A Hyperbranched Polysilane-Based, Borane Cocatalyst for the Metallocene-Catalyzed Polymerization of Propylene

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ABSTRACT: The synthesis of a vinyl-terminated, hyperbranched polysilane and the additional hydroboration with bis(pentafluorophenyl) borohydride are reported. Quantitative transformation was proved by ^{1}H NMR and FT-IR analysis. The polymeric borane was tested as cocatalyst in the metallocene-catalyzed polymerization of propylene. The corresponding catalyst system comprising *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta-2-methyl-1-η^5-indenyl)ethane]zirconocene dichloride and the polymeric borane was activated in situ in the presence of triisobutylaluminum (TIBA). Polymerizations were performed at temperatures of 30 and 50 °C with a propylene concentration of 3 mol/L in toluene solution using various cocatalyst: catalyst ratios (10:1, 50:1, and 100:1). This polymer-supported catalyst system produces polypropylenes with excellent activities and good molecular weights. These results were compared with an additional set of polymerization experiments using molecular dispersed $B(C_6F_5)_3$ as cocatalyst, resulting in significantly reduced polymerization activities. This indicates a hindered catalyst mobility inside the hyperbranched cocatalyst matrix, leading to a higher concentration of active species within the hyperbranched nanostructure.

Introduction

Activation of metallocene catalysts for α-olefin polymerizations[1,2] concentrates on the formation of the active species via borane or borate cocatalysts introducing weakly or noncoordinating borate counterions.[3−5] Especially the application of borate cocatalysts enhances the active site concentration and helps to improve molecular weights and therefore material properties significantly.[6−9] For commercialization, these homogeneous systems have to be adapted to existing industrial processes, which require a control of the polymer morphology toward an adjustable particle size.[10] Conventional supporting materials in commercial processes are silica or aluminum oxides that give excellent particle morphologies with $TiCl_3$-based ZN catalysts.[11,12] However, these strategies have disadvantages, particularly for the support of asymmetric, dual-side metallocenes which produce high-performance thermoplastic polypropylene elastomers.[28,30] The reason is based on the influence of the supporting material surface on the specific stereoerror formation mechanism of these new polymerization catalysts. In this context it is obvious to explore new anchoring processes on apolar organic substrates that have less interaction with the catalyst species.[13−15] In recent literature an interesting approach from Mager et al.[16] is reported focusing on modified dendrimers that comprise borate functionalities which activate metallocene dialkyl species. However, the perfect nature of such dendrimers requires a rather difficult synthesis. We focus here on easily accessible hyperbranched polysilanes,[29] converting the remaining vinyl end groups into perfluorinated phenylboranes by a simple hydroboration step. This approach guarantees the absence of any polymerization-inhibiting inorganic salts that would be present in the respective polyborate activators. A major advantage of hyperbranched polymers is the distribution of functional end groups throughout their globular structure, in contrast to perfectly branched dendrimers.[17,18] This should also lead to an encapsulation of the active sites inside the polymeric matrix,[19] whereas catalysts immobilized with dendrimeric systems are exclusively located on the particle surface.[20]

Results and Discussion

Synthesis of the Polysilane Cocatalyst. The catalytic hydrosilylation reaction of the AB_2 monomer methyldiundecenylsilane **1** (Figure 1) affords a hyperbranched polycarbosilane **2** in up to 99% yield using bis(trioctylbenzylammonium) tetranitritoplatinate as catalyst precursor.[29] This polyaddition leads to hyperbranched macromolecules with one terminal Si−H group and $(n + 1)$ vinyl end groups unreacted throughout the polymer structure[29] ($n =$ degree of polymerization). The resulting polycarbosilane showed an increased chemical and thermal stability compared to that of the monomer. The terminal vinyl groups were converted into the boranes **4** by a direct and clean hydroboration reaction with bis(pentafluorophenyl) borohydride **3**, which was generated by treatment of bromopentafluorobenzene-1 with *n*-BuLi and subsequent BCl_3 addition at −70 °C (Figure 2). Chloride/hydride exchange proceeded via the addition of $Me_2Si(H)Cl$ at 0 °C.[31] The hydroboration reaction was monitored by FT-IR- and ^{1}H NMR spectroscopy which revealed complete conversion of all vinyl end groups into borane functions.

