Kinetic and Active Centre Studies on the Polymerization of Propylene using $MgCl_2$ Supported Ziegler – Natta Catalysts and 1,3 Diether Donors

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Summary: All polymerization experiments were carried out in a Büchi glass reactor capable of operating at propylene pressures of 1-7 atmospheres. Two types of $MgCl_2$ supported catalysts with controlled morphology were studied, viz., catalyst systems containing either a 1,3 diether (Catalysts A and D), 9,9-bis (methoxymethyl) fluorene, or a simple diester (Catalysts B, C and E) such as diisobutylphthalate, used as reference systems. The kinetic behaviours of these catalysts were investigated for propylene polymerization. The 1,3-diether based systems proved to be excellent catalyst systems for propylene polymerization showing high polymerization activities and stable rate-time profiles and produced spherical polymer particles. Catalyst pre-treatment was found to play an important role in controlling the morphology of the final polymer. A tritiated alcohol radio-quenching technique was used to determine the concentrations active centres: values of 7.5 and 5.1 mol/mol % respectively were obtained for catalysts A and D and 3.5, 2.9 and 2.2 mol/mol % respectively were obtained for catalysts B, C and E. Catalysts A and D showed very high polymerization activities and also higher C_o^* values. All polymers produced were characterized by SEM, DSC, extraction and molecular weight determinations.

Keywords: active centre determination; $MgCl_2$ supported catalysts; polypropylene (PP); Ziegler Natta polymerisation

Introduction

Control in Ziegler – Natta polymerization has come a long way. It is now possible to control the stereoisospecificity of polypropylene polymerization in the absence of an external electron donor, and to produce polymer with a high isotactic index, and at the same time to control the morphology of the polymer that is formed. The past decade has seen the advent of a new generation of $MgCl_2$ supported catalysts in polypropylene (PP) manufacture. These catalysts, consisting of $MgCl_2$, $TiCl_4$, and a diether as the internal donor, typically a 2,2-disubstituted 1,3-dimethoxypropane, are generally referred to as fifth-generation catalysts and show particularly high activity in propylene polymerisation.[1–3] Compared to fourth-generation catalysts, comprising $MgCl_2$, $TiCl_4$ and a diester such as diisobutyl phthalate (DIBP), the diether-based systems give narrower molecular weight distribution PP, and require relatively low hydrogen concentration for effective molecular weight control.[4] Diester-based catalysts normally require the presence of an alkoxysilane donor as external donor, added with the trialkylaluminium cocatalyst.

For the present study five $MgCl_2$ supported catalyst systems were prepared, two fifth-generation systems and three fourth-generation systems and were used for a comparative study of the polymerization of propylene. Particular attention was paid to the determination of the numbers of active centres, as determined by quenching using tritiated ethanol, the stability of the rate-

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time profiles, and morphology of the polymer that was produced.

Experimental Part

Catalysts

The catalysts used in the present work were prepared using procedures similar to these reported previously.[5] For catalysts A and D, the internal donor was a diether, 9,9-bis(methoxymethyl)fluorene,[2] and in catalysts B, C and E, the internal donor was a diester DIBP. Analytical details for these catalysts are listed in Table 1.

It is to be noted that Catalysts A and D have similar average particle sizes and contain similar amounts of diether, Ti and Mg. However, Catalysts B, C and E have very different average particle sizes and contain different amounts of DIBP. The Ti loading of Catalysts A and D was higher than that for Catalysts B, C and E.

Diluents and Chemicals

EC180, a high boiling solvent, consisting of about equal amounts of 2,2,4,4,6- and 2,2,4,6,6- isomers of pentamethylheptane, was dried using a mixture of 4A and 13X molecular sieves. $AlEt_3$ was diluted with EC180 to prepare a 1 M solution before use. Dicyclopentyldimethoxysilane (DCPDMS) was used as a 0.25 M solution in EC180. Propylene was purified before use by passing through a column of 4A and 13X molecular sieves.

Tritiated water was supplied by UKAEA Radiochemical Centre, Amersham, UK, in batches of 1ml, each with an activity of 1 *Ci*, equivalent to 2.2×10^{12} dpm.

Table 1.
Catalyst Compositions.

