Polymerization of hex-1-ene by homogeneous zirconocene and hafnocene catalysts in compressed solution

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Poly(hexene) with very high molecular weight is produced at 250 MPa (2500 atm) with $(C_5HMe_4)_2HfCl_2$–methyl aluminoxane (MAO) as catalyst; the dependence of the polymerization on the reaction pressure (0.1 MPa–1.5 GPa) and the substituent pattern of a zirconocene catalyst is described.

While poly(ethene) and poly(propene) dominate in terms of production volumes the polyalkene industry, polymers of higher α-alkenes find use due to their special physical properties.[1] In catalytic alkene polymerization the molecular weights of the produced polyalkenes and reaction rates decrease in the order propene > but-1-ene > pent-1-ene > hex-1-ene.[2] So far, the polymerization of hexene has been achieved using homogeneous organoyttrium catalysts (M_n = 24000–64000) and zirconium catalysts with chelating binaphthoxide ligands (M_w = 674000; M_w/M_n = 2.23).[3] Furthermore, Chien has shown the efficiency of homogeneous metallocene-based catalysts such as methyl aluminoxane (MAO)-activated *rac*-$C_2H_4(indenyl)_2ZrCl_2$ which yields poly(hexene) (PH) with molecular weights of up to M_n = 97000 [1.8×10^5 g(PH) mol (Zr)$^{-1}$ h^{-1}] at low reaction temperatures.

Here we report zirconocene and hafnocene catalysed polymerization reactions of hexene under high pressure.† Polymerization conditions at high pressure were optimized using $(C_5H_5)_2ZrCl_2$–MAO as catalyst, and best results were obtained in reactions with hexene as monomer *and* solvent and using only a minimum amount of toluene for premixing (10 min) of the catalyst precursor and MAO. Normal-pressure polymerization was suppressed by precooling hexene prior to addition to the activated catalyst.‡

At 500 MPa polymerization of hexene by $(C_5H_5)_2ZrCl_2$–MAO was fast and gave poly(hexene) as a viscous oil with molecular weights in the range 24000–29000 (Fig. 1). The molecular weight distributions were observed to be narrow (M_w/M_n = 1.54–1.57). However, for a reaction time of 23 h, the polydispersity increases to M_w/M_n = 3.43 which can presumably be ascribed to the high conversion (96%) reached in this reaction. Further experiments with a reaction time of 2 h and pressures between 0.1 MPa and 1.5 GPa revealed that rates and molecular weights are considerably enhanced as the pressure was increased (Figs. 2 and 3). The catalytic activity [2.1×10^6 g(PH) mol (Zr)$^{-1}$ h^{-1} at 0.1 MPa] was accelerated 25-fold at 500 MPa [5.4×10^7 g(PH) mol (Zr)$^{-1}$ h^{-1}] and droped at higher reaction pressures to 4.7×10^7 g(PH) mol (Zr)$^{-1}$ h^{-1} at 1.5 GPa. This was likely to arise from the high viscosities[6] of the reaction medium under these conditions slowing down the rates of diffusion of the monomers to the catalyst centres. The molecular weights (M_w = 3300 at 0.1 MPa) were found to increase nine-fold at 500 MPa and lower at higher reaction pressures (M_w = 9800 at 1.5 GPa), this being more pronounced than for the catalytic activities. As a plausible explanation it can be assumed that high viscosities are decreasing the rate of chain propagation since chain termination

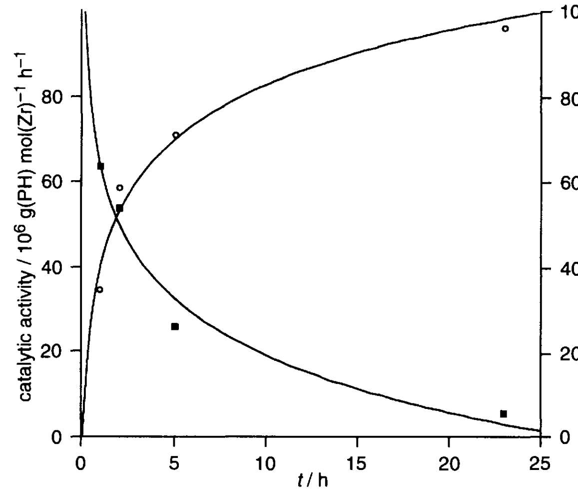

Fig. 1 Catalytic activity (■) and conversion (○) *vs.* time for the polymerization of hexene by $(C_5H_5)_2ZrCl_2$–MAO at 24 °C and 500 MPa; [Zr] = 3.6×10^{-6}, [Al] = 3.6×10^{-2} mol dm^{-3} in 24.6 ml hexene, 0.4 ml toluene