Catalyst Activation. The *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cylopenta-2-methyl-1-η^5-indenyl)ethane]zirconocene dichloride **5** (Figure 3) precursor[21] was treated in situ with excess of triisobutylaluminum (TIBA, ratio: 100:1) and subsequently reacted with the polymeric borane **4** to give the active catalyst species **6** in an

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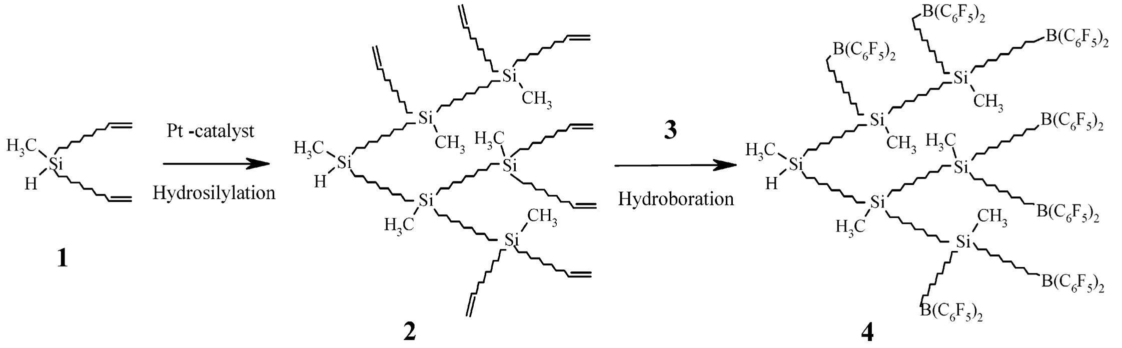

Figure 1. Synthesis of poly(methyldiundecenylsilane) **2** from methyldiundecenylsilane **1** and subsequent hydroboration with bis(pentafluorophenyl) borohydride **3** to the cocatalyst **4**.

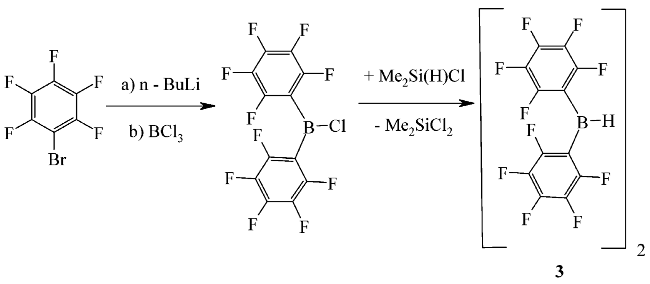

Figure 2. Synthesis of bis(pentafluorophenyl) borohydride **3**.

equilibrium. The results of the polymerization experiments were additionally referred to runs in homogeneous solution using the respective zirconocene compounds and TIBA/$B(C_6F_5)_3$.[22] This allows a comparison of a hyperbranched, polymeric system and a homogeneously dissolved, molecular cocatalyst comprising a similar electronic structure.

Propylene Polymerization Experiments. The polymerizations were performed in an autoclave with constant propylene concentrations of 3.00 mol/L at temperatures of 30 °C (5 bar) and 50 °C (6.5 bar). The cocatalyst:catalyst ratios were 10:1, 50:1, and 100:1. Injection of the preactivated catalyst/cocatalyst solution via a pressure buret started the polymerizations. Both borane cocatalysts were suitable activators for the polymerization of propylene with **5**/TIBA (Table 1).

