., in the area of medical and

cosmetic applications [9]. However, for an efficient application of metallocene catalysts in modern polymerization processes (drop-in technology) they have to be supported on carrier materials [10–12]. By applying these particle-forming processes, it is possible to prevent the polymer particles from sticking together and to the walls of the reactor (reactor fouling), because the catalyst serves as a template for polymer particle growth [13, 14]. Among the variety of carriers, silica appeared to be a reasonable support because it possesses high surface area and porosity, has good mechanical properties, and is stable and inert.

The most common method of applying metallocenes to heterogeneous polymerizations is to support the complexes on solids such as silica, alumina, magnesium dichloride, or other supports [15–18]. There are different routes to immobilize catalysts, for example (Fig. 1).

(A) Initial adsorption of MAO to the support followed by adsorption of the metallocene.

(B) Direct adsorption of the metallocene/MAO adduct on the support.

(C) Direct adsorption of the metallocene on the carrier surface leading to physisorption or chemisorption of the metallocene (direct heterogenization).

(D) Covalent bonding of the metallocene by its ligand environment to the carrier followed by activation with external MAO.

The supporting procedures can have different effects of varying severity on the polymerization characteristics of the metallocenes. Method C can afford polymers with higher molecular masses than those produced with the corresponding homogeneous counter-

¹ The text was submitted by the author in English.