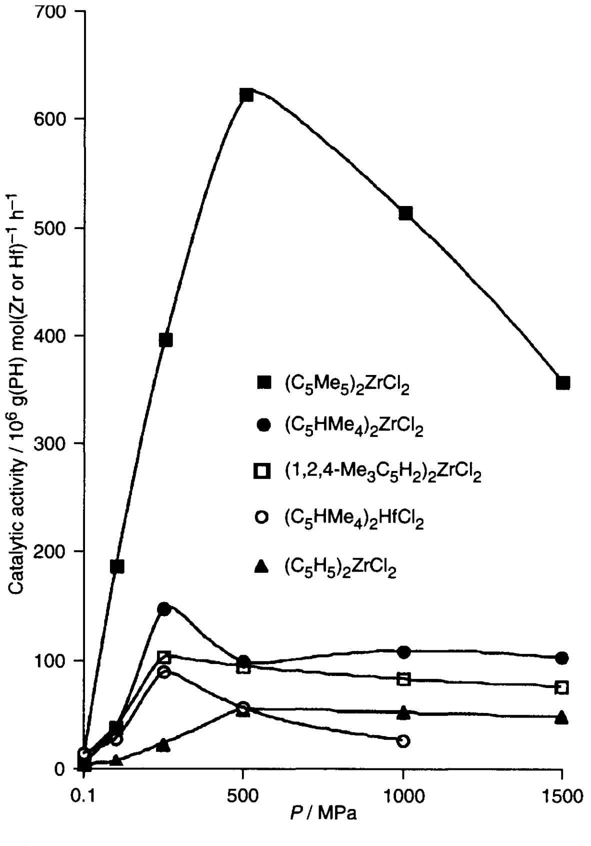

Fig. 2 Pressure dependence of catalytic activities for the polymerization of hexene by MAO-activated $(C_5H_{5-n}Me_n)_2ZrCl_2$ (n = 0: 3.6×10^{-6}; n = 3, 4: 1.8×10^{-6}; n = 5: 3.6×10^{-7} mol dm^{-3}) and $C_5HMe_4)_2HfCl_2$ (2.0×10^{-6} mol dm^{-3}) respectively; [Al]/[Zr(Hf)] = 10000

via β-H transfer to the metal should be independent of the monomer concentration.

A series of several Kaminsky-type catalysts with methyl substituents attached to the C_5 rings $(Me_nC_5H_{5-n})_2ZrCl_2$–MAO ($n = 0, 1, 3, 4, 5$)[7] has been employed. Pressure dependence observed for $(C_5H_4Me)_2ZrCl_2$–MAO is in accordance with that of the C_5H_5 derivative with the methyl substituents leading to a slight increase of molecular weights and activities. However, for $(1,2,4\text{-}C_5H_2Me_3)_2ZrCl_2$–MAO the influence of three Me groups at each C_5 ring on the polymerization behaviour is substantial. Molecular weights show a maximum value of $M_w = 548\,000$ at *ca.* 100 MPa, and catalytic activities go through a maximum of 1.0×10^8 g(PH) mol $(Zr)^{-1}$ h^{-1} at *ca.* 250 MPa. Poly(hexene) with high molecular weight[8] of $M_w = 1\,570\,000$ ($M_w/M_n = 2.44$) was obtained in polymerizations brought about by $(C_5HMe_4)_2ZrCl_2$–MAO at an optimum pressure of *ca.* 250 MPa. Surprisingly, the highest activity was observed for $(C_5Me_5)_2ZrCl_2$–MAO which polymerizes hexene at 500 MPa with a rate of 6.2×10^8 g(PH) mol $(Zr)^{-1}$ h^{-1}, a value two orders of magnitude higher than at atmospheric pressure [3.9×10^6 g(PH) mol $(Zr)^{-1}$ h^{-1}].

