

# Ethylene polymerization with high activity catalysts prepared from titanium tetrachloride and magnesium diene adducts

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Magnesium (isoprene)<sub>2</sub> adducts were prepared in THF and transferred to toluene solutions. The products from the reaction of these solutions with TiCl<sub>4</sub> gave highly active catalysts for ethylene polymerization when used with aluminium trialkyl co-catalysts. Results of polymerizations under various conditions are given. Comparison experiments were carried out with catalysts prepared from magnesium myrcene and magnesium diphenyl butadiene adducts. Reaction products of TiCl<sub>4</sub> and magnesium diene mixtures were separated into soluble and insoluble fractions and analysed.

**Keywords** Polymerization; ethylene; Ziegler catalyst; magnesium adducts; titanium tetrachloride; high activity

## INTRODUCTION

The change from a conventional Ziegler catalyst producing 1500 g polyethylene/gram Ti to high activity catalysts producing in excess of 5000 kg/gram, the so-called second generation catalysts<sup>1,2</sup>, requires an increase in the intrinsic activity of a given site, an increase in the number of active sites or both. Methods used to increase the number of active sites include ball-milling and absorption or deposition of transition metal compounds on a support. Wilchinsky<sup>3</sup> has shown that milling produces an increase in activity, in propylene polymerization, with decreasing crystallite size for a TiCl<sub>3</sub><sup>1/3</sup>AlCl<sub>3</sub> catalyst, until the crystallites reach about 50 Å. Supported catalysts comprise a much wider variety of systems. One of the earliest, although of relatively low activity by present day standards, was the Cabot<sup>4</sup> catalyst consisting of a transition metal compound deposited on a metal oxide. Solvay and Cie<sup>5</sup> reported much improved catalysts based on Mg(OH)Cl as a reactive support and other companies followed with magnesium compounds ranging from inert MgCl<sub>2</sub><sup>6</sup> to reactive organomagnesiums<sup>7,8</sup> where MgCl<sub>2</sub> may be formed *in situ*. High activity catalysts other than those based on transition metal/magnesium include tetra-*n*-butyl transition metal complexes supported on alumina or silica patented by ICI<sup>9</sup>, and Union Carbide's supported silylchromate catalyst<sup>10</sup> which is more akin to the Phillips chromia-alumina catalyst than to a Ziegler type.

Haward *et al.*<sup>11</sup> reporting in detail on the Shell catalysts obtained by reacting Grignard compounds with TiCl<sub>4</sub>, showed that increase in activity for ethylene polymerization resulted from an increase in the number of active sites from about 1% of total added titanium in a standard Ziegler catalyst<sup>12</sup>, to as many as 50% in the new system. It was also shown<sup>13</sup> that limited quantities of ethers, including THF, did not affect the yield of polymer. From this it seemed possible that the scope of organomagnesium reduced TiCl<sub>4</sub> systems could be extended by using

a variety of magnesium compounds which could be prepared in ethers and transferred to hydrocarbon solvent with subsequent removal of uncomplexed ether. Suitable materials for initial experiments in this direction were the magnesium isoprene and magnesium butadiene adducts recently described<sup>14</sup> in the literature. According to Yasuda *et al.* the 1:2 Mg:isoprene adduct was easily prepared under mild conditions and was readily soluble in toluene. The 1:2 ratio of magnesium to tetrahydrofuran in the adduct also meant that when it was reacted with TiCl<sub>4</sub> at 1:1 or 1.5:1 ratios, the THF:Ti ratios would still be within the range which Haward *et al.* found acceptable. The macrocyclic nature of the 1:2 Mg:isoprene adduct<sup>14b</sup> differentiated it from other organomagnesium reagents which had been used in analogous catalyst preparations.

## EXPERIMENTAL

Polymerizations were carried out at atmospheric pressure in glass 4-necked flanged 700 ml reactors sealed with Teflon gaskets. The reactors were equipped with 4-bladed paddle stirrers run at 1000 rpm, gas/solvent inlet tube, outlet to a paraffin oil bubbler via a reflux condenser, thermometer and catalyst addition point.