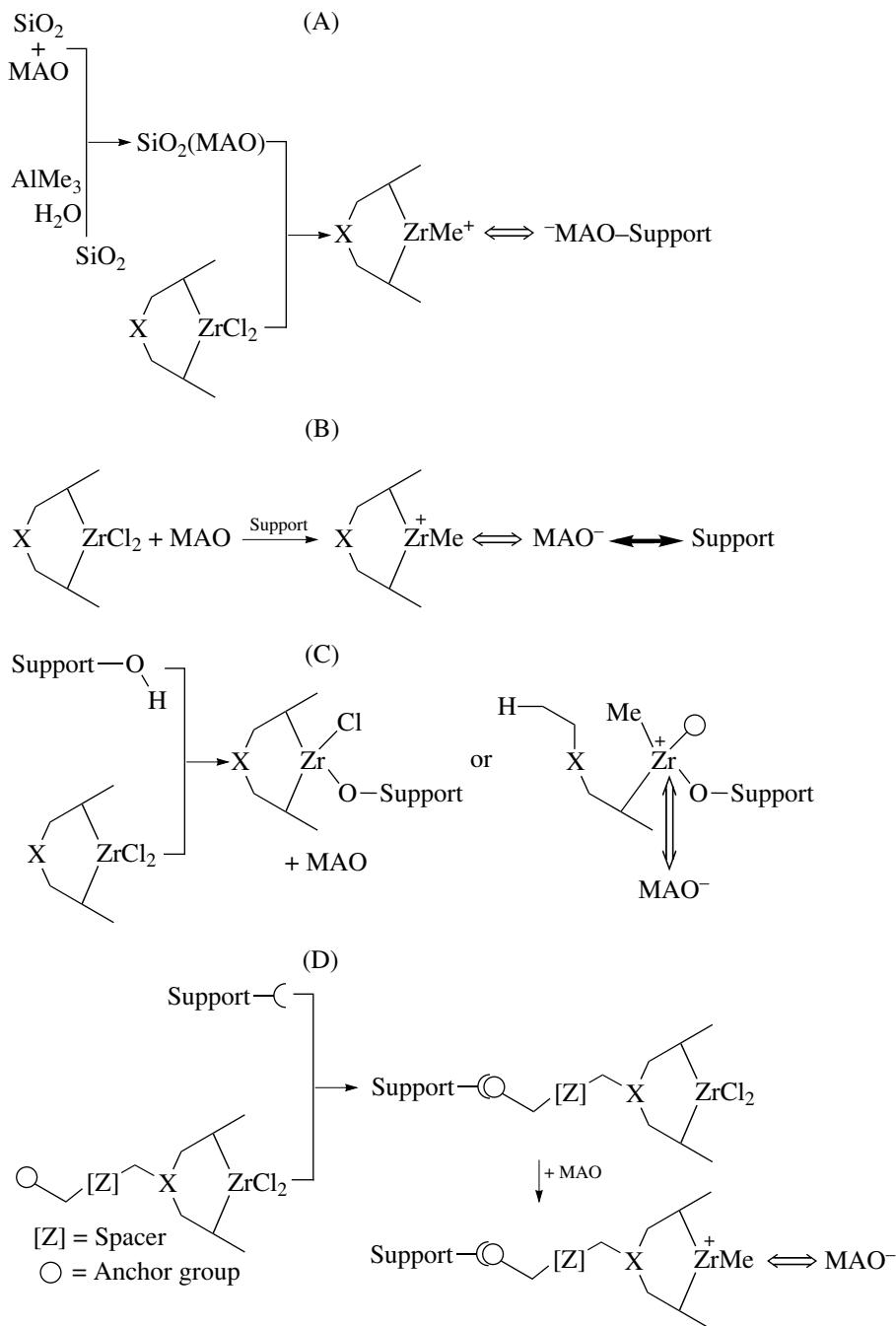


Fig. 1. Different methods to support metallocene/MAO catalysts on silica support.

parts [19], but can also (which is likely also true of method B) change the metallocene structure and, therefore, its stereospecificity due to interaction with surface electron donor groups, such as silanol groups [20, 21]. So the nature of the tacticity changes if the syndiotactic working metallocene $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$ is heterogenized first on a support in the described way. The *mmmm* pentads, measured by ^{13}C NMR, increase from 0.4 to 96%, representing an isotactic polymer.

Difficulties can also arise with method D: a variant of this procedure is the synthesis of the covalently attached metallocene directly on the surface of the support [22]. However, the anchor groups on which the synthesis takes place are not always chemically uniform (vicinal and geminal silanol groups).

Indirect heterogenization (method A) is the most promising procedure, as the single-site character, the stereospecificity, and many other polymerization characteristics of metallocenes are only, if at all, slightly

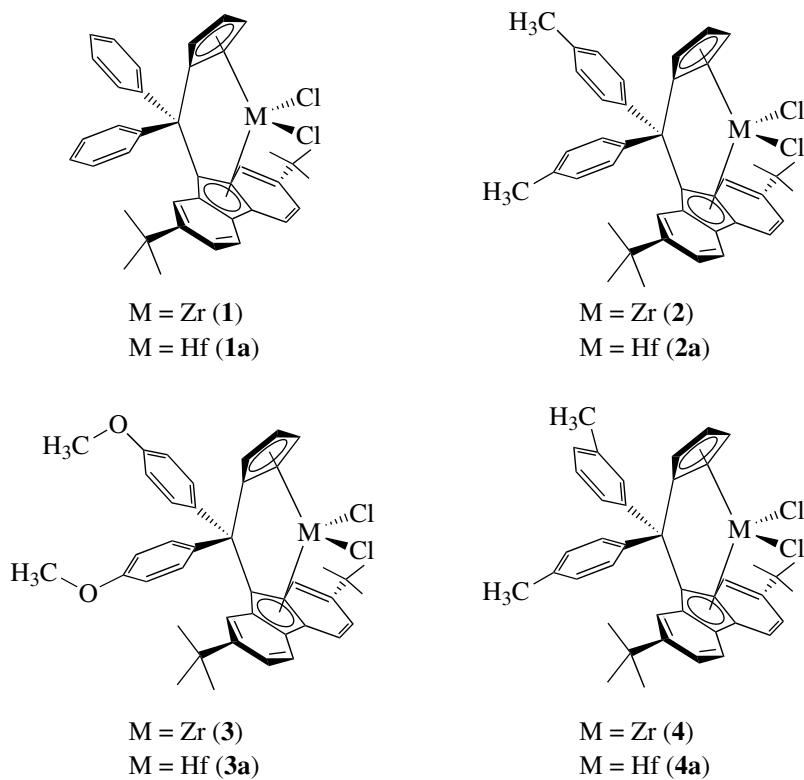


Fig. 2. Structures of synthesized C_3 -symmetric zirconocenes and hafnocenes for the syndiospecific polymerization of propene.

altered by the support process [23]. It is thought that the MAO on the silica is bound by reactions with the OH group on the surface or by loosed ionic interactions.

