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Ultrahigh Molecular Weight Polypropene Elastomers by High Activity “Dual-Side” Hafnocene Catalysts

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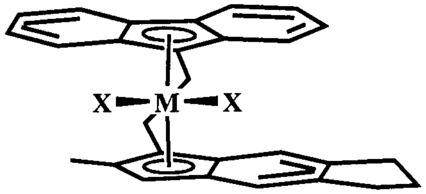
Introduction. The design of metallocene catalysts has led to a series of new polypropene microstructures, like highly syndiotactic materials, hemi-isotactic chains,[1] and atactic−isotactic block structures.[2] Recently, we described an asymmetric *ansa*-zirconocene dichloride complex (**1**) that is able to introduce single stereoerrors into an isotactic polypropene chain as a function of monomer concentration.[3] Using **1**/MAO in toluene solution, we could reach good activities (up to 4 × 10³ kg PP (mol Zr h mol C_3)$^{-1}$) and a medium molecular weight ($M_w \approx 1.7 \times 10^5$ g/mol) affording elastic polypropenes. However, one major requirement for the practical application of these new materials is a molecular weight high enough to ensure satisfying tensile and creep properties below and above room temperature. At the same time, the activity of the catalysts has to reach values suitable for application in conventional solution, bulk, or gas-phase processes.

We report here on a series of new asymmetric zirconocene dimethyl (**2**), hafnocene dichloride (**3**), and hafnocene dimethyl (**4**) complexes for the homopolymerization of propene in toluene solution and in liquid monomer after MAO and borate activation. Whereas **2**/borate affords elastic polypropenes with $M_w \leq 350\,000$ g/mol and gives activities up to 40 000 kg PP (mol Zr h)$^{-1}$, **4**/borate produces elastic polypropenes with ultrahigh molecular weights between 700 000 and 5 000 000 g/mol, variable isotacticity (15 ≤ [mmmm] ≤ 40), and activity up to 50 000 kg PP (mol Hf h)$^{-1}$.

Results and Discussion. The complexes *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta-2-methyl-1-η^5-indenyl)ethane]dimethylzirconium (**2**), *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta-2-methyl-1-η^5-indenyl)ethane]hafnium dichloride (**3**), and *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta-2-methyl-1-η^5-indenyl)ethane]dimethylhafnium (**4**) were prepared according to literature procedures[3−5] in isolated yields between 75 and 95% and were sufficiently characterized by NMR, mass spectroscopy, and elemental analysis techniques. Polymerization experiments[6] were performed in toluene solution and in liquid propene at temperatures between 10 and 50 °C in a 0.5 L V4A steel reactor equipped with internal temperature control and an efficient cooling system (T_p = constant = 2 °C). The activator trityltetrakis(pentafluorophenyl)borate was added to a solution of **2** or **4** in liquid propene at the desired temperature. Water impurities were scavenged before metallocene addition by triisobutylaluminum. The polymerization reaction was quenched by injection of methanol; excess monomer was vented off, and the polymer was dried in a vacuum at 90 °C.



	M	X
1:	Zr	Cl
2:	Zr	CH_3
3:	Hf	Cl
4:	Hf	CH_3

Previous polymerization experiments performed with **1** (Table 1, entries 1 and 2) in toluene solution indicated an increase of M_w with raising monomer concentration and showed that at least a significant part of chain termination ensued from transfer to aluminum.[7] These findings prompted us to move to liquid propene as polymerization medium and to switch from MAO to borate activation in order to increase the molecular weight further and to see whether activity could also benefit from the new reaction protocol. Indeed, using **2**/borate, we could nearly double the molecular weight ($M_w = 3.5 \times 10^5$ g/mol) and also find an up to 10-fold increase of the activity compared to the MAO experiments in solution (entries 3 and 4).

The existing literature provides a few examples that an exchange of zirconium by hafnium in isostructural complexes leads to a up to 3 times increased molecular weight.[8] Unfortunately, the activity of the Hf(IV) complexes was reported to be negligible compared to the Zr analogues after MAO activation.[9] We found the same low activity for the $HfCl_2$ complex **3** after MAO activation in toluene solution (entries 5 and 6). In addition, also the molecular weight did not even exceed that of the products resulting from **1**/MAO.

However, the situation changed when the Hf−dimethyl complex **4** was activated with trityltetrakis(pentafluorophenyl)borate. The activity increased again to values comparable to **2**/borate and even higher (entries 7−9). Obviously, the low activity of **3**/MAO is not an intrinsic property of Hf(IV)- based catalysts but results

Table 1. Polymerization Results of Catalyst 1−4

entry	catalyst	activator	solvent	T_p [°C]	activity[a,b]	mmmm [%]	M_w [g/mol][c]	M_w/M_n
1	**1**	MAO	toluene	30	2000	32	170 000	2.0
2	**1**	MAO	toluene	50	4000	54	100 000	2.0
3	**2**	borate	C_3H_6(l)	10	10000	17	350 000	3.0
4	**2**	borate	C_3H_6(l)	50	40000	27	200 000	4.8
5	**3**	MAO	toluene	30	150	31	55 000	2.0
6	**3**	MAO	toluene	50	320	40	27 000	2.1
7	**4**	borate	C_3H_6(l)	0	6000	17	4 900 000	6.9
8	**4**	borate	C_3H_6(l)	20	23000	24	1 600 000	2.6
9	**4**	borate	C_3H_6(l)	50	50000	34	700 000	3.5

[a] Toluene: kg PP (mol cat.)$^{-1}$ [C_3]$^{-1}$ h^{-1}, [C_3] = 3 mol/L. [b] Liquid propene: kg PP (mol cat.)$^{-1}$ h^{-1}. [c] HT-GPC (Waters alliance 2000), 1,2,4-trichlorobenzene; 145 °C; universal calibration against polystyrene standards; $K = 0.02$ mL/g; $\alpha = 0.76$.