All glassware was heated to 130°C for 4 h, assembled hot and allowed to cool under nitrogen. 500 ml of dry air-free isooctane solvent was added to the reactor under nitrogen pressure and then saturated with purified monomer for 30 min prior to catalyst addition. Catalyst components were added by syringe. Monomer was fed to the reactor via a calibrated GAP flow meter and vented through the bubbler. Monomer uptake was measured by adjusting the input flow to give zero flow at the bubbler and noting the flow rate at set intervals. The total monomer input agreed well with the final yield of polymer. Polymerization temperature was controlled as required, by Isomantle heaters or acetone/Drikold cooling bath.

Polymerization grade ethylene and propylene were purified by passage through a column of hydrogen reduced BASF 3-11 catalyst and successive columns of activated alumina and 3-A molecular sieves, and contained <5 ppm H<sub>2</sub>O and <2 ppm O<sub>2</sub>. Hydrocarbon solvents were dried over sodium lead alloy and distilled from lithium butyl. After peroxide removal with ferrous sulphate and preliminary drying, THF was further dried over CaH<sub>2</sub> and distilled onto molecular sieves. Isoprene (BDH) was dried over CaH<sub>2</sub> and distilled through columns containing KOH, to remove inhibitor, and 3-A molecular sieves for final drying. All distillations were carried out under dry nitrogen. Aluminium alkyls (Schering AG) and TiCl<sub>4</sub> (BDH) were used as received and diluted as required.

Chloride was determined potentiometrically after hydrolysis of the sample in dilute nitric acid and removal of solvent. Magnesium in TiCl<sub>4</sub>/magnesium diene reaction products was determined after hydrolysis of samples in toluene with dilute H<sub>2</sub>SO<sub>4</sub>. After boiling to remove volatile organic material, the aqueous solution was neutralized, buffered to pH 10 and filtered to remove titanium hydroxide. The final solution was titrated against EDTA using Solochrome Black 6B indicator. Titanium was determined by the peroxide method. Simple hydrolysis of toluene samples with dilute H<sub>2</sub>SO<sub>4</sub> left some titanium in the organic phase. Boiling to remove toluene precipitated some titanium and was also unsatisfactory. The method finally adopted was to evaporate toluene from a sample in a crucible and to fuse the residue with potassium pyrosulphate before applying the peroxide method. Ti(III) was determined by titration of a stirred mixture of toluene solution and 1 N H<sub>2</sub>SO<sub>4</sub> containing 4 g K CNS, with ferric ammonium sulphate under nitrogen. Immediately after hydrolysis the initial hydrolysed solution was often deeply coloured but became more or less colourless towards the end point. The method was checked against known TiCl<sub>3</sub> samples.

The 1:2 magnesium isoprene adduct was prepared according to the method of Yasuda<sup>14b</sup>. The product was not isolated from the THF solvent but was diluted with toluene and heated to distill off THF and any residual isoprene. After the bulk of the THF had been removed, further toluene was added and the distillation repeated. A small amount of precipitate formed and traces of metallic magnesium were deposited on the walls of the flask. A similar procedure using vacuum distillation to permit use of lower temperature resulted in considerably more decomposition. The yellow toluene solution was filtered and analysed for active magnesium before use. Residual THF levels were very variable ranging from 1.1:1 THF:Mg to 3.2:1.

Magnesium myrcene and magnesium diphenylbutadiene adducts were initially prepared according to Baker *et al.*<sup>15</sup> using FeCl<sub>3</sub> and ethyl bromide as catalysts. Reactivity using magnesium turnings, for ease of separation, was low and it was found that improved catalyst free products could be obtained by using residual magnesium turnings from previous magnesium isoprene adduct preparations. This active magnesium was thoroughly washed with THF before adding THF and the required quantity of myrcene or diphenylbutadiene. Stirring in a sealed bottle at 20°C for 3 days gave 35–40% diene conversion. Transfer to toluene was achieved as described above but distillation under vacuum was used to remove THF. Residual diene remained in the toluene

solution. Toluene soluble material was filtered off but with diphenylbutadiene, it was difficult to remove sufficient THF without extensive precipitation, leading to rather dilute toluene extracts.

Reaction between TiCl<sub>4</sub> and the magnesium adducts was carried out in sealed, crown capped bottles. The calculated quantity of adduct solution in toluene was syringed dropwise into a dilute solution of TiCl<sub>4</sub> in toluene in a bottle containing several grams of glass balls. The exothermic reaction produced a dark brown suspension of solid in a brown or orange solution. The bottles containing the catalyst were rolled for several hours to disperse material adhering to the bottle walls.

