Organometallics in ethylene polymerization with a catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$: 2. Polymerization process in pseudo-solution

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A study has been made of ethylene polymerization in pseudo-solution with a catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$ in the presence of hydrogen as a regulator of polyethylene molecular weight. The polymerization process in pseudo-solution by adjustment of hydrogen makes it possible to produce polyethylene having a wide range of molecular weights. For this purpose melt indices between 0°–50°C/min are desirable and these values are not reached with a suspension type of ethylene polymerization with a catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$. The effect of the molar ratio cocatalyst/catalyst (Al/Ti and Mg/Ti) on the catalyst activity and on the polyethylene molecular weight was studied, together with the content of hydrogen as a regulator of the molecular weight. The catalyst productivity increased to some limiting molar ratio Mg/Ti and Al/Ti and further increase of organometallics in the catalyst system did not influence the polymer molecular weight. In the case of ethylene polymerization with this catalyst combination in the presence of hydrogen, some activation of the catalyst was observed. Two mechanisms, which may account for the activation effect of the hydrogen are discussed.

INTRODUCTION

By the use of catalyst systems containing an organomagnesium cocatalyst it is possible to obtain polyethylene at yields which are high enough to eliminate any necessity for additional purification of the polymer. Generally, with these catalyst systems the resulting polyethylene is of ultramolecular weight[1,2]. Because pronounced active transfer reactions are absent, very high molecular weight products are obtained.

In our earlier paper[3] we reported the use of a catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$ for the preparation of polyethylene of very high molecular weight. We obtained polymer products with limiting viscosity number between 11 and 14 dl/g. We also found that a catalyst complex of $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$ was a very active catalyst for ethylene polymerization.

Using the suspension polymerization conditions with such a catalytic system[4] (polymerization temperatures between 50°–90°C) does not permit us to obtain polyethylene with a wide range of molecular weights. By adjustment of very large amounts of hydrogen (10–60 vol%), used as modifier, a full commercial range of molecular weights has not been covered. At normal polymerization temperatures (50°–90°C) the hydrogen is not an effective regulator of the molecular weight of ethylene polymerization with a catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$.

Higher reaction temperatures permit the realization of a polymerization process in pseudo-solution. Under these conditions the hydrogen favourably affected polymer molecular weight. From the practical viewpoint the attainment of a polymerization process in a pseudo-solution by adjustment of hydrogen makes it possible to prepare polyethylene having a wide range of molecular weights. For this purpose polyethylene melt indices between 0–50 dg/min are desirable and these values are not reached with a conventional suspension type of ethylene polymerization[4].

In order to determine the maximum catalyst productivity of the system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$ used to obtain polyethylene in pseudo-solution with a wide range of molecular weights, experiments were carried out at different molar ratios of cocatalyst/catalyst (Mg/Ti and Al/Ti), using a higher reaction temperature (polymerization process in pseudo-solution) and hydrogen as a regulator of polyethylene molecular weight.

EXPERIMENTAL

As the materials and methods used in this investigation have already been described in our previous paper[5], supplementary data will be given.

The dependence of molar ratios Mg/Ti and Al/Ti on the catalyst productivity of the system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$ and on the polyethylene molecular weights (melt indices) were studied under the following standard conditions: titanium tetrachloride concentration, 0.05 mmol/dm^3; polymerization temperature, 130°C; reaction medium, 1 dm^3 iso-octane; polymerization time, 15 min; total pressure (ethylene + hydrogen), 10 kg/cm^2.

RESULTS AND DISCUSSION

In connection with their importance as solid phase components in the catalyst system for low pressure ethylene polymerization to linear polymers, the catalyst complexes formed

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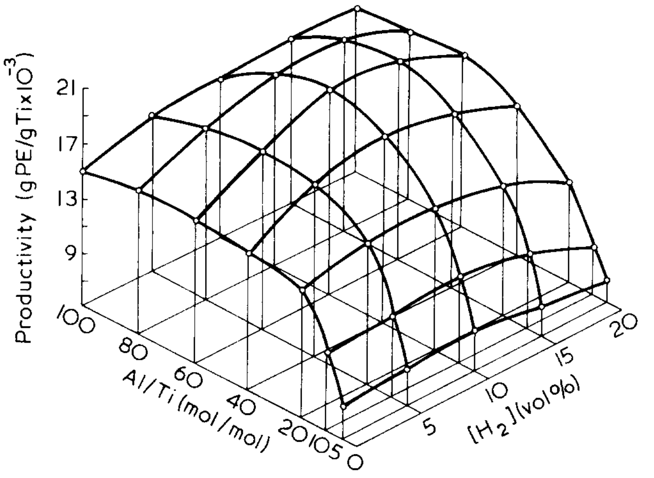

