Polymer Bulletin 34, 413–418 (1995)

Polymer Bulletin

Copolymerization of ethylene and 1-octadecene with the Cp_2ZrCl_2/MAO and Cp_2HfCl_2/MAO catalyst systems

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Received: 1 December 1994/Accepted: 2 January 1995

Summary

The comparison of the copolymers obtained with the Cp_2ZrCl_2/MAO and Cp_2HfCl_2/MAO catalyst systems showed that the catalyst having hafnocene was much more reactive towards 1-octadecene than zirconocene. The comonomer concentration had to be three times higher in the zirconocene copolymerization than in the hafnocene copolymerization when the level of 6 mol-% was reached. Although the hafnocene catalyst was more reactive towards 1-octadecene, the molecular weights were higher than in the copolymers obtained with the zirconocene catalyst.

The total activity of the zirconocene was 10 times higher than with the hafnocene catalyst. With the zirconocene catalyst the activity towards ethylene was constantly increasing by increasing the comonomer concentration but stayed nearly constant with the hafnocene catalyst. It seemed that there is no rate enhancement effect upon comonomer addition with the hafnocene catalyst.

Introduction

The finding that the activity of metallocenes can be increased by replacing alkyl aluminiums with methylaluminoxane (MAO) started the active research in the metallocene field (1-3). Since the beginning of 80's the research has risen dramatically and the first metallocene products are now available commercially. The polymerization research is focused on the zirconium based metallocenes leaving the other group 4A metals behind. The most important reason for this is the unstable titanium species at elevated temperatures and lower activities with the hafnium based metallocenes.

Only a few studies have looked the differencies in the polymerizations with hafnocenes and zirconocenes (4,5). Chien and He (6) compared the zirconocens and hafnocenes in copolymerization of ethylene and propylene, while Ewen *et al.* concentrated on the comparison of polypropylenes obtained with different stereorigid metallocenes (7,8). Since the different metallocenes give different molecular weight at the same conditions, they can be used to obtain bimodal or broad molecular weight distributions (9,10).

This study compares ethylene/1-octadecene copolymerizations performed with Cp_2ZrCl_2/MAO and Cp_2HfCl_2/MAO catalyst systems.

Experimental

Materials. Cp_2ZrCl_2 and Cp_2HfCl_2 were commercial products (from Aldrich), methylaluminoxane was 10 weight-% in toluene (from Schering AG) and n-heptane grade was GR (from J.T. Baker). Ethylene was grade 3.5 (from AGA) and 1-octadecene was for synthesis (from Aldrich). Ethylene, 1-octadecene and n-heptane were further purified by conducting them through columns containing molecular sieves, CuO and Al_2O_3, and ethylene before their addition to the reactor.

Copolymerization. Copolymerization was performed in n-heptane in a 0,5-dm^3 reactor under a constant overpressure of 1,5 bar. Predetermined amount of n-heptane was added into the evacuated and N_2-flushed reactor. This was followed by 1-octadecene, which was pumped into the reactor. Total volume of the reaction medium was 300 millilitres in every run. After this MAO/toluene solution was pumped into the reactor. Ethylene was added up to the polymerization pressure and it was controlled automatically with a pressure transducer and a magnetic valve. Copolymerization was initiated by pumping the catalyst/toluene solution into the reactor (in-situ start). The Al/M (M=Zr, Hf) mole ratio was 2400. Copolymerization was stopped by degassing the reactor, after which the organic layer was washed with a mixture of ethanol and diluted hydrochloric acid and water and n-heptane was gently evaporated. The polymer was further washed with acetone in order to extract the unreacted comonomer. The product was then dried under vacuum at 80°C overnight.