Unless otherwise specified the catalyst used was prepared from magnesium (isoprene)<sub>2</sub> and TiCl<sub>4</sub> at a 1.5:1 molar ratio and contained THF:Ti in a ratio of 3.5:1.

## RESULTS AND DISCUSSION

In initial experiments on ethylene polymerization using AlEt<sub>3</sub> as cocatalyst at 50°C, four catalysts were compared which differed only in the amount of THF present, i.e. THF:Ti equal to 1.4:1, 3.5:1, 2.0:1 and 3.5:1. Using 0.2 mM Ti/litre and 8 mM/litre of AlEt<sub>3</sub>, yields obtained in one hour were 45.1 g, 46.3 g, 35.0 g and 59.4 g respectively. There was no correlation between yield and THF level but it was observed that, perhaps fortuitously, the yields were inversely related to the temperatures at which THF was removed during transfer of the magnesium isoprene adduct to toluene, which were 80°, 75°, 110° and 20°C (vacuum) respectively.

Haward<sup>13</sup> showed that for Grignard reduced TiCl<sub>4</sub>, the yields with higher aluminium alkyl cocatalysts were 4–5 times greater than for AlEt<sub>3</sub> or AlEt<sub>2</sub>Cl. Direct comparison of ethylene polymerizations carried out with magnesium isoprene treated TiCl<sub>4</sub> for 1 h at atmospheric pressure gave quite a different order of reactivity with yields of 46 g, 6 g, 30 g and 31 g produced with AlEt<sub>3</sub>, AlEt<sub>2</sub>Cl, AlBu<sup>n</sup><sub>3</sub>, and AlBu<sup>t</sup><sub>3</sub>.

The effect of temperature on rate of ethylene polymerization is shown in *Figure 1*. Up to 50°C the rate increases initially but soon reaches a steady state. At higher temperatures the rate increases as before but reaches a maximum and then decreases rapidly. An Arrhenius plot for the lower temperatures (*Figure 2*) using the steady state rates gives an overall activation energy of 13.6 kcal, almost identical to that found by Berger and Grieveson<sup>16</sup>, for  $\gamma$ -TiCl<sub>3</sub>/AlEt<sub>2</sub>Cl catalyst. Their results differ however, in that although the rate decreases at higher temperatures, the formation of a steady state was apparently retained. Both Berger<sup>16</sup> and Haward<sup>11</sup> maintain that the higher temperature behaviour is due to a decrease in the ethylene concentration in solution to below the level required to balance the increase in ethylene required for a rate increase, i.e. ethylene starvation, rather than destruction of active centres.

At a constant titanium level, polymerizations were carried out with ethylene at 50°C with aluminium:titanium ratios from 5:1 to 80:1. The results are shown in *Figure 3*. Yield increased throughout the range of alkyl concentrations although the rate of increase decreased markedly at high levels. It is likely that initially the number of active sites increases rapidly with alkyl concentration but the rate falls off as all the suitable titanium atoms react. Berger<sup>16</sup> observed that rate of ethylene polymerization with the TiCl<sub>3</sub>/AlEt<sub>2</sub>Cl catalyst