By adding the metallocene, a complexation takes place, forming ionic interactions as well, similar to those found in the activation of metallocenes with MAO in a solvent. It could be shown that the metallocene on the silica surface cannot be leached by triisobutylaluminium (TIBA) in high amounts. But if the supported metallocene is treated with external MAO, a detachment takes place and great quantities of the activated metallocene are observed in the solution [24]. In most cases, the activity of supported metallocene catalysts and the tacticities of the obtained polypropenes are less, compared with homogeneous catalysts. Therefore we synthesized new highly syndiotactic working zirconocenes [25].

EXPERIMENTAL

Material: All procedures were carried out under argon using Schlenk techniques. MAO and MAO/SiO₂ were purchased from Crompton, propene from Messer-Griesheim, and argon from Gerling, Holz Corp. The gases, as well as toluene, were purified by passage through columns filled with Cu catalyst (BASF R3-11) and a molecular sieve of 10 Å. Argon was dried by passage through columns filled with Al₂O₃ and molecular sieve of 4 Å. The synthesis of the zirconocenes 1–4

and hafnocenes 1a–4a (Fig. 2) were performed according to the general procedure reported in [7–9].

Polymerizations in slurry and solution: The experiments were carried out in 0.5 l Büchi Type I autoclave equipped with an additional internal cooling system. Monomer feed of the gaseous monomers was maintained with a Peteric 3002 pressure flow controller. The reaction was monitored by a Büchi Data System bds 488. The polymerization conditions with supported zirconocene catalysts for the syndiospecific polymerization of propene are summarized below:

Reaction volume—100 ml
 Solvent—Toluene, hexane
 Monomer—Propene
 Monomer concentration—0.06–6.2 mol/l
 Polymerization temperature—0–60°C
 Catalyst concentration— 2.85×10^{-5} mol/l
 Cocatalyst—TIBA
 TIBA : Zr ratio—30 : 1000
 Al(MAO) : Zr ratio—30 : 1000

For standard experiments, the reactor evacuated at 95°C for 1 h and charged subsequently with 100 ml toluene, 100 mg TIBA. Propene was added afterwards. Polymerization was started by addition of the metallocene catalyst. During the reaction, the total pressure

Activities and syndiotacticities of polypropenes prepared by the catalysts **1–4** and the polymerization in solution, slurry, bulk and gas phase at 30°C

Catalyst	Solution	Slurry	Bulk	Gas phase
1	2800 (94)	1800 (93)	990 (92)	1100 (78)
2	5200 (93)	3100 (92)	1100 (94)	940 (82)
3	7000 (92)	2100 (90)	— —	830 (82)
4	6900 (84)	— —	270 (76)	— —

Note: Activity: $\text{kg}_{\text{PP}}/(\text{mol}_{\text{Zr}} \text{ h mol}_{\text{propene}}/\text{L propene})$; $rrrr$ pentad in % (values in parentheses).

was kept constant by supplying propene. Polymerization was quenched by injection of 5 ml of ethanol or 5 ml of a saturated solution of 2,6-di-*tert*-butyl-4-methylphenol in ethanol and the polymer solution was stirred overnight with dilute hydrochloric acid followed by neutralization with NaHCO_3 , washing with water, evaporation of toluene, and drying.