Activities. The observed polymerization activities[23] reveal a broad variation depending on temperature and cocatalyst/catalyst ratio, independent of the particular borane structure. Generally, increasing the temperature from 30 to 50 °C leads to higher values, as expected. An even stronger effect is caused by raising the cocatalyst:catalyst quotient, reflecting the reversibility of alkyl group exchange between the Lewis acidic zirconocenium ions and the borane agents.[9] The activities reached at borane:Zr = 10:1 can be enhanced by a factor of about 10 by switching to a ratio of 100:1. The top activity (Table 1, Pborane **6**) comes already close to values that are typical for borate activators like $Ph_3C^+[B(C_6F_5)_4]^-$,[24] which proceed irreversibly based on the formation of covalent trityl−carbon bonds.[25]

Interestingly, activation through the polymeric borane **4** leads in all cases to higher activities compared to that of $B(C_6F_5)_3$ (Table 1), although the missing third electron-withdrawing pentafluorophenyl group in **4** results in a reduced Lewis acidity. This effect might find an explanation by assuming a longer retention period of the polymerization active zirconocenium ion **6** (Figure 3) inside the hyperbranched matrix due to a hindered freedom of movement compared to polymerization reactions in homogeneous solution. The average period in which each zirconocene molecule exists in its polymerization active form is therefore enhanced by the polymeric cocatalysts, leading to a shift of the activation equilibrium to **7** (Figure 4). This would afford the observed higher activity values (Figure 4; “$A_{support}$”) relative to the situation in solution **8** (“$A_{solution}$”).[26]

Polypropylene Characteristics. The molecular weights of the polypropylenes prepared in the present study using $B(C_6F_5)_3$ or the polymeric borane **4** as activators are generally higher compared to solution experiments under MAO activation, probably due to hindered chain-transfer reactions to MAO species.[27] A tendency for higher molecular weights by using the polymeric activators relative to $B(C_6F_5)_3$ can be identified. A maximum M_w value of 270 000 was reached at a ratio of 100:1 and T_p = 30 °C (Table 1, Pborane **5**). Broader polydispersities and significantly reduced molecular weights are found for both polymeric (Table 1, Pborane **1**) and molecular dispersed $B(C_6F_5)_3$ (Table 1, borane **1**) activators at low borane/Zr ratios, indicating a slow activation reaction. At higher ratios (50:1; 100:1) the polydispersities are in the range expected for this catalyst family, and the molecular weights reach constant maximum values for both activating compounds.

All polypropylenes are isotactic materials bearing variable [mmmm] pentad concentrations. The microstructures are identical to solution experiments and are found to be independent of the nature of the activating species. The occurring stereoerrors, identified by the pentad distribution, are typical for variable tacticity PP prepared with these asymmetric, dual-side catalysts that afford increased [mmmm] pentad contents (30−50%) by raising the polymerization temperature from 30 to 50 °C.[28,30]

Conclusions

Hyperbranched polyborane cocatalysts, like **4**, are proved to be excellent activating systems for our asymmetric, “dual-side” metallocene catalysts leading to homo-polypropylene elastomers. Both $B(C_6F_5)_3$ and **4** result in polymers with increased molecular weight relative to solution experiments with MAO.[24] Significantly increased activities were found for the polymeric activators relative to the molecular dispersed borane cocatalyst. We attributed this effect to the particular nature of the hyperbranched nanostructure of **4**, leading to a reduced catalyst mobility that enhances the concentration of active species. This is a major advantage compared to perfect dendrimers (besides the easier synthesis), which provide activating borate units only on the outer particle sphere. In contrast to conventional

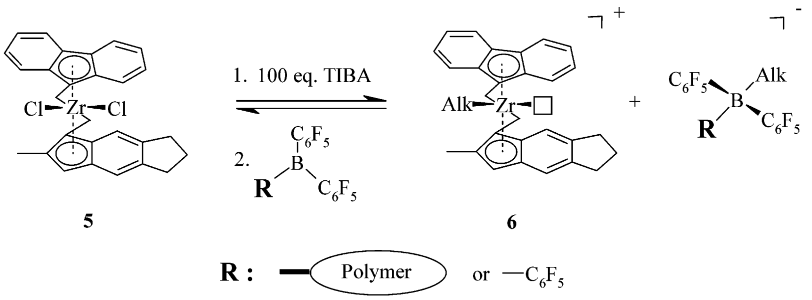

Figure 3. Catalyst activation.