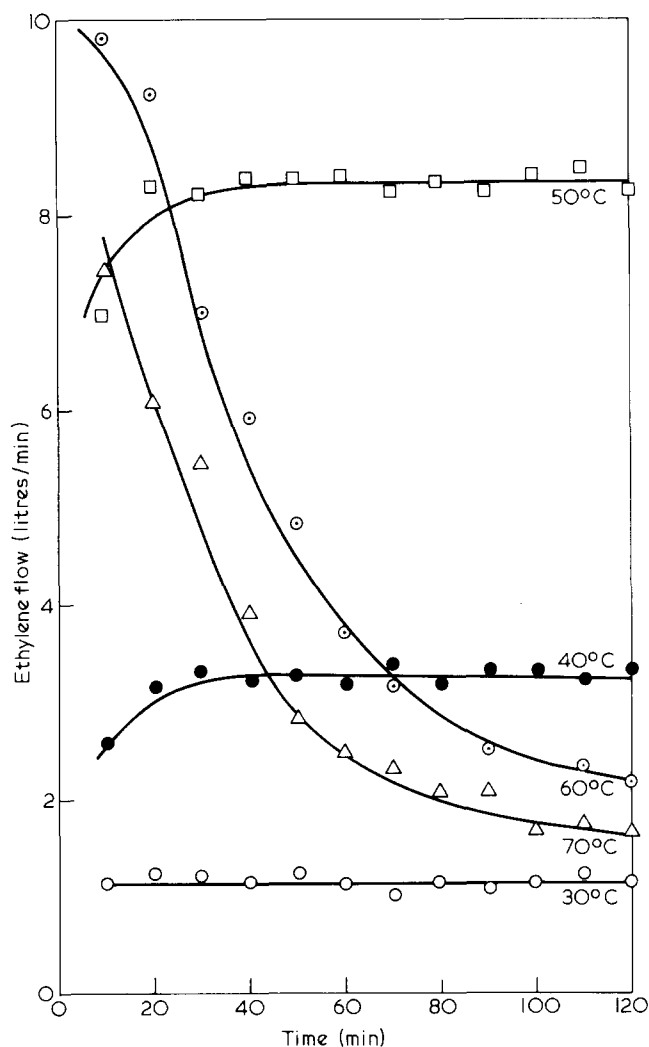


Figure 1 Ethylene flow versus time.  $\text{TiCl}_4/\text{Mg}(\text{isoprene})_2$  catalyst.  $\text{Ti} = 0.2 \text{ mM l}^{-1}$ ;  $\text{AlEt}_3 = 8.0 \text{ mM l}^{-1}$

was independent of alkyl concentration above 1 mM/litre while Fukui<sup>17</sup>, with the catalyst  $\text{TiCl}_3/\text{AlEt}_3$ , obtained an increase in rate with increase in alkyl concentration similar to that found in the present work.

A further series of experiments was made where the  $\text{AlEt}_3:\text{Ti}$  ratio was kept constant but the overall catalyst level was varied (Figure 4). An Al:Ti ratio of 5:1 was used, rather than the standard 40:1 previously adopted, in order to restrict the amount of  $\text{AlEt}_3$  required at high catalyst levels. At this ratio, steady state polymerization was not maintained and after the initial increase, rates slowly declined. The yields did not fall off at high catalyst levels as predicted on the basis of increasing mass transfer control.

A 'maximum kinetic rate of polymerization' of 30–40 kg/g  $\text{TiCl}_3/\text{h}/\text{atmosphere}$  of ethylene has been calculated by Haward for the Grignard based catalyst and at a practical level of operation 2.5–3.5 kg/g  $\text{TiCl}_3/\text{h}/\text{atmosphere}$  of polymer was obtained using a 50/50 ethylene hydrogen mixture at 80°C. Using the magnesium isoprene based catalyst with ethylene at 50°C, 3.3 kg polymer/g  $\text{TiCl}_3/\text{h}/\text{atmosphere}$  was obtained at 0.2 mM/litre Ti and 4.0 kg at 0.05 mM/litre Ti. Allowing for the difference in polymerization temperature and the reduction in yield due to hydrogen, the two catalysts are of comparable activity. An increased quantity of polymer could obviously be obtained with longer polymerization

time, as rates are evidently constant with time, and with increased pressure.

Haward<sup>18</sup> reported the polymerization of propylene with the Grignard reduced  $\text{TiCl}_4$  catalyst. As expected for a catalyst containing brown  $\text{TiCl}_3$  with little or no crystalline ordering, the isotacticity of the polypropylene was low, amounting to about 40% in agreement with our