Characterization. 1-Octadecene content of the copolymers was determined with a Varian 400 Unity NMR spectrometer operating at 110 °C from the methylene, branching, α, β and γ carbons. The monomer triad distributions were calculated according to Randall (11). Molecular weight distributions were investigated with a Waters high-temperature GPC device equipped with three TOSOH mixed bed columns with exclusion limit for polystyrene 4×10^8. Solvent 1,2,4-trichlorobenzene was used at a flow rate of 1,0 cm^3/min. The columns were calibrated universally with broad molecular weight distribution linear low density polyethylenes. Differential scanning calorimetry curves were obtained with heating rate 10 °C/min from -10 to 180 °C. The same sample was heated to the end temperature twice and between the runs it was cooled back to -10 °C with a cooling rate 10 °C/min. Only the second heating curve was analyzed.

Results and discussion

The results from the copolymerizations are seen in Table 1. Table 2 shows the monomer triad distributions of the selected hafnocene and zirconocene samples. It can be noted that the only differencies can be seen in the O-centered triads: the amount of OEE+OOE triad is higher in the polymers obtained with the zirconocene catalyst. The same tendency, although smaller, can be seen in the amount of EOE triad.

Figure 1 shows the activity of the catalyst plotted against the concentration of the comonomer in the reactor. There it can be seen that the total activity of the zirconocene was 10 times higher than with the hafnocene catalyst. The activity towards ethylene was constantly increasing by increasing the comonomer concentration with the zirconocene catalyst but stayed nearly constant with the hafnocene catalyst. It seemed that there is no rate enhancement effect and that the activity started to decrease a little with the hafnocene catalyst.

In the figure 2 it can be seen that the hafnocene catalyst is much more reactive towards the 1-octadecene comonomer than the zirconocene catalyst. For example, 3 times more comonomer was needed in the reaction medium with the zirconocene than with the hafnocene catalyst in order to obtain 6 mol-% 1-octadecene containing copolymer.

Table 1. The properties of the ethylene/1-octadecene copolymers obtained with Cp_2ZrCl_2/MAO (**I**) and Cp_2HfCl_2/MAO (**II**) catalyst systems. t = 70 °C, p(ethylene) = 1,5 bar, Al/M (M=Zr, Hf) = 2400

Sample	Comonomer mol-% (wt-%)	$\bar{M}_w$ g/mol	$\bar{M}_w/\bar{M}_n$	T_m °C	ΔH_f J/g	Total activity kg/g cat×15min
(I)						
EBH19	0,4 (3,5)	52 000	2,2	129,2	127,6	7,8 (7,5) (*
EOD1	0,8 (6,8)	30 000	2,3	127,5	123,9	7,3 (6,8)
EOD2	1,2 (9,9)	23 000	1,9	124,2	110,2	11,7 (10,5)
EOD3	1,8 (14,2)	21 000	2,0	117,5	87,0	11,8 (10,0)
EBH17	2,0 (16,1)	21 000	2,1	116,6	85,3	12,1 (10,2)
EBH18	2,4 (18,1)	18 000	2,3	113,7	75,5	13,0 (10,5)
EOD4	4,3 (28,8)	8 000	2,0	95,7	25,7	19,0 (13,1)
EOD5	6,3 (37,7)	5 000	2,0	-	-	28,3 (16,7)
(II)						
EOD7	1,5 (12,1)	41 000	2,1	125,7	79,3	2,1 (1,8)
EOD8	2,4 (18,1)	33 000	2,1	122,5	78,2	2,5 (2,0)
EOD9	3,5 (24,6)	28 000	2,1	119,0	45,2	2,5 (1,9)
EOD6.01	4,3 (28,8)	22 000	2,1	111,4	34,2	2,6 (1,8)
EOD3.01	4,8 (31,6)	19 000	2,1	94,3	22,1	2,8 (1,9)
EOD10	6,7 (39,3)	15 000	2,1	89,9	9,0	2,7 (1,5)

*) Activity towards ethylene = total activity x (1 - comonomer wt-%/100)

Table 2. The monomer triad distributions of selected samples. E = ethylene monomer unit, O = 1-octadecene monomer unit

Triad / Sample	EBH18(* Zr-2,4 mol-%	EOD4 Zr-4,3 mol-%	EOD8 Hf-2,4 mol-%	EOD6.1 Hf-4,3 mol-%
OOO	0,000	0,000	0,000	0,000
EOO+OOE	0,005	0,009	0,000	0,003
EOE	0,023	0,036	0,021	0,031
OEO	0,000	0,000	0,000	0,000
OEE+EEO	0,035	0,084	0,046	0,113
EEE	0,937	0,871	0,933	0,852