	Catalyst				
	A	B	C	D	E
Ti/wt %	3.70	1.90	2.25	3.4	1.6
Mg/wt %	12.4	18.6	17.1	11.5	19.9
DIBP/wt %	–	11.5	7.2	–	5.2
Diether/%	11.4	–	–	11.6	–
Particle size/μm	40	10	60	40	80

All experiments were carried out in a dedicated radiochemistry laboratory using established safety procedures.

Polymerizations

All polymerizations were carried out in a 0.5 L Büchi glass reactor using 250–300 ml EC180 and at a constant total pressure of 6 bar.[5] The instantaneous rate of polymerization was recorded automatically and was determined from the relationship:

$$R_p = Y\Delta C / c\Delta t[Ti] \qquad (1)$$

in which R_p is the instantaneous rate of polymerization, Y is the polymer yield in gram, Δ C is the number of counts during the interval Δ t; c is the total number of counts and [Ti] is the catalyst concentration in mmol L^{-1}. The units of R_p are therefore in g polymer (mmol Ti)$^{-1}$ h^{-1}.

The order of addition of catalyst and cocatalyst components is very important in Ziegler – Natta polymerization and the following orders were strictly adhered to. For diether systems the cocatalyst solution was added first followed by the catalyst slurry. For phthalate systems the order was first the cocatalyst solution, then the external donor solution, and finally the catalyst slurry.

The relevant components were first precontacted in the presence of propylene at 25 °C and then prepolymerization with propylene at a total pressure of 6 bar with a partial pressure of hydrogen of 0.25 or 0.5 bar was carried out for 30 min before the main polymerization at 50 °C and a total pressure of 6 bar (0.25 bar hydrogen and 5.75 bar propylene).

Results and Discussion

Rate – Time Profiles

The rate – time plots for the various pretreated (precontacted and prepolymerized) catalyst systems, A, B, C, D and E, for propylene polymerization were determined and are shown in Figure 1.

For Catalyst A the instantaneous rate of polymerization decreases during the first 30 min but then remains constant at high

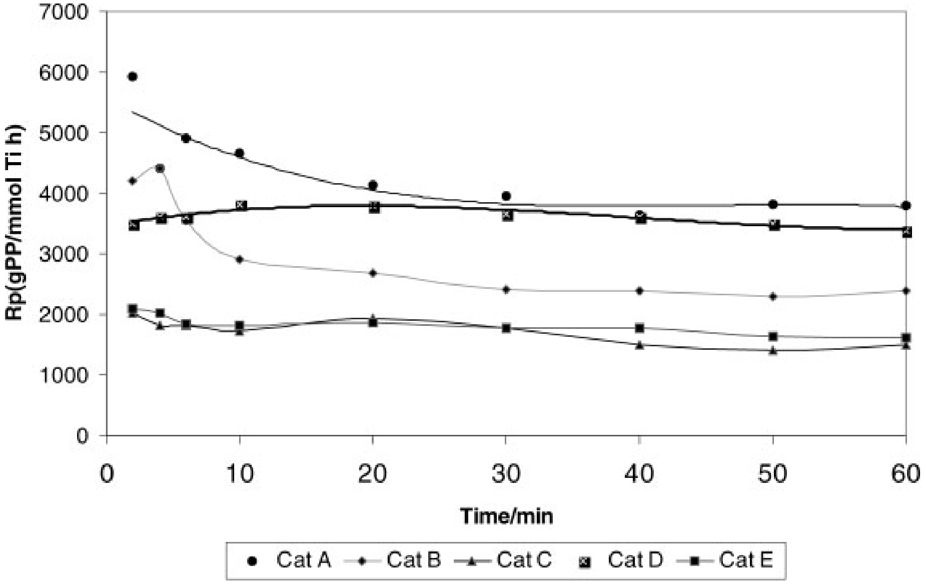

Figure 1.
Rate-time Profiles for Propylene Polymerization using Pretreated Catalysts A, B, C, D, and E. Polymerization Conditions: [Ti] = 0.04–0.08mmol dm^{-3}; [Al] = 8.0 mmol dm^{-3}; Temp = 50 °C; Donor = none (for Catalyst A & D); for B, C & E: [Al]/[Si] = 20; [Si]/[Ti] = 7.5–10; H_2 = 0.25–0.50 bar; Pressure = 6 bar; Polymerization Time = 1 h; vol diluent = 250 cm^3.

value. Catalyst D shows an instantaneous rate of polymerization which increases gently during the first 20 min to reach a maximum value which then decreases very gently. Catalysts C and E show lower but remarkably constant rates of polymerization. Only Catalyst B shows instability during the first 10 min of polymerization.