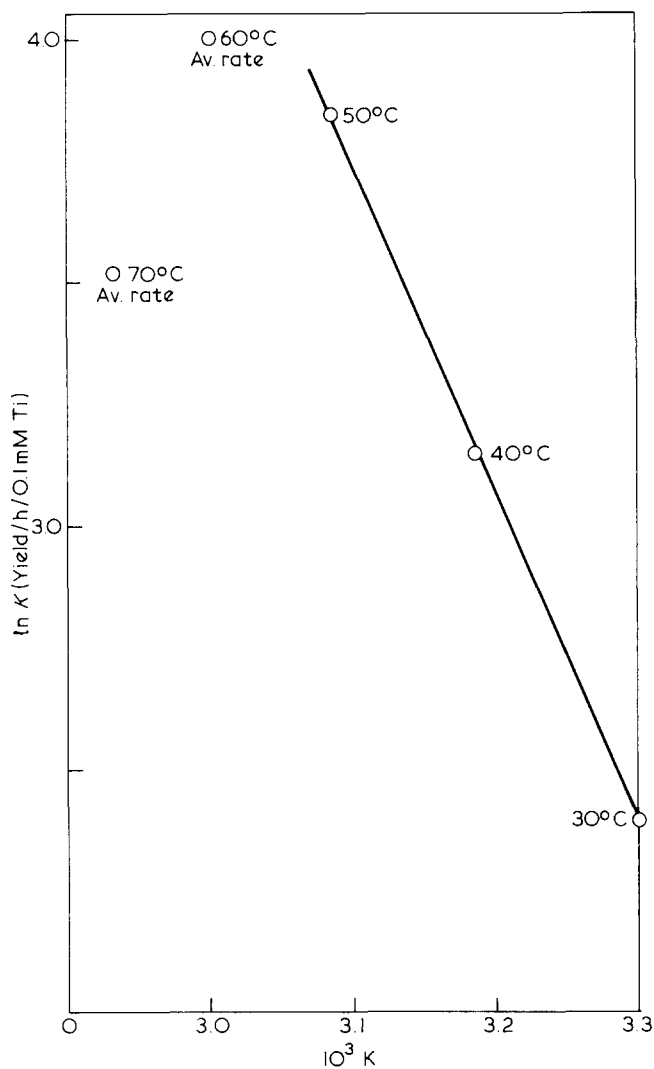


Figure 2  $\ln K$  with increasing temperature.  $\text{TiCl}_4/\text{Mg}(\text{isoprene})_2$  catalyst.  $\text{Ti} = 0.2 \text{ mM l}^{-1}$ ;  $\text{AlEt}_3 = 8.0 \text{ mM l}^{-1}$

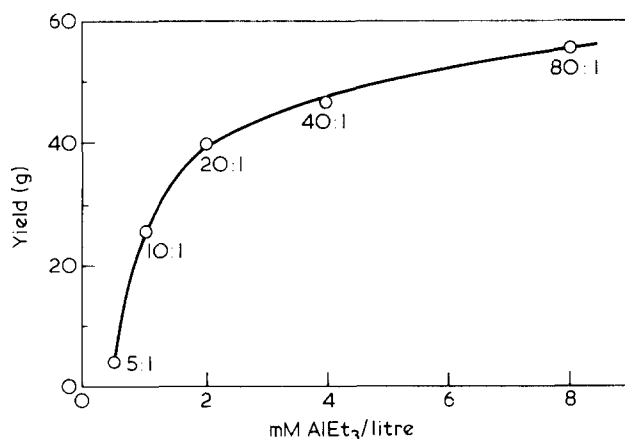


Figure 3 Yield versus mM  $\text{AlEt}_3$ .  $\text{TiCl}_4/\text{Mg}(\text{isoprene})_2$  catalyst.  $\text{Ti} = 0.2 \text{ mM l}^{-1}$ ; temperature = 50°C; time = 1 h