*) Catalyst - 1-octadecene content of the polymer

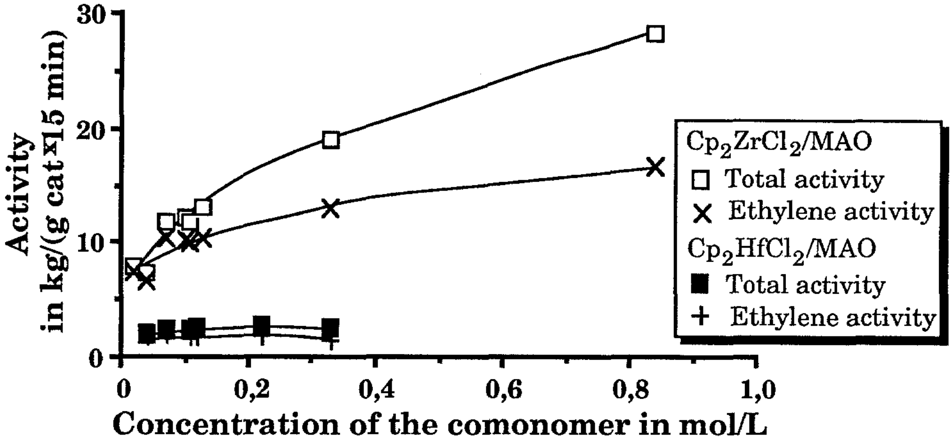

Figure 1. The dependence of the activity on the comonomer concentration in the reactor.

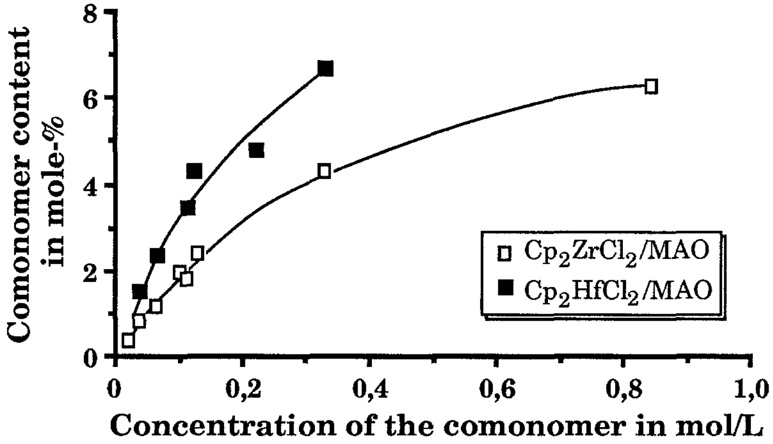

Figure 2. The dependence of the activity on the comonomer concentration in the reactor.

It is well known that the comonomers seem to work as chain transfer agents and decrease the molecular weight of the copolymer. Figure 3 shows this clearly. When the hafnocene catalyst was used the molecular weight of the copolymer did not decrease as dramatically as when the zirconocene catalyst was used.

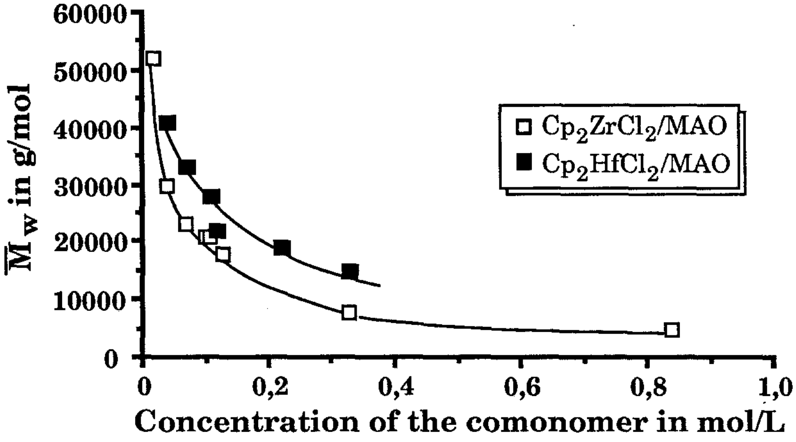

Figure 3. The dependence of the molecular weight of the polymer on the concentration of the comonomer in the reactor.