Polymerization in gas phase: Polymerizations were carried out in a 2 l Büchi type II autoclave equipped with a helical stirrer. Monomer feed of propene was maintained with a Brooks TR 5850 mass flow controller (500 ml/min); the reaction was controlled and monitored using a Simatic S5 from Siemens. The reactor was filled with 380 g pre-dried NaCl and evacuated at 95°C for 1.5 h with stirring (100 rpm). The reactor bed

medium was treated with a toluenic solution of TIBA (0.6 mol/l) 30 min prior to introduction of the supported metallocene. The catalyst was prepared externally: the required amount of metallocene in toluene was injected into a toluenic suspension of MAO/SiO_2 (0.1 g/ml). The resulting suspension was allowed to mix for 10 min and was then introduced into the reactor with a syringe. After introduction of the catalyst, the reactor was evacuated for 10 min with stirring (300 rpm) in order to evaporate the surplus toluene. The reaction was started by quick pressurization (ca. 20 s) of the reactor with the monomer gases and starting the stirrer (200 rpm). During polymerization, the total pressure was kept constant by supplying propene at fixed flux ratios. The reaction was terminated by depressurization followed by short evaluation of the reactor and finally injection of 5 ml of ethanol or 5 ml of a saturated solution of 2,6-di-*tert*-butyl-4-methyl-phenol in ethanol.

RESULTS AND DISCUSSION

The activities of the propene polymerization and the tacticities of the obtained polypropenes were shown to depend on the catalyst structure as well as on the polymerization process (table).

Generally, the observed activities yielded with these catalysts are among the highest values ever reported for the production of syndiotactic polypropene [26]. Particularly, employing the catalysts in the slurry procedure, excellent activities are yielded compared to other studies [27] (3100 $\text{kg}_{\text{PP}}/(\text{mol}_{\text{Zr}} \text{ h mol}_{\text{propene}}/\text{l})$ at 30°C with catalyst **2**). By supporting the metallocene, an exceptionally small decrease in catalyst activity is observed.

Figure 3 shows the dependence of the polymerization process and polymerization temperature on the catalyst activity for catalyst **2**. It is worth mentioning that

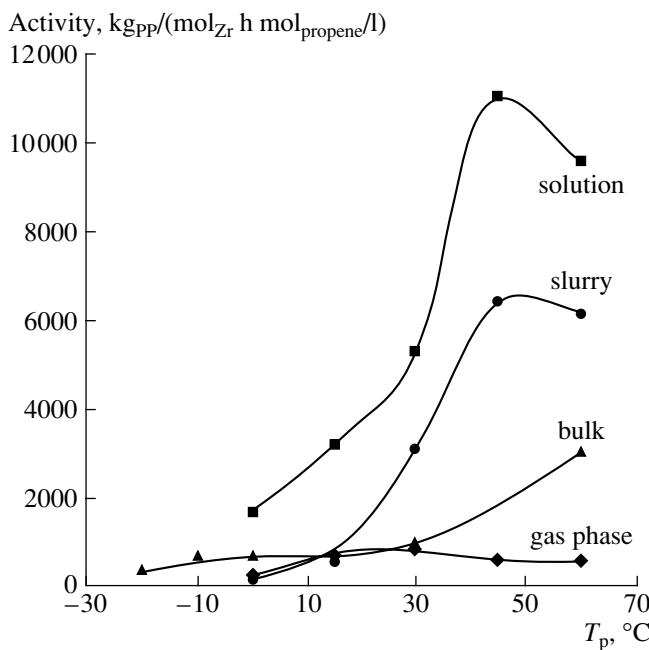


Fig. 3. Activity of the syndiotactic propene polymerization with catalyst **2** by different polymerization temperatures.

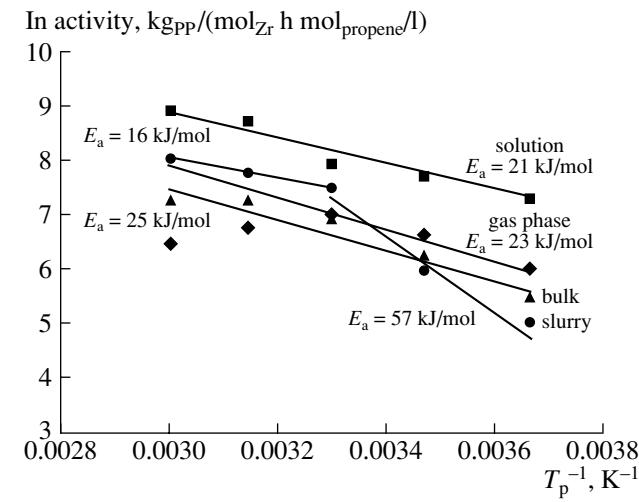


Fig. 4. Arrhenius plot for the different propene polymerization processes using catalyst **1**.