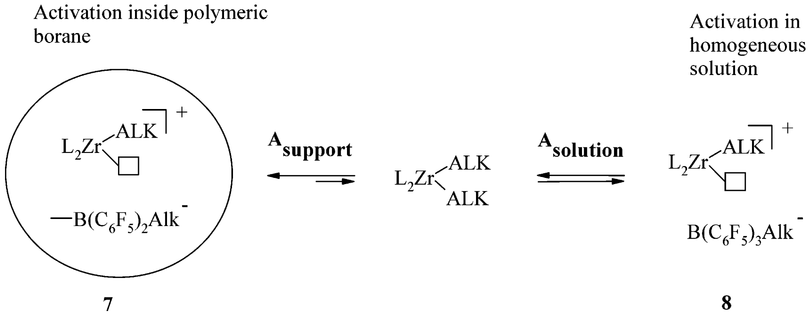

Figure 4. Schematic activation processes with polymeric borane activator (heterogeneous) and $B(C_6F_5)_3$ activator (molecular disperse).

Table 1. Polymerization Results with 5/TIBA /$B(C_6F_5)_3$ (Boranes 1−6) and 5/TIBA/4 (Pboranes 1−6)

run	[cat.][a]	ratio[b]	temp[c]	pressure[d]	time[e]	yield[f]	M_w[g]	activity[h]	*D*	[mmmm][i]
borane **1**	20	10:1	30	5	10	1.33	100 000	100	3.9	30.5
borane **2**	10	10:1	50	6.5	5	1.32	110 000	600	2.4	50.4
borane **3**	10	50:1	30	5	15	8.25	210 000	1000	2.1	29.1
borane **4**	5	50:1	50	6.5	5	1.46	110 000	1200	2.3	49.1
borane **5**	5	100:1	30	5	6	9.03	210 000	6000	2.3	32.8
borane **6**	5	100:1	50	6.5	6	13.46	150 000	9000	3.6	56.8
Pborane **1**	10	10:1	30	5	5	2.11	40 000	900	8.8	30.1
Pborane **2**	5	10:1	50	6.5	12	3.48	90 000	1200	2.6	48.7
Pborane **3**	5	50:1	30	5	9	4.05	250 000	1800	2.0	31.1
Pborane **4**	2.5	50:1	50	6.5	4	5.44	120 000	10400	2.7	49.4
Pborane **5**	2.5	100:1	30	5	14	13.06	270 000	7600	1.9	26.4
Pborane **6**	1.5	100:1	50	6.5	5	4.34	130 000	12100	2.1	51.2

[a] [μmol]. [b] Cocatalyst: catalyst. [c] [°C]. [d] [bar]. [e] [min]. [f] [g]. [g] Calibrated relatively against PP standards. [h] kg of PP/[molZr] × [C_3] × h. [i] Isotacticity [%].

supports, like silica or alumina, we find no influence of this polymer-based supporting method on the PP microstructure. This lack of influence is considered as an additional advantage of the here presented approach. Thus, there is no hindrance of a solid support surface, which in most cases affects the intrinsic stereoerror formation mechanism of the particular metallocene catalyst, to fine-tune the polymer microstructure and hence the final polymer properties. It will be interesting to find out whether this concept of hyperbranched support materials, which is at the borderline between homogeneous and heterogeneous catalysis, can also be used to control particle-forming processes.

Experimental Section

General Remarks. Methyldiundecenylsilane, the corresponding polysilane,[29] and *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta-2-methyl-1-η^5-indenyl)ethane] zirconocene dichloride[30] were prepared and characterized by published procedures. All synthetical work was done with standard Schlenk techniques under an argon atmosphere. Triisobutylaluminum (1 M in hexane) was purchased from Crompton and $B(C_6F_5)_3$ (0.5 mmol in hexane) from Nippon Shokubai. Bromopentafluorobenzene, BCl_3, *n*-BuLi (1.6 mol in hexane), and $Me_2Si(H)Cl$ were purchased from Aldrich. Toluene p.A. for propylene polymerization, benzene, and pentane were purchased from Merck and dried via distillation over $LiAlH_4$.

Measurements. NMR spectra were recorded on a Bruker AC 400 at ambient temperatures and referenced to TMS. FT-IR measurements were performed on a Bruker IFS 113-V and a Perkin-Elmer 1310 infrared spectrometer. PP analysis: ^{13}C NMR spectra were recorded on a Bruker AMX 500 spectrometer ($C_2D_2Cl_4$, 90 °C, 125 MHz, 5 mm probe) in the inverse gated decoupling mode with a 3 s pulse delay and a 45° pulse to attain conditions close to the maximum signal-to-noise ratio. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 2000, 140 °C in 1,2,4-trichlorobenzene) relative to polypropylene standards.