Figure 4 shows how the melting point of the polymer is affected by the content of the comonomer in the polymer. It can be seen that the melting point of the polymers decreases linearly when the comonomer content is increasing. However, more comonomer incorporation in the polymers obtained with the hafnocene catalyst was needed in order to affect the melting point of the polymers.

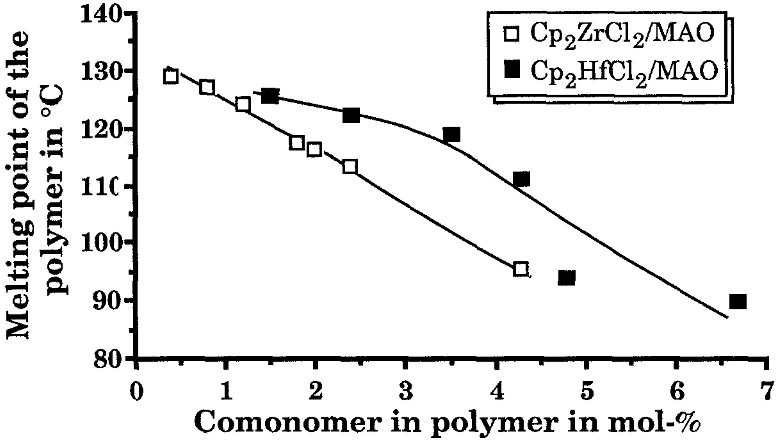

Figure 4. The dependence of the melting point of the polymer on the comonomer content of the polymer.

In the figure 5 the dependence of the heat of fusion on the comonomer content of the polymer can be seen. It shows that there is no difference in the heat of fusion is at the same level in both the zirconocene and the hafnocene polymers. The comonomer content of the polymers is at the the same level.

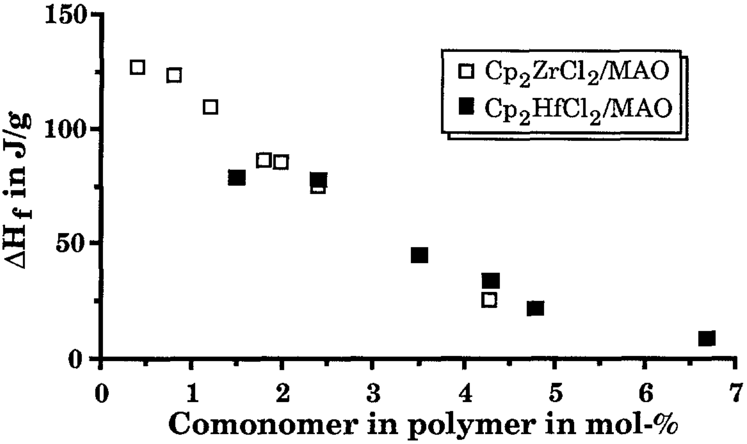

Figure 5. The dependence of the heat of fusion on the comonomer content of the polymer.

Conclusions

The copolymerizations of ethylene and 1-octadecene with the Cp_2ZrCl_2/MAO and Cp_2HfCl_2/MAO catalysts systems revealed some interesting results:

i) The rate enhancement effect was not in work with the hafnocene catalyst.
ii) The activity of the hafnocene catalyst was 10 times lower than the activity of the zirconocene catalyst.
iii) The reactivity of 1-octadecene was 3 times higher with the hafnocene catalyst.
iv) The molecular weight was higher in the copolymers obtained with the hafnocene catalyst.
v) The melting point of the polymers could be linearly decreased by increasing the comonomer content of the polymer. However, the heat of fusion of the hafnocene polymers was higher with the same comonomer content.

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