Active Centre Determination

Active centre concentrations were determined using quenching by means of tritiated ethanol. However since the ethanol contained both tritiated and non-tritiated molecules, where $H = {}^1H$ = hydrogen; $T = {}^3H$ = tritium, the following reactions will take place:

$$\text{Ti}^*\text{-P} + \text{EtOT} \xrightarrow{k_T} \text{Ti-OEt} + \text{P-T}$$

$$\text{Al-P} + \text{EtOT} \xrightarrow{k'_H} \text{Al-OEt} + \text{P-H}$$

$$\text{Ti}^*\text{-P} + \text{EtOH} \xrightarrow{k_H} \text{Ti-OEt} + \text{P-H}$$

$$\text{Al-P} + \text{EtOT} \xrightarrow{k'_T} \text{Al-OEt} + \text{P-T}$$

Hence

$$[\text{MPB}]_t = [\text{MPB}]_0 + \int_0^t R_{ta}\, dt$$

$$\therefore [\text{MPB}]_t = [\text{MPB}]_0 + R_{ta}\, dt$$

For each catalyst system, the correction factor, K, for the kinetic isotope effect due to the slower rate of reaction of EtOT compared to EtOH was determined via the slow addition method.[6]

$$K = \frac{\text{Specific activity of polymer} \times \text{Yield (slow addition)}}{\text{Specific activity of polymer} \times \text{Yield (fast addition)}}$$

Values of K so obtained were as follows.

Catalyst:	A	B	C	D	E
K:	2.1	1.5	2.3	1.3	2.0

A typical MPB versus time pilot for Catalyst A is shown in Figure 2.

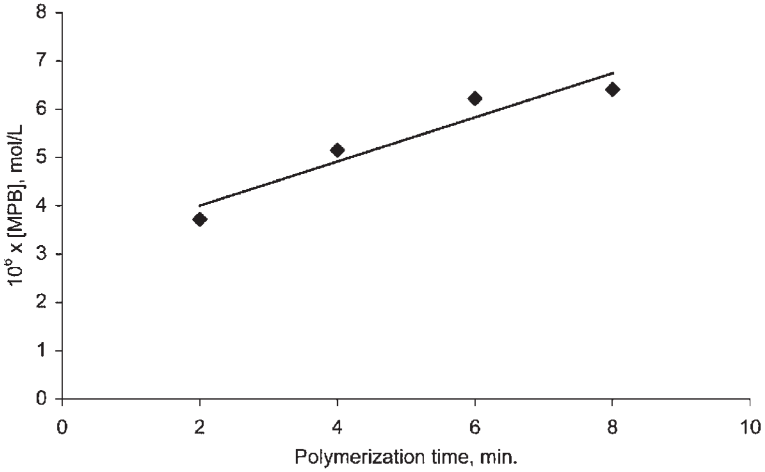

Figure 2.
Variation of metal-polymer bond concentration with polymerization time for Catalyst A.

Extrapolation to $t = 0$ yields $[MPB]_0$ from which C_0^* may be calculated. Relevant values of C_0^* together with k_p values are listed in Table 2.

It is evident that the higher polymerization activities shown by Catalysts A and D arise because of their higher concentrations of active centres rather than any increase in k_p values which remain relatively constant and more or less within experimental error, estimated at ±20%.

Polymer Fractionation

Samples of quenched polymer (0.5–2 g) after different polymerization times were subjected to Soxhlet extraction with boiling heptane for 20 h to remove the substantially atactic polymer.

Table 2.
Propagation Rate Coefficients and Active Centre Determinations at 50 °C.

Catalyst	R_p		% C_o^*/mol (mol Ti)$^{-1}$	k_p/L mol^{-1} s^{-1}
	g PP (mmol Ti)$^{-1}$ h^{-1}	mol $C_3=$ (mol Ti)$^{-1}$ s^{-1}		
A	4552	30.1	7.5	201
B	2889	19.1	3.9	245
C	2030	13.4	2.9	231
D	3921	25.9	5.3	244
E	1900	12.6	2.2	284

Table 3.
Active Centre Determinations from Fractional Polymers.

