Olefin Polymerization

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Hydridoboranes as Modifiers for Single-Site Organochromium Catalysts: From Low- to Ultrahigh-Molecular-Weight Polyethylene**

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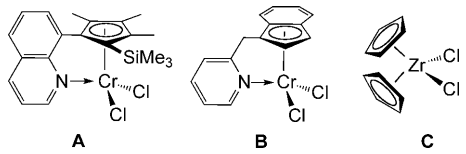
Molecular single-site catalysts allow the precise synthesis of polyolefins with a range of specific properties. Organochromium complexes show advantageous properties in the polymerization and copolymerization of ethylene.[1] Depending on the catalyst system used, low-molecular-weight up to ultrahigh-molecular-weight polyethylenes (UHMW-PEs) with a narrow molecular weight distribution can be obtained. The molecular weight of the polyethylene produced by a single catalyst system can be reduced by the use of chain-transfer reagents.[2,3] We now report on the use of hydridoboranes as additives, which in the presence of single-site cyclopentadienylchromium complexes[4] are able to increase the molecular weight of polyethylene accurately up to the UHMW-PE range. These observations are in contrast to the situation when boranes are used as chain-transfer reagents in metallocene-catalyzed olefin polymerization.[5]

The influence of several modifiers on ethylene polymerization was investigated by using **A** and **B** as catalyst precursors and methylaluminoxane (MAO) as the activator and compared with the results obtained with zirconocene dichloride **C**.[6,7] Although 200–300 equivalents of the respective modifier were used, this amount did not result in a considerable decrease in the catalytic activity (see Table 1). This finding indicates that the chosen modifiers readily allow the coordination of the incoming ethylene monomer.

As expected, organoaluminum compounds tend to lead to lower molecular weight (MW), as a result of chain-transfer reactions from Cr to Al. Whereas trimethylaluminum ($AlMe_3$) has little effect (Table 1, entries 2 and 8), triethylaluminum ($AlEt_3$) leads to a strong decrease in the PE chain lengths. A similar difference in chain-transfer efficiency has been observed recently for catalytic carboalumination reactions in the presence of complex **A**.[8]



Although phenylsilane does not have a significant effect (Table 1, entries 4 and 10), boranes display considerable influence. Whereas trialkylboranes lead, as expected, to lower MW, the use of 9-borabicyclo[3.3.1]nonane (9-BBN) as an additive produces high-molecular-weight polyethylenes up to the ultrahigh range (Table 1, entries 6 and 12). We were able to control the increase in MW by using different amounts of 9-BBN (Figure 1). In contrast, different amounts of alkylaluminum compounds produce correspondingly lower molecular weights. Thus, by varying the amount and nature of the modifiers we are able to selectively control the MW over a broad range from 50000 up to 5000000 $g\,mol^{-1}$ without changing the reaction conditions or the catalytic system.

The role of 9-BBN compared to established chain-transfer reagents was investigated in a series of control experiments: *B*-benzyl-9-BBN leads to lower MW. Since other trialkylboranes react in a similar way, the B–H function is essential. Therefore, other hydridoboranes (BH_3 and Et_2BH) and also hydridoalanes (diisobutylaluminum hydride) were tested, but

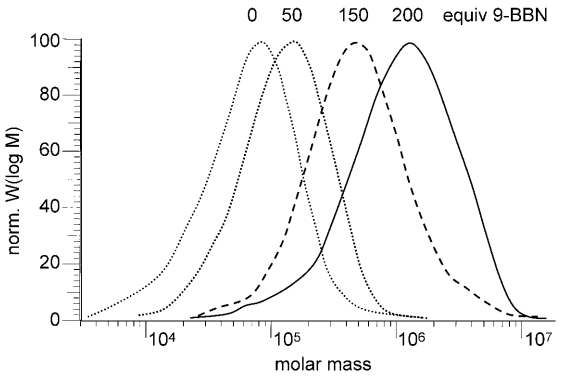


Figure 1. Gel-permeation chromatography (GPC) plots of polyethylenes synthesized with **A**/MAO and different amounts of 9-BBN to control the MW.[9]

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Table 1: Ethylene polymerization with **A**, **B**, and **C** as catalyst precursors and various modifiers.[a]