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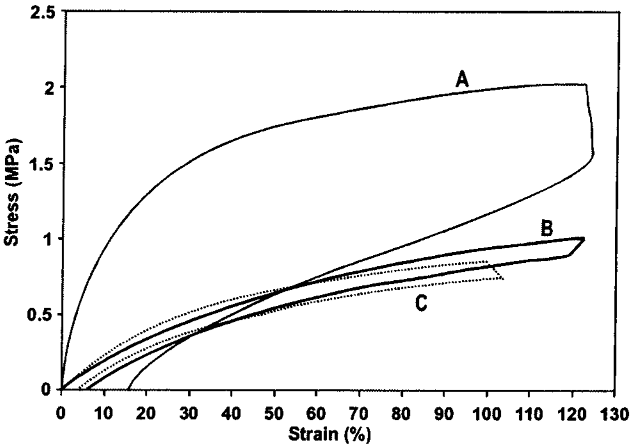

Figure 1. Stress−strain hysteresis curves (strain test ASTM D638) for homopolypropenes of different molecular weight (M_w: A, 3.5×10^5; B, 1.6×10^6) and of Kraton (C).

most probably from a slow and inefficient activation through MAO.[10]

The excellent catalytic performance of **4**/borate is complemented by the high molecular weight of the polymer products. At 0 °C polymer chains with ultrahigh molecular weight (entry 7, $M_w = 4.9 \times 10^6$ g/mol)[11] are accessible. A temperature increase leads to a decline of the molecular weight (e.g., 20 °C: $M_w = 1.6 \times 10^6$ g/mol). However, even at technical process temperatures elastic homopolypropenes with very high molecular weights (e.g., entry 9, 50 °C: $M_w = 7 \times 10^5$ g/mol)[12] are produced.

Thermoplastic polyolefins of low crystallinity suffer from high set values in stress−strain hysteresis experiments due to a facile and irreversible deformation of the small crystalline substructures upon mechanical stress. This behavior can be observed for our elastic materials of the first generation ($M_w = 1.7 \times 10^5$, zirconium catalysts)[13] and is still present in homopolypropenes of $M_w = 3.5 \times 10^5$ (Figure 1A, set 18−19%; Table 1, entry 3). The same hysteresis experiment[14] performed on one of our el-UHMPP samples (Figure 1B, $M_w = 1.6 \times 10^6$; Table 1, entry 8) reveals a significant reduction of the set to 5−7%. The resulting stress−strain curve depicted in Figure 1B is nearly identical to that of a SBS block copolymer (Kraton) under similar test conditions and demonstrates that new homopolypropenes of designed microstructure and molecular weight are accessible that start to penetrate into the property range of classical engineering thermoplastic materials.

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(5) The zirconium (hafnium)−dimethyl complex **2 (4)** was prepared by treating a toluene solution of **1 (3)** with 5 equiv of methyllithium in diethyl ether. The excess of methyllithium was quenched with dibromoethane. The solvents were removed, and the residue was extracted with hexane. Evaporation of the hexane yielded **2 (4)** as pure yellow powders.

(6) A 0.5 L Büchi steal autoclave with mechanical stirring was charged with 250 mL of toluene or 250 mL of liquid propene. After equilibration to the desired reaction conditions (T_p, [C_3]) the polymerizations were started by adding a toluene solution of the respective complex, followed by the addition of the cocatalyst (**1, 3**: MAO; **2, 4**: borate). The reaction was quenched by injection of methanol.

(7) High-resolution ^{13}C NMR spectroscopy performed on lower molecular weight products clearly showed the signals of isopropyl chain ends, resulting from transfer to aluminum and hydrolytic workup of the product. Vinyl and vinylidene chain ends could not be identified. A similar observation was made by Brintzinger et al. for other highly substituted C_2-symmetric metallocenes. Cf.: Lieber, S.; Brintzinger, H.-H. *Macromolecules* **2000** *33,* 9192.

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(11) The broad molecular weight distribution results most likely from the insolubility of the ultrahigh molecular weight products in liquid propene at 0 °C. It is clear that a significant part of the material is of much higher molecular weight which might be an indication that 5×10^6 g/mol is not the upper limit that can be reached with our catalysts. A significant narrowing of the polydispersity could be observed after repeated molecular weight determination of the same material. This indicates a significant polymer degradation depending on temperature, time, and stirring, applied for preparation of GPC samples.

(12) These ultrahigh molecular weight polypropenes still contain variable amounts of isolated stereoerrors, indicated by low concentrations of the mrmr pentad (cf. ref 3). For other, mostly atactic homopolypropene elastomers, cf.: Sassmannshausen, J.; Bochmann, M.; Rösch, J.; Lilge, D. *J. Organomet. Chem..* **1997**, *548,* 23.

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(14) Tensile Test ASTM D638.

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