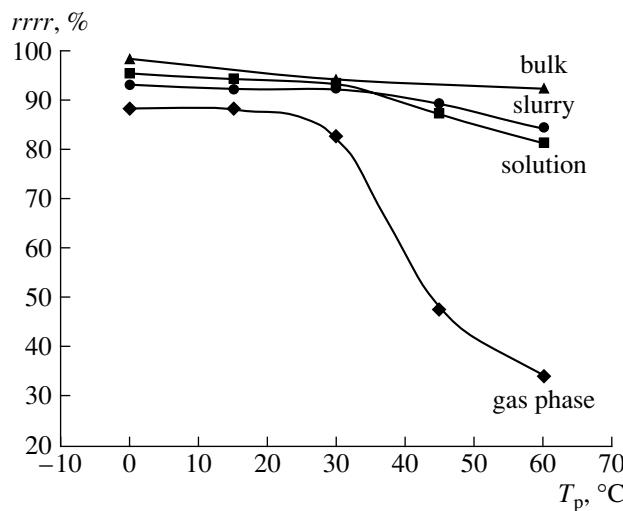


Fig. 5. *rrrr*-Pentad for syndiotactic polypropenes synthesized by different polymerization processes with catalyst **2**.

due to a better comparison of the processes, the catalyst activities reported in this paper are related to the monomer concentration. In the case of gas phase polymerizations, the highest activity was attained at 30°C, decreasing at higher temperatures. On the other hand, employing the other processes, catalyst activity increases from -20 to 45°C without showing deactivation of the catalytic species for the bulk process. The slurry process shows the best activities. Due to avoidance of bimolecular deactivation, higher stability is expected for supported catalysts. Therefore, the course of catalyst activity in the gas phase process seems to be surprising at first sight. Nevertheless, it can be explained by monomer sorption effects. The polymerization of olefins over solid catalysts is a complex reaction, involving both physical and kinetic effects [28, 29]. Monomer sorption plays a key role in determining the local monomer concentration at the active site [30]. The extent of sorption decreases as polymerization temperature increases. For this reason, decreased activity in gas phase polymerizations could be traced to the lower monomer concentration at the active site, recalling that only the bulk concentration of propene was kept constant in this procedure. Obviously, methyl substitution in the Ph₂C-bridge (catalyst **2**) leads to higher activities. However, the thermal stability of complex **2** is reduced, since the maximum catalyst activity is observed at 45°C. Activities of the supported metallocene are approximately constant for higher temperatures. Complexes **3** and **4** were shown to behave similar to complex **2**.

By plotting the logarithm of the activity versus $1/T$, the activation energies (E_a) can be calculated (Fig. 4).

For all catalysts values, about 20–25 kJ/mol were detected. Catalyst **1** gives similar values for the solution, bulk and gas phase procedure. Only the calculation of E_a for the slurry process is different. E_a was quantified to be nearly two times as large at tempera-