Entry	Pro-catalyst	c_{cat} [μmol]	Modifier	Modifier/Cr	Activity [g mmol^{-1} h^{-1}]	M_w[b] [10^5 g mol^{-1}]	PE [g]	$t_{polym.}$ [min]	M_w/M_n[b]	Crystallinity[c] [%]	T_m[c] [°C]
1	**A**	4.42	–	–	3243	5.3	2.9	12	3.1	65	135.4
2	**A**	5.82	$AlMe_3$	290:1	2200	3.2	4.3	20	3.4	74	133.3
3	**A**	5.36	$AlEt_3$	200:1	3298	0.5	5.9	20	3.2	80	130.5
4	**A**	5.36	$PhSiH_3$	200:1	2972	4.7	4.0	15	3.1	63	134.0
5	**A**	6.05	BEt_3	250:1	3529	3.1	7.1	20	3.7	68	134.0
6	**A**	4.66	9-BBN	200:1	2908	31.4	2.7	12	5.1	53	133.9
7	**B**	6.99	–	–	3017	13.1	4.2	12	2.9	53	132.4
8	**B**	6.07	$AlMe_3$	280:1	3553	12.8	4.3	12	2.5	57	133.9
9	**B**	6.38	$AlEt_3$	200:1	3439	0.9	4.4	12	2.4	81	131.9
10	**B**	6.38	$PhSiH_3$	200:1	2850	13.5	3.6	12	3.0	56	133.7
11	**B**	8.51	BEt_3	200:1	2731	4.2	7.8	20	3.0	60	132.9
12	**B**	6.38	9-BBN	200:1	2834	48.9	6.0	20	3.5	51	134.7
13	**C**	10.30	–	–	2332	6.0	4.8	12	2.4	57	132.3
14	**C**	10.30	9-BBN	200:1	1181	4.3	3.4	17	3.7	67	133.6

[a] Conditions: co-catalyst PMAO, Al/Cr 1000:1, RT, 150 mL toluene, 1 bar C_2H_4. [b] Determined by GPC. [c] Determined by differential scanning calorimetry.

they strongly decrease the catalytic activity. Catecholborane entirely stops the catalysis, presumably because of the presence of the oxygen function.[10]

Sterically hindered phenols, however, could have an entirely different effect on a polymerization reaction. Busico et al.[11] used 2,6-di-*tert*-butylphenol to trap free $AlMe_3$, which is present[12] in MAO and, to a lower amount, in PMAO[13] solutions. The bulky alkyl groups of this phenol prevent it from binding to the metal center, but it reacts with $AlMe_3$. The use of 2,6-di-*tert*-butylphenol in our catalytic system results in a constantly high activity and a product with an ultrahigh MW. This finding indicates that the dominant chain-termination step is chain transfer to aluminum rather than one of the other termination reactions. This is in line with earlier results from Theopold, who described a low tendency for β-hydride elimination with chromium(III) systems.[14]

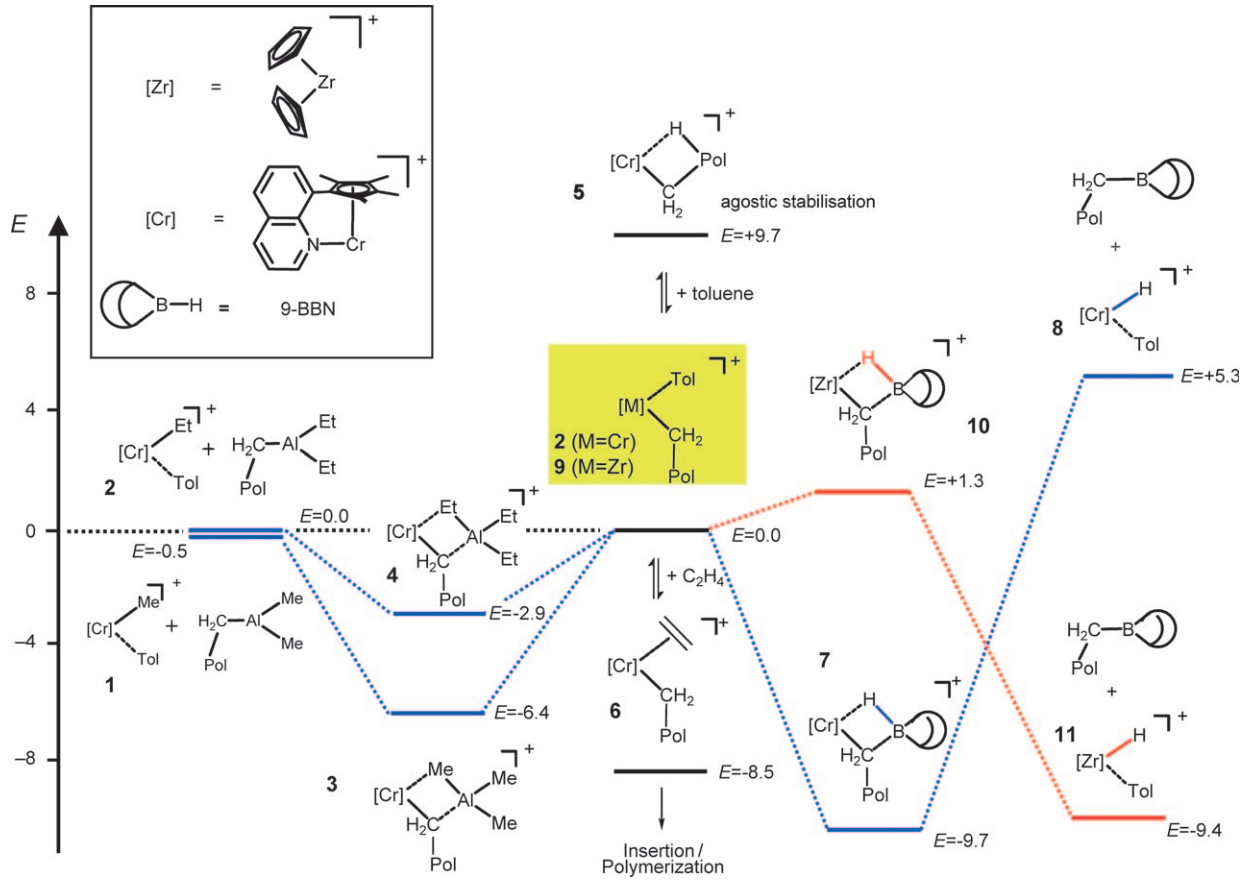
Although both additives lead to UHMW-PE, the mechanisms are quite different. The sterically hindered phenol reacts quickly with the residual $AlMe_3$ and thus prevents chain transfer. In contrast, 9-BBN reacts only slowly with MAO or $AlMe_3$ (see the Supporting Information). The same is true for the hydroboration of ethylene. Furthermore, unchanged or a decreased MW is observed when trialkylboranes are used as additives (BEt_3, *B*-benzyl-9-BBN). Consequently, 9-BBN and not a by-product causes the observed effect immediately after addition. The addition of 9-BBN at a later stage (for example, 2 or 4 min after the start; see Figure S1 in the Supporting Information) results in bimodal MW distributions with M_w maxima around 10^5 and 10^6 g mol^{-1}, respectively.