The polymerization activities of the zirconocene catalysts $(Me_nC_5H_{5-n})_2ZrCl_2$–MAO increase at 500 MPa in the order $Me_0 < Me_1 < 1,2,4\text{-}Me_3 < Me_4 \ll Me_5$. Even though quantitative interpretation of the activity values appears to be difficult the observed tendency might be rationalised in terms of electronic properties. At high pressure activities seem to be governed by the electronic features of the substituted cyclopentadienyl ligand. These dominate the influences from sterical hindrance of the active metal centre.

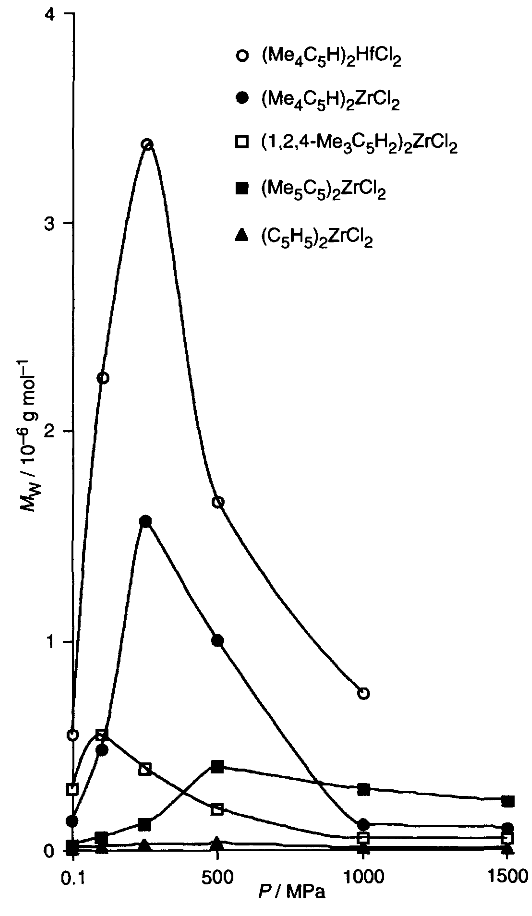

Fig. 3 Pressure dependence of molecular weights for the polymerization of hexene by MAO-activated $(C_5H_{5-n}Me_n)_2ZrCl_2$ and $(C_5HMe_4)_2HfCl_2$ respectively; catalyst concentrations same as in Fig. 2

$(C_5HMe_4)_2HfCl_2$–MAO yields poly(hexene) with higher molecular weight than the corresponding zirconium analogue following a general trend for group 4 metallocene catalysts.[9] At an optimum pressure of *ca.* 250 MPa very high molecular weight poly(hexene) ($M_w = 3\,380\,000$; $M_w/M_n = 2.70$) could be produced as a rubber-like solid.

A Special Grant for Promotion of Research from the Institute of Physical and Chemical Research (RIKEN) is gratefully acknowledged. A. F. thanks the Ciba-Geigy Foundation (Japan) for the Promotion of Science for the award of a fellowship.

Footnotes

† Polymerization in solution under pressure has previously been utilized in free-radical processes for which an activation volume $\Delta V^{\neq}$ of *ca.* -10 cm^3 mol^{-1} has been determined.[5]

‡ *General procedure*: A 25 ml Teflon sample holder was charged at room temperature in a Schlenk tube with argon, 0.2 ml of the metallocene catalyst $(C_5H_{5-n}Me_n)_2ZrCl_2$ in dry toluene ($n = 0, 1$: 9×10^{-8}; $n = 3, 4$: 4.5×10^{-8}; $n = 5$: 9×10^{-9}; $(C_5HMe_4)_2HfCl_2$: 5×10^{-8} mol) and a solution of MAO in toluene (mass% Al = 5.98; 10 000-fold excess). After 10 min dry, cold (−78 °C) hexene (24.6 ml, 0.2 mol) was added *via* cannula and the sample holder firmly closed by a screw cap and immediately cooled to −78 °C. Pressure was applied by a direct piston-cylinder apparatus with a hydraulic press during warming to room temperature. After 2 h the pressure was released, the viscous reaction mixture transferred to a glass beaker, and MeOH (10 ml) added. The polymer was separated from the decomposition products of MAO by filtration. Removal of the volatiles and drying in high vacuum afforded the polymer as a colourless, highly viscous oil or rubber-like solid. The yield was determined by weighing and the molecular weight by gel permeation chromatography (GPC).

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Received, 7th December 1995; Com. 5/07971C