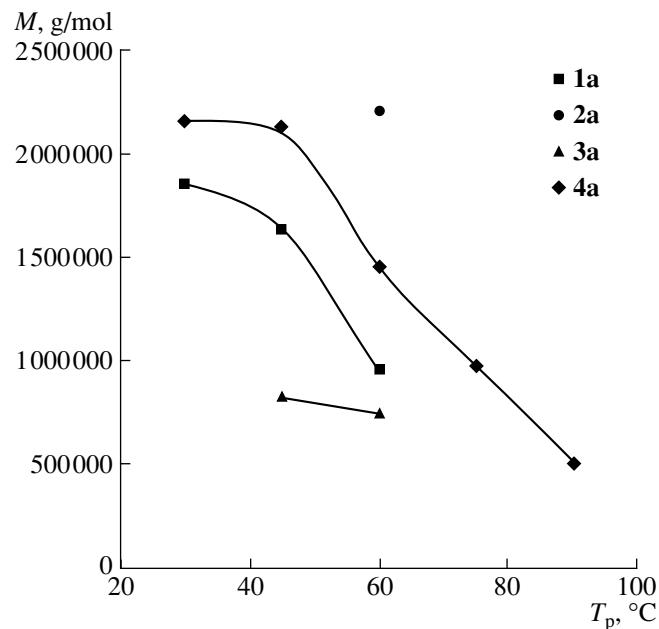


Fig. 6. Molar masses of syndiotactic polypropenes using different C_8 -symmetric hafnocenes.

tures between 0 and 30°C. In the range between 30 and 60°C, it was determined to be about 16 kJ/mol. This behavior is supposed to be traced to diffusion- and pre-polymerization effects [28].

Highly stereoregular syndiotactic polypropene is obtained with the catalyst systems used in this study reaching stereoregularities of $rrrr = 99\%$ and melting temperatures of 153°C (see Fig. 5 and table).

Analysis of the polymers by ¹³C NMR spectrum of the polymers produced in the different processes confirms the presence of mm stereodefects as the predominant source of stereo irregularity in the polymer microstructure. This is in accordance with an enantiomeric site control mechanism [31].

The microstructure of the produced polypropenes strongly depends on the polymerization temperature as well as on the applied polymerization process as shown in Fig. 5 for catalyst **2**. The highest degree of stereoselectivity, i.e., the highest value for the *rrrr* pentad, is obtained for the bulk polymerization. At 60°C, the solution process with the homogeneous catalyst is much less syndiotactic than the bulk and slurry process with the supported catalyst. This decline is more distinctive regarding the gas phase process. For this process, the syndiotactic pentad content decreases from 88% at a polymerization temperature of 0°C to 34% at 60°C. Thus, for each process, the highest stereoregularity is obtained for polymers produced at low polymerization temperatures, which is in accordance with an enantiomeric site control mechanism. The dependence of the polymerization process on the stereoregularity can be interpreted by the role of the monomer concentration. Polymerizing in liquid propene, the monomer

concentration is about 9 times higher than in the case of applying process solutions or slurry. In gas phase polymerizations, the monomer concentration constitutes only 2% of that. This decrease in monomer concentration results in an increase of stereodefects, leading to a lower stereoselectivity.

The molar masses, determined by viscosimetry, cover a wide scope, from 59000 to 1780000 g/mol. Apparently, the structure of the metallocene has no great influence on the molar mass of the produced polypropylenes. For every process, the highest molar masses are obtained for polymers produced at low polymerization temperatures. Supported catalysts in the bulk process give by 0°C about 30% higher molar masses than the solution process with the homogeneous catalyst. The monomer concentration plays here again the main role.

Even higher molecular masses can be obtained using the analogous hafnium complexes (**1a–4a**) instead of zirconium. At a polymerization temperature of 25°C in the solution process, molar masses of 2300000 are reached (Fig. 6).

Hafnocene **2a** and **4a** give the highest molar masses. With the increasing polymerization temperature, they decrease to 500000 by 90°C. The hafnocenes are very stable even at higher polymerization temperatures.

CONCLUSIONS

Supporting of C_s -symmetric catalysts in which the fluorenyl ligand is substituted in 2,7-position, it is possible to produce highly syndiotactic polypropene. As the substitution of the bridge for the different metallocenes does not significantly influence the polymerization performance, the effects observed in propene polymerization were found to be strongly dependent on the applied polymerization process and temperature. The bulk process in liquid propene with the supported zirconocenes offers high activities with very good syndiotacticities compared with the homogeneous catalyst in the solution process.

It could be shown that the polymerization behavior is not so much the result of the supporting itself, as an effect of the monomer concentration. Therefore, an efficient application of syndiotactic working catalysts in liquid propene or suspension is possible in existing polymerization processes (drop-in technology).

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