Figure 1 The catalyst productivity vs. Al/Ti molar ratio and amount of hydrogen used (Mg/Ti molar ratio = 6)

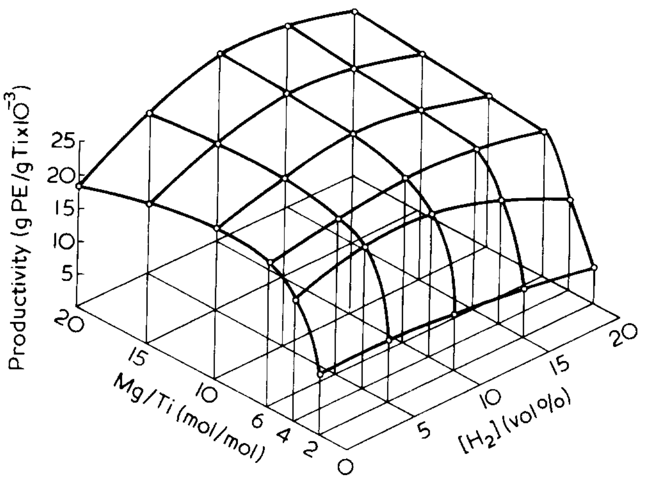

Figure 2 The catalyst productivity vs. Mg/Ti molar ratio and amount of hydrogen used (Al/Ti molar ratio = 40)

from titanium tetrachloride and organometal cocatalysts have frequently been discussed in the literature. Their nature and activity appears to be dependent on many factors, such as the choice of organometal compound, the concentration of reactants, the way the latter are mixed, the nature of the solvent, the duration of the reaction, etc.; but probably one of the most important factors is the molar ratio between titanium tetrachloride and organometallics in the catalyst system[6].

To obtain some information on the influence of the molar ratio cocatalyst/catalyst (Mg/Ti and Al/Ti) on the catalyst activity and on the polyethylene molecular weight, experiments were carried out at standard reaction conditions: fixed concentration of titanium tetrachloride, constant polymerization temperature, the same preparation of catalyst complex, the same previously treated reaction medium (iso-octane).

Figure 1 shows the polymer yield (catalyst productivity in g polyethylene/g titanium) vs. molar ratio Al/Ti and amount of hydrogen used as a chain transfer agent. The polymer yield increased to molar ratio Al/Ti = 40 and above that molar ratio showed practically no dependence on the content of the diethylaluminium chloride in the catalyst system. Analogous results were obtained for the same catalyst combination used for suspension polymerization of ethylene, with the difference that in suspension polymerization the catalyst productivity increased to Al/Ti molar ratio = 10 and then remained constant[5].

In the same manner the effect of molar ratio Mg/Ti on the catalyst productivity is shown in *Figure 2*. It is again seen that above some limiting value of molar ratio cocatalyst/catalyst (in this case above Mg/Ti molar ratio = 6) the polymer yield did not depend on the amount of diphenylmagnesium in the system. The limiting molar ratio for suspension polymerization of ethylene with the same catalyst combination is Mg/Ti = 3 (ref 5).

The comparison of the optimal ratios cocatalyst/catalyst (Mg/Ti and Al/Ti) responsible for the catalyst activity of the system in the suspension process and in the process in pseudo-solution, shows that to prepare catalysts of equal activity the ethylene polymerization in solution demanded a larger excess of organometallics.

As shown by *Figures 3* and *4*, hydrogen affected the polymer molecular weight produced with this three-component system in the ethylene polymerization in pseudo-solution. Under these conditions it could be seen quite readily that in the presence of 5–20 vol% hydrogen the polymer melt indices increased over wide ranges.