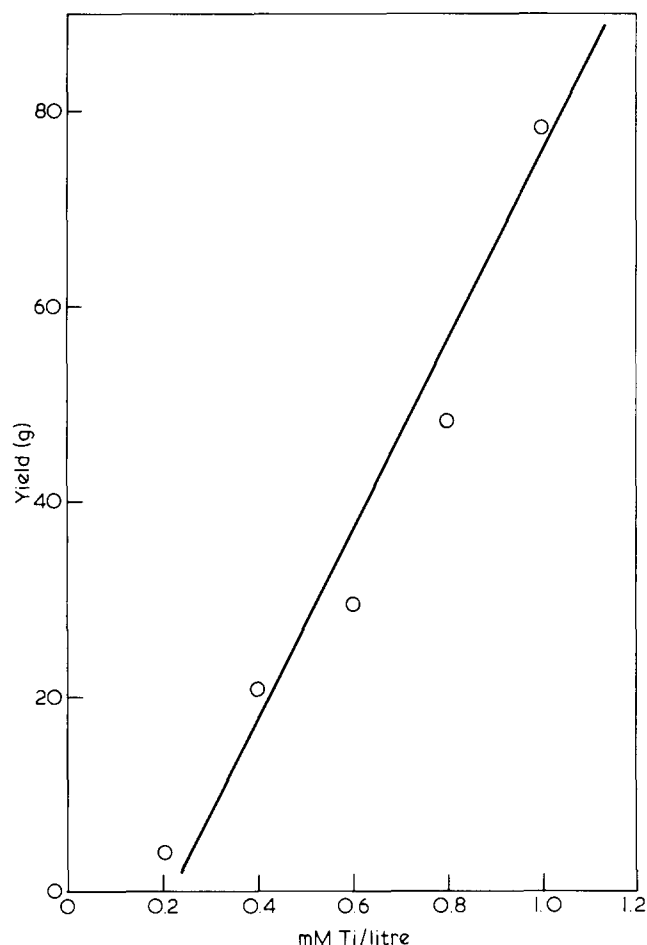


Figure 4 Yield versus mM Ti.  $\text{TiCl}_4/\text{Mg}$  (isoprene) $_2$  catalyst.  $\text{AlEt}_3:\text{Ti} = 5:1$ ; temperature =  $50^\circ\text{C}$ ; time = 1 h

own findings with the corresponding supported Grignard/ $\text{TiCl}_4$  system<sup>8</sup>. It was surprising therefore, to find that the reaction product from the magnesium isoprene adduct had no activity for propylene polymerization even at very high catalyst levels. This may be attributed to the presence of THF in the latter catalyst which could block the small number of active sites ( $\approx 3\%$  of total Ti) available for propylene polymerization<sup>18</sup>. Although not active towards propylene, the magnesium isoprene system did copolymerize ethylene and propylene giving a moderate yield of 36 g blocky polymer in 2 h using 8 mM  $\text{AlEt}_3$ /litre and 0.2 mM/litre Ti at  $50^\circ\text{C}$ . With an ethylene propylene input ratio of 1:1.33 by volume a 60/40 copolymer was obtained.

The work reported so far was based on a catalyst prepared at a magnesium:titanium ratio of 1.5:1. In Table 1, polymer yields for other ratios are given for the magnesium (isoprene) $_2$  adduct and compared with results for magnesium myrcene and magnesium diphenylbutadiene (DPB) adducts, together with the  $\text{Ti}^{3+}$  content of the respective catalysts. The myrcene catalyst proved to be extremely active at a high Ti:Mg ratio. Ti(111) contents were relatively low even with high Mg:Ti ratios. Other workers have reported complete reduction to Ti(111) with Grignard based catalysts, and even some further reduction to Ti(11) at lower ratios. The effect of increasing THF levels in the catalyst with increasing proportion of magnesium adduct is reflected in the lower yield of polymer. At Ti:Mg ratios of 1:2 and 1:3 for example, the

Ti:THF ratios were of the order of 1:6 to 1:9. Free myrcene and diphenylbutadiene in the catalyst did not appear to have much effect.

Most reactions between magnesium diene adducts and  $\text{TiCl}_4$  were carried out at ambient temperature and resulted in satisfactory catalysts. It was suspected, however, that low temperature preparations would give improved activity as any organotitanium species formed would have a longer life time with more controlled decomposition, and over-reduction of titanium would be eliminated. The results of a series of experiments using catalysts prepared at lower and higher temperatures are given in Table 2 for ethylene polymerization and show that  $0^\circ\text{--}20^\circ\text{C}$  is the optimum range.

One other variable which was examined was the order of mixing the magnesium adduct and the  $\text{TiCl}_4$ . Normally, the magnesium solution was added to the titanium, to control reduction by retaining an excess of titanium chloride. Since it had been found that reduction to Ti(111) was incomplete under these conditions, the reverse order of addition was expected to give greater reduction and hence greater activity. In fact there was a dramatic yield decrease in polymerizations with the catalyst prepared in the latter manner. Under comparable conditions the reduction was about 65% and 60% for magnesium (isoprene) $_2$  and magnesium diphenylbutadiene respectively with no effect on Ti(111) content.

The polyethylenes described here were all prepared in the absence of a molecular weight regulator, such as hydrogen, and hence had very high molecular weights. However it was possible to get an indication of the effect of

Table 1

Catalyst	Ti : Mg Ratio	Yield (g h <sup>-1</sup> )	Ti (111) (%)
$\text{TiCl}_4/\text{Mg}$ (isoprene) $_2$	2 : 1	42	61
"	1 : 1	48	87
"	1 : 1.5	29	89
"	1 : 2	16	90
"	1 : 3	2	87
$\text{TiCl}_4/\text{Mg}$ DPB	1 : 1	16	76
"	1 : 1.5	39	78
"	1 : 2	7	79
$\text{TiCl}_4/\text{Mg}$ myrcene	2 : 1	49	56
"	1 : 1	8	71
"	1 : 2	0	64