These experimental observations can be explained by an interaction of the hydridoborane with the Lewis-acidic chromium center competing with an Al-R-Cr interaction. The distinctive feature of these chromium catalysts is that the borane–catalyst adduct does not lead to chain transfer during formation of a chromium hydride species. These interpretations are supported by DFT calculations (Scheme 1).

The basis of our interpretation of the 9-BBN effect is a competing equilibrium of different adducts of the coordinatively unsaturated catalyst with 9-BBN, alkylaluminum compounds, solvent molecules, and ethylene. Experimental and theoretical results in cyclopentadienylchromium-catalyzed olefin polymerization are in accordance with active species that are coordinatively unsaturated and cationic.[1,4] The energy surface for olefin insertion is influenced by the interaction of the active catalyst with additional coordinating molecules. It has been shown for zirconium- and titanium-based catalysts that calculations on cationic complexes without external interactions (for example, counterion, solvent molecule) give unrealistic pictures of the energy surface.[15] In the absence of ethylene, borane, or alkylaluminum compounds, the cyclopentadienylchromium complex is stabilized by interaction with the toluene solvent molecules, so that the interaction with the counterion ($MeMAO^-$) is only electrostatic in nature and similar for all cationic species. We have identified the intermediates and transition states pertaining to the termination reaction with $AlMe_3$ (**2**→**3**→**1**; Scheme 1 and see Scheme S1 in the Supporting Information). The two transition states have low relative energies of up to 33 kJ mol^{-1}.[15b,16] This finding justifies the assumption of fast equilibria between the aforementioned catalyst adducts. The chain transfer to aluminum compounds is almost isoenergetic, so that the amount of the alkylaluminum compound controls the probability of chain-transfer reactions occurring. Chain termination with $AlEt_3$ is characterized by lower energy barriers for the two transition states compared to the $AlMe_3$ termination (see Scheme S2 in the Supporting Information). This is a likely reason for their different effect on the chain-transfer reaction.

Chain transfer to boron is energetically disfavored, thus 9-BBN is not able to terminate the growing polymer chain and eventually acts as a placeholder for ethylene, thereby preventing the chain termination by alkylaluminum compounds. Ultimately this leads to ultrahigh molecular weights.

Interestingly the chain transfer to boron is energetically disfavored only for the investigated chromium complexes, not for zirconocene complexes. We calculated the corresponding energies for the chain transfer from zirconocene, and the DFT results are in accordance with the well-known chain-transfer activity of hydridoboranes in metallocene-catalyzed polymer-



Scheme 1. Calculated energies of the proposed different influence of Al–R and B–H on the chain termination during ethylene polymerization. Method: DFT B3LYP/6-311g*. The profiles are plotted for zero-point-vibration-corrected energies. The relative energies are in kJ mol^{-1}. Dimerization energies for AlR_3 and R_2BH were taken into account. CH_3CH_2- was used as a model for the polymer chain. CH_2-Pol = growing polymer chain.

izations.[2,5] Consequently, the addition of 9-BBN results in decreased molecular weights (see Table 1, entries 13 and 14).

The described effect of 9-BBN allows the homogeneous catalytic formation of precise molecular weight polyethylenes. Our mechanistic interpretations explain earlier experimental observations concerning the formation of UHMWPE when organochromium catalysts are immobilized.[17]

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