However, when the molar ratio Al/Ti increased from 10–100 the melt index at a constant content of hydrogen de-

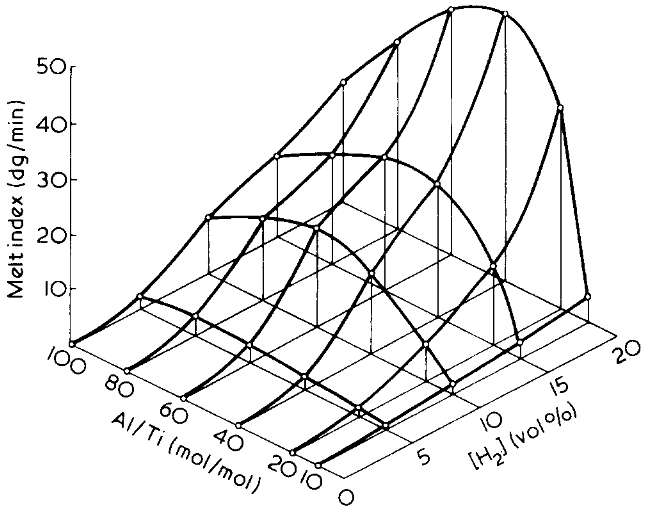

Figure 3 The polyethylene melt index vs. Al/Ti molar ratio and amount of hydrogen used (Mg/Ti molar ratio = 6)

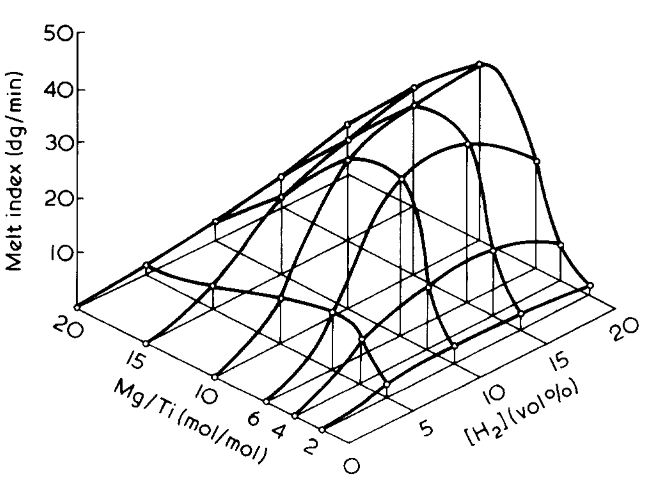

Figure 4 The polyethylene melt index vs. Mg/Ti molar ratio and amount of hydrogen used (Al/Ti molar ratio = 40)

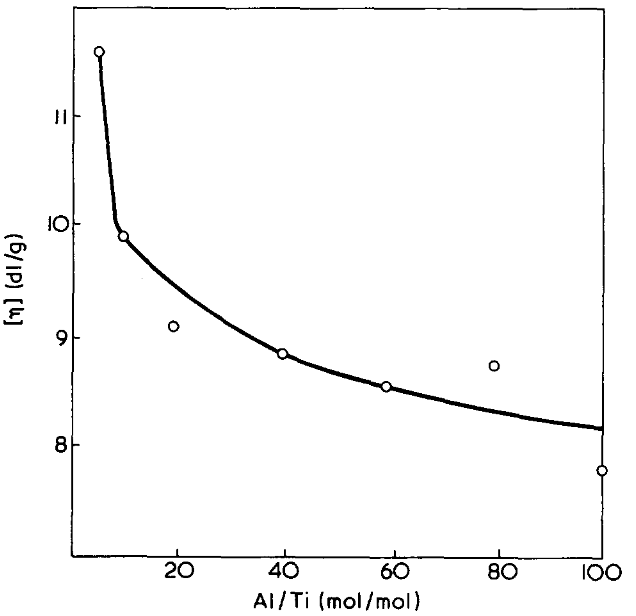

Figure 5 The effect of Al/Ti molar ratio on the polymer limiting viscosity number in the absence of hydrogen (Mg/Ti = 6)