$\text{AlEt}_3 = 8$  mM/litre  $\text{TiCl}_4/\text{Mg}$  isoprene and  $\text{TiCl}_4/\text{Mg}$ DPB = 0.1 mM/litre  
Temp. =  $50^\circ\text{C}$ .  $\text{TiCl}_4/\text{Mg}$  myrcene = 0.05 mM/litre

Table 2

Catalyst	Ti : Mg Ratio	Temp. of mixing ( $^\circ\text{C}$ )	Yield/h (g)	Ti (111) (%)
$\text{TiCl}_4/\text{Mg}$ (isoprene) $_2$	1 : 1	-25	23.4	85
"	1 : 1	0	34.9	86
"	1 : 1	+20	52.6	86
"	1 : 1	+40	19.7	83
$\text{TiCl}_4/\text{Mg}$ DPB	1 : 1	-25	10.4	83
"	1 : 1	0	14.5	86
"	1 : 1	+25	11.5	87
"	1 : 1	+40	7.7	83

Ti = 0.1 mM/litre.  $\text{AlEt}_3 = 8$  mM/litre. Polymerization at  $50^\circ\text{C}$

certain parameters on molecular weight by measuring melt flow index using a 21.6 kg weight although the flows even with this loading were extremely low. Results in Table 3 show an increase in flow with increase in AlEt<sub>3</sub>:Ti ratio and with increase in temperature of polymerization. Flow increased for samples from the first 30 min of polymerization and then became steady.

Catalysts prepared with all magnesium diene catalysts at a ratio of Mg:TiCl<sub>4</sub> of 1:2 settled rapidly to give a brown solid and clear orange solution. These could be easily separated by decantation. At 1:1, 1.5:1 and 2:1 ratios of Mg:Ti, the solid remained suspended for long periods but could be filtered off using a No. 4 sinter. In the case of the 2:1 catalyst the filtrate was dark brown. (Reactions where the magnesium adduct contained an excessive amount of residual THF tended to produce a sticky brown residue which could not be easily separated.) The separated solids when reslurried in toluene had the same order of catalytic activity as the original mixtures and produced fine powdery polymers. The filtrates were either completely inactive or produced a gram or two of stringy polymer.

The chemical analysis for inorganic elements is given in

Table 3

MFI @ 21.6 kg/190°C	Ti conc. (mM/litre)	Al conc. (mM/litre)	Temp. of polymerization (°C)	Polymerization time (min)
0.009	0.2	16	50	60
0.006	0.2	8	50	60
0.003	0.2	4	50	60
0.002	0.2	2	50	60
0.001	0.2	1	50	60
0.000	0.2	8	30	60
0.000	0.2	8	40	60
0.006	0.2	8	50	60
0.036	0.2	8	60	60
0.106	0.2	8	70	60
0.033	0.2	8	50	15
0.021	0.2	8	50	30
0.009	0.2	8	50	60
0.008	0.2	8	50	90
0.010	0.2	8	50	120

Table 4

Catalyst	Soluble fraction				Insoluble fraction				
	Ti : Mg (Ti in mM/ml)	Ti : Cl	Ti : Cl after correction for MgCl <sub>2</sub>	Ti <sup>3+</sup>	Ti : Mg (Ti in mM/ml)	Ti : Cl	Ti : Cl after correction for MgCl <sub>2</sub>	Ti : Cl after correction for RMgCl	Ti <sup>3+</sup>
TiCl <sub>4</sub> /Mg isoprene 2 : 1	1 : 0 (0.0038)	1 : 2.9	—	0	1 : 0.51 (0.07)	1 : 4.1	1 : 3.1	1 : 3.5	64%
1 : 1	1 : 0 (0.006)	1 : 2.2	—	63%	1 : 1.24 (0.029)	1 : 4.5	1 : 2.2	1 : 3.3	76%
1 : 2	1 : 0.7 (0.018)	1 : 1.3	1 : 0	84%	1 : 2.6	1 : 5.3	1 : 0.2	1 : 2.8	86%
TiCl <sub>4</sub> /Mg myrcene 2 : 1	No Mg or Ti	—	—	—	1 : 0.5 (0.046)	1 : 4	1 : 3	1 : 3.5	56%
1 : 1	1 : 0.01 (0.006)	1 : 2.3	1 : 2.1	52%	1 : 1.1 (0.035)	1 : 4.3	1 : 2	1 : 3.2	71%
1 : 2	1 : 0.72 (0.039)	1 : 1.7	1 : 0.4	64%	1 : 11.4	1 : 29	1 : (2.3)	—	—

Table 4 for magnesium isoprene and magnesium diphenylbutadiene catalysts at various ratios.

