Polymerization of Ethylene over Catalysts Composed of Diethylaluminium Chloride and Metal Chlorides

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Polymerization of ethylene took place over catalytic systems composed of Et_2AlCl combined with metal chlorides in the absence of transition metal compounds, indicating that the Al–C bonds are the polymerization centres.

The activity of Ziegler–Natta catalysts for olefin polymerization is increased substantially by supporting the Ti compounds on a solid carrier.[1–5] A variety of metal chlorides have been reported as carriers, the most common being $MgCl_2$. The marked improvement in activity resulting from the use of $MgCl_2$ has recently been shown to be attributable to a considerable increase in the propagation rate constant as well as the number of active species.[6,7] In the patent literature[8] Battelle describe catalysts apparently free from transition metals using magnesium or aluminium acetates. It is also well known that organometallic aluminium derivatives effectively catalyse the oligomerization of ethylene.[9] It would be expected, therefore, that high polymerization of ethylene would proceed over such derivatives if the propagation rate constant could be increased to a great extent while the chain-transfer rate constant remained unchanged.

Accordingly we have examined the polymerization of ethylene by using Et_2AlCl combined with such metal chlorides as $MgCl_2$, $AlCl_3$, $ZnCl_2$, PCl_3, and $SnCl_4$. The metal chloride (10 mmol) (except for $SnCl_4$ and PCl_3) was dissolved in refluxing 2-ethylhexan-1-ol (EHA) or tetrahydrofuran (THF) (90 mmol). Immediately before polymerization, heptane or toluene as solvent (15 cm^3), Et_2AlCl (2.0 mmol), and a portion of the metal chloride (0.13 mmol) solution in EHA or THF were introduced into the polymerization vessel under nitrogen. The polymerization of ethylene was carried out at 40 °C for 24 h under an initial pressure of 25 bar in a 100 cm^3 stainless steel reactor equipped with a magnetic stirrer. Polymerization was terminated by adding an excess of dilute hydrochloric acid in methanol. The molecular weight distribution of the polymer was measured at 150 °C by gel permeation chromatography (Shodex LC HT-3) using *o*-dichlorobenzene as solvent. For comparison the polymerization was also examined under the same conditions using Et_2AlCl alone or EtBuMg combined with $MgCl_2$ as catalyst, and also in a glass reactor in place of the stainless steel reactor.

Table 1. Results for ethylene polymerization with the catalytic systems of Et_2AlCl–MCl_x.[a]

Catalytic system	Solvent	$P(C_2H_4)$ /bar	Temp. /°C	Time /h	Reactor	Polymer yield /mg	Molecular weight $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Et_2AlCl	Heptane	25	40	24	Stainless	0	—	—
EtBuMg–$MgCl_2$	"	"	"	"	"	0	—	—
Et_2AlCl–$MgCl_2$	"	"	"	"	"	273	5.3×10^5	2.3
"	"	1	20	72	Glass	41[c]	—	—
"[b]	Toluene	25	40	24	Stainless	143	—	—
"[b]	"	1	20	72	Glass	86[d]	—	—
Et_2AlCl–$AlCl_3$	Heptane	25	40	24	Stainless	67	—	—
Et_2AlCl–$SnCl_4$	Toluene	"	"	"	"	24	—	—
Et_2AlCl–PCl_3	Heptane	"	"	"	"	5	2.6×10^3	1.7
Et_2AlCl–$ZnCl_2$	Toluene	"	"	"	"	3	—	—

[a] Et_2AlCl, 2.0 mmol; EtBuMg, 2.0 mmol; MCl_x, 0.13 mmol; EHA, 1.17 mmol; solvent, 15 cm^3. [b] $MgCl_2 \cdot 2THF$ was used in place of $MgCl_2$–EHA. [c] Et_2AlCl, 10 mmol; $MgCl_2$, 0.50 mmol; EHA, 5.85 mmol; heptane, 75 cm^3. [d] Et_2AlCl, 2.0 mmol; $MgCl_2 \cdot 2THF$, 1.0 mmol; heptane, 15 cm^3.

All the catalytic systems were apparently soluble in the solvent. Table 1 gives the results for the polymerization. No polymer was obtained using Et_2AlCl alone or EtBuMg combined with $MgCl_2$ whereas the catalytic systems composed of a combination of Et_2AlCl and the metal chlorides gave a linear polyethylene of high molecular weight with a relatively narrow polydispersity of 1.7—2.3. This narrow polydispersity of the molecular weight may arise because the catalytic systems are homogeneous. Among the metal chlorides investigated, $MgCl_2$ showed the highest activity.

The present results strongly suggest that the propagation reaction takes place by the insertion of ethylene monomers, co-ordinated or not, into the Al–C bonds, and that the propagation rate constant is markedly increased by modifying Et_2AlCl with the metal chlorides.

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