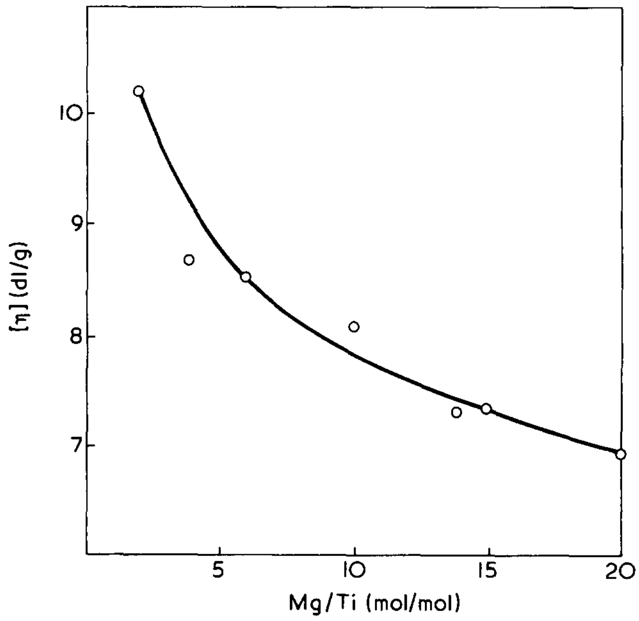

Figure 6 The effect of Mg/Ti molar ratio on the polymer limiting viscosity number in the absence of hydrogen (Al/Ti = 40)

pended on the molar ratio Al/Ti and showed a maximum (*Figure 3*). It is also seen that at a fixed content of hydrogen the polymer melt index depends on the molar ratio Mg/Ti and shows a similar maximum (*Figure 4*).

In the light of these results it will be clear that organometal compounds act as a chain transfer agent when the molar ratio increases to the optimal values. On the other hand at a higher ratio cocatalyst/catalyst (above the optimal values), effects due to organometal compounds acting as an agent in the resulting ligand rearrangement in the octahedral surroundings of the active sites cannot be excluded. We might, therefore, expect compositional and structural changes of the active centres when the amount of organometal cocatalysts in the catalyst system exceeds that of the optimal concentrations.

The influence of molar ratio cocatalyst/catalyst in the absence of hydrogen on the molecular weight is shown in *Figures 5* and *6*. The results in *Figures 5* and *6* clearly show that the polyethylene molecular weight decreased more considerably at molar ratios Al/Ti and Mg/Ti close to the optimal ratios. At higher molar ratios Al/Ti and Mg/Ti organometal compounds actually do not act as active chain transfer agents.

Generally, the presence of hydrogen in the Ziegler–Natta catalyst system reduced the activity of the catalyst. Haward *et al.*[1] reported that with similar magnesium-reduced titanium catalyst systems the activity decreased in the presence of hydrogen, used as a regulator of polyethylene molecular weight.

In this case, for ethylene polymerization with a catalyst combination $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$ in the presence of hydrogen, some activation of the catalyst was observed. An analogous activation effect of hydrogen has been observed by several authors for different Ziegler–Natta catalyst systems used for α-olefin polymerization[7–9]. A number of mechanisms have been offered to explain the activation effect of hydrogen.

We assume that two possible mechanisms may be considered.

(1) At normal temperatures of polymerization (suspension process) in the presence of hydrogen, the resulting catalyst–hydride bond can be considered as a termination step, since this bond will not be immediately available for further chain propagation. At the higher reaction temperatures, the catalyst–hydride bond is not a latent site for polymer propagation and is alkylated.

(2) The chain propagation occurs at a low valence transition metal centre disposed on the solid catalyst surface. The catalyst surface ensures proper distribution of the active sites and proper orientation of the olefin molecules as they are fed into the active centre to produce the polymer chain. The polymer chains grow upon the catalyst surface. In the absence of an active chain transfer agent some of the active sites are 'exposed' for the ethylene insertion to the active centre and some of the sites are 'blocked' and, to a certain extent, are covered with polymer chains growing up from neighbouring active sites.

The use of an active chain transfer agent (hydrogen) during the polymerization step leads to a different picture in the growth reaction. As the polymer chains are desorbed easily in the presence of hydrogen, more active sites are exposed and more monomer is adsorbed on the catalyst surface, to some extent reducing prohibitive physical blocking of the polymerization sites.

It is to be expected that at a higher content of hydrogen the catalyst activity falls off with hydrogen content and this is probably due to further reduction of the ethylene partial pressure in the polymerization system. The second mechanism is in agreement with the results of Boucheron[10].

Quite generally, both proposed mechanisms could conceivably operate together, but these assumptions are being tested.

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