Synthesis of Bis(pentafluorophenyl) Borohydride. This compound was prepared by a modified literature procedure.[31] A three-necked round-bottom flask fitted with a reflux condenser, a dropping funnel, and a stopper was charged with 15 mL of bromopentafluorobenzene in dry pentane and cooled to −70 °C. 68.5 mL of *n*-BuLi (1.6 mol in hexane) was added dropwise to the reaction mixture. After complete addition, the resulting suspension was stirred for 2 h. The precipitate was separated, washed several times with pentane, and dried. It was again dissolved in pentane and cooled to −70 °C. BCl_3 was added slowly and in order to remove all educts, and the compound was washed with pentane. The white precipitate was redissolved in 50 mL of freshly distilled dimethylchlorosilane and stirred for an additional 4 h. The resulting product was recrystallized and filtered.

Yield: 46% (white crystalline powder); purity 99%. ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 4.2 (br). ^{19}F NMR (C_6D_6, 400 MHz, δ in ppm): main component (80%): −134.5 (2F), −147.8 (1F), −160.5 (2F); component (10%): −130.2 (2F), −143.0 (1F), −161.5 (2F). IR (Nujol, NaCl, λ^{-1} in cm^{-1}): 1652, 1550, 1522, 1406, 1394, 1379, 1315, 1282, 1143, 1112, 1018, 974, 766, 679, 661, 623. GC-MS (CI): m/z 346 (M^+).

Synthesis of the Polymeric Cocatalyst. A freshly prepared solution of bis(pentafluorophenyl) borohydride in 5 mL of toluene was added dropwise to a solution of poly(methyldiundecenylsilane) in 3 mL of toluene. The mixture was treated in an ultrasonic bath for 10 min and stirred for an additional hour. The product was washed two times with benzene to remove all educts. Yield: 98%; M_w = 37 500 g/mol. IR (Nujol, NaCl, λ^{-1} in cm^{-1}): 3698, 3551, 3496, 2926, 2655, 1648, 1522, 1467, 1777, 1291, 1251, 1094, 975, 794.

The conversion was monitored via FT-IR by disappearance of the characteristic vinyl end groups, for instance the $=$C−H stretching bond at 3077 cm^{-1}, the C$=$C stretching resonance at 1641 cm^{-1}, and the $=$C−H deformation bond at 992 cm^{-1}. The deformation frequency of the borohydride at 1550 cm^{-1} disappeared simultaneously. Also, ^{1}H NMR showed no vinylic protons of the educt $=CH_2$ (4.97 ppm) groups and the $-CH=$ (5.82 ppm) groups.

Catalyst Activation. The activation process was performed by the following procedure: The desired amount of dichlorozirconocene precursor was dissolved in 10 mL of dry toluene under an argon atmosphere, and 100 equiv of TIBA was added. Addition of the adequate amount of $B(C_6F_5)_3$ or the polymeric borane **4** (0.5 mmol/mL in toluene) gave the active species.

Propene Polymerization Reactions. The polymerization reactions were performed in a 0.5 L Buechi steel reactor at constant pressure (±0.1 bar) and temperature (±1 °C). After addition of 200 mL of toluene, subsequently, the polymerization temperature was adjusted, the reactor was charged with propene up to the desired partial pressure, and the preactivated catalyst solution was injected into the autoclave via a pressure buret. The monomer consumption was measured by a calibrated gas flow meter (Bronkhorst F-111C-HA-33P), and the pressure was kept constant during the entire polymerization period (Bronkhorst pressure controller P-602C-EA-33P). Pressure, temperature, and consumption of propylene were monitored and recorded online. The polymerization reactions were stopped by injecting 1 mL of methanol. The reaction mixture was poured into acidified methanol (500 mL), where the polymer precipitated. The product was filtered, washed with methanol, and dried in a vacuum at 50 °C overnight.

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