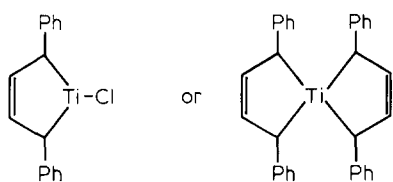
The orange to yellow solutions obtained by filtering reactions at 2:1 and 1:1 Ti to Mg ratios contained virtually no magnesium but the dark brown filtrate obtained at 1:2 contained a considerable quantity of both magnesium and titanium. It was suspected that colloidal material was passing through the sinter in the latter separation. The surprising feature of the solutions was the low chlorine to titanium ratio and high Ti (III) content. This suggests some kind of complex formation either with the myrcene or isoprene dimer and THF. Normally, hydrocarbon soluble titanium complexes of ethers are associated with Ti (IV) but even then solubility is low (c.f. TiCl<sub>4</sub>·2THF). Corresponding Ti (III) complexes tend to be associated and insoluble. Recently it has been shown<sup>19</sup> that phosphine stabilized, chloride free complexes can be readily obtained from Mg (butadiene)·2THF and TiCl<sub>4</sub>. Some are soluble in hexane but all are based on zero valent titanium.

The analytical results for the insoluble brown solids pose the same kind of problem. All the information available from the literature indicates that these products should contain amorphous TiCl<sub>3</sub>, or TiCl<sub>3</sub> and TiCl<sub>2</sub>, intimately mixed with MgCl<sub>2</sub>. In accordance with Haward's work, Zakharov *et al.*<sup>20</sup> state that reduction of TiCl<sub>4</sub> with BuMgCl produces TiCl<sub>3</sub> and MgCl<sub>2</sub> while Petkov<sup>21</sup>, using a rather complex catalyst prepared from TiCl<sub>4</sub>, AlEt<sub>2</sub>Cl and Mg(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> obtained TiCl<sub>3</sub> containing about 25% TiCl<sub>2</sub> at a ratio of Mg:Ti equal to 2:1. In complete contrast the reaction of TiCl<sub>4</sub> with MgCl<sub>2</sub> itself<sup>6d</sup> results in very little fixation of titanium unless the mixture is ball-milled. The breakdown of the crystal structure of MgCl<sub>2</sub> under these conditions allows increased TiCl<sub>4</sub> interaction and formation of an active catalyst containing Ti (IV).

The overall Ti:Cl ratio for the solids from magnesium dienes can be explained easily only if the product is a mixture of TiCl<sub>3</sub> and RMgCl. For Mg(isoprene)<sub>2</sub> products, extracting the amount of chloride required for RMgCl from the overall ratios leaves Ti:Cl ratios of 1:3.5, 1:3.3 and 1:2.8 which agrees well with the expected order of reduction for the 2:1, 1:1 and 1:2 TiCl<sub>4</sub>:Mg diene

reaction ratios and with the order, if not the exact value, for Ti (111) content. Organic material was found in the brown solids but could not be quantitatively examined since it appeared to be partially polymerized. The Mg (myrcene) results at 2:1 and 1:1 Ti:Mg reaction ratio corrected for RMgCl give Ti:Cl ratios of 1:3.5 and 1:1.32, again consistent with the expected extent of reduction. (The 1:2 sample was obviously not properly separated as mentioned previously.) However it is difficult to envisage a suitable monovalent organic residue arising from the known diene structures.

If it is assumed that MgCl<sub>2</sub> is formed, as the literature suggests for analogous systems, the figures for Ti:Cl, after correction for MgCl<sub>2</sub>, become 1:3.1, 1:2.2 and 1:0.2 for Mg(isoprene)<sub>2</sub> + TiCl<sub>4</sub> at the relevant reaction ratios and 1:3 and 1:2 for the first two myrcene experiments. Such ratios are not in accord with Ti (111) species unless cyclotitanium species are involved. Compounds such as



could be postulated for diphenylbutadiene but not for Mg (isoprene)<sub>2</sub> or Mg myrcene where the ligands are essentially both isoprene dimers.

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