Catalyst	Type of fraction	I.I. %	% C_o^*/mol (mol Ti)$^{-1}$	k_p/L. mol^{-1}. s^{-1}
A	Insoluble	93.5	6.0	247
	Soluble	6.5	1.5	64
B	Insoluble	93.4	2.7	338
	Soluble	6.6	0.8	83
C	Insoluble	90.1	2.2	278
	Soluble	9.9	0.7	83
D	Insoluble	96.8	3.9	325
	Soluble	3.2	1.2	34
E	Insoluble	91.3	1.6	273
	Soluble	8.7	0.5	80

Table 3 lists I.I. values, calculated from the difference between values for total polymer and insoluble polymer, together with relevant active centre and propagation rate coefficient values.

As expected[7] the calculated k_p values for centres producing soluble polymer (mainly atactic) are much lower than k_p values for centres producing insoluble polymer (mainly isotactic). It is easier, evidently, to produce polymer chains with a helical configuration than to produce polymer molecules with a random configuration.

Morphology Studies

A selection of $MgCl_2$ supported catalysts and polymer samples were studied by means of scanning electron microscope (SEM). Catalyst samples were handled under an inert atmosphere of dried nitrogen. All samples were sputter coated with gold and then viewed using a JEOL, JSM-6300 Scanning Electron Microscope. A SEM micrograph of a representative sample of Catalyst A particles is shown in Figure 3. This picture clearly shows that the catalyst particles have a characteristic spherical shape and a narrow particle size distribution (PSD) in the range 20–60 μm. The SEM micrograph at a higher magnification, Figure 4, shows that the particles have a relatively smooth outer surface.

The same characteristics were found for Catalysts B, C, D and E. However some catalysts showed surfaces containing cracks, e.g., Catalysts A, B, C and D but not Catalyst E.

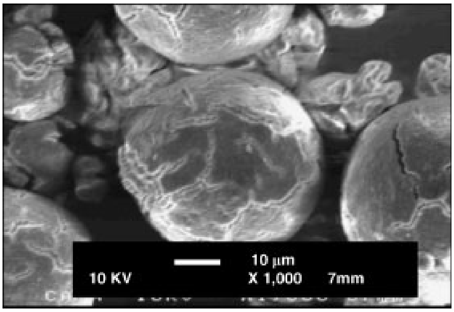

Figure 4.
SEM micrograph of Cat-A.

In general the polymers replicated the spherical nature of the catalyst supports (see Figure 5 and Figure 6).

Conclusions

The higher polymerization activities shown by $MgCl_2$ supported Ziegler – Natta catalysts

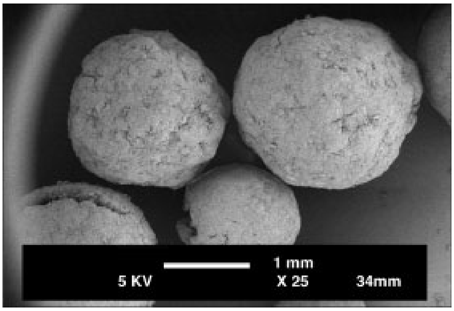

Figure 5.
SEM micrograph of PE.

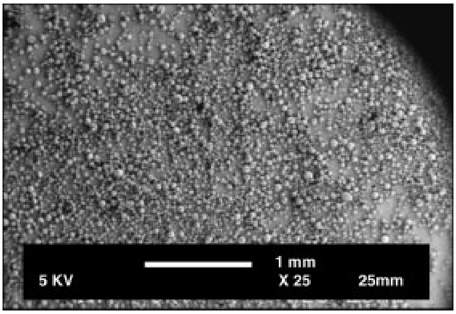

Figure 3.
SEM micrograph of Cat-A.

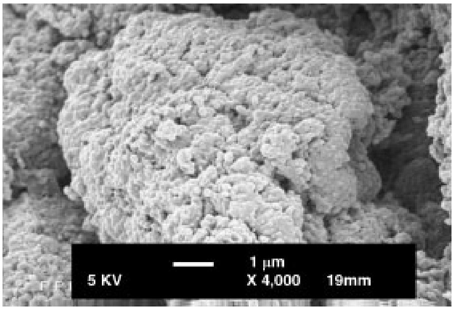

Figure 6.
SEM micrograph of PE.

containing 1,3-diethers arise from increased numbers of stabilized active centres.

Outstanding control of polymer morphology is possible through the use of $MgCl_2$ supported Ziegler – Natta catalysts.

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