Polymerization catalysts for propene from the reduction of titanium tetrachloride with halogen-free magnesium alkyls

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(*Received* 4 *September* 1980)

Previous work on magnesium reduced titanium catalysts for propene polymerization has been extended by producing a number of catalysts containing less magnesium and chloride (per titanium atom) than previously and by eliminating the 'stranger' bromide ion from the solid phase. These materials show increased activity, but poor stereoregulation. Phases with both magnesium and aluminium ions in the '$TiCl_3$' lattice were slightly more active, and more stereospecific.

INTRODUCTION

We[1] and others[2] have previously reported on the activity of alkyl magnesium reduced titanium chloride in the polymerization of ethene and propene[3]. These catalysts are highly active for ethene polymerization, and reasonably so for propene, but they produce only 35–40% crystalline polypropene, and are unlikely to be industrially useful for propene polymerization.

Such materials are highly amorphous, as X-ray studies show[4], and the high activity for ethene is due to a large number of active sites[1]; the same may be true for propene[2]. This noncrystalline nature is thought to be the reason for the poor stereoregulation and it appeared logical to attempt the preparation of titanium chloride phases containing less magnesium and, preferably, no extraneous halogen (c.f. the bromide ion deposited in reactions of RMgBr). The most straightforward way to do this is to use as reductant a dialkyl magnesium rather than a Grignard reagent: thus instead of

$$RMgX + TiCl_4 \longrightarrow TiCl_3.MgClX + R\cdot$$

we may expect

$$R_2Mg + 2TiCl_4 \longrightarrow 2TiCl_3.MgCl_2 + 2R\cdot$$

This product phase is likely *a priori* to give more stereoregular polymerization, but probably reduced rates, since it is more likely to be able to crystallize as a $TiCl_3$ phase and exclude the magnesium.

We report here on our studies, following on some preliminary work, using as reductants didodecyl magnesium (as a slurried solid), a solution of an equimolar mixture of magnesium *n* and *s* butyls, and solutions of the recently reported[5] complexes formed between magnesium and aluminium alkyls; both types of alkyl solutions were in aliphatic hydrocarbons. A further variant studied has been the order of addition of the reagents, i.e. whether the magnesium alkyl is added to excess titanium tetrachloride or *vice versa*. We also report on catalysts prepared from magnesium alkyl chlorides, rather than bromides.

EXPERIMENTAL

Materials

Polymerization grade propene (ICI Plastics Division) was purified by successive passage over copper and molecular sieve, as previously described[2]. Nitrogen (BOC, oxygen free grade) was purified similarly.

Polymerization diluent was 'Isopar C', supplied by Esso Chemicals. It was purified immediately before use by refluxing over, and distillation from, $LiAlH_4$ under N_2. n-Heptane was treated similarly. Aluminium alkyls (Schering A G) were used as supplied.

Dialkyl magnesiums were prepared by a standard procedure[6], from the alkylmagnesium bromide in ether. This solution was treated with 1,4-dioxan, to precipitate $MgBr_2$, and the supernatant liquid evaporated to dryness, finally heating at 0.1 mm Hg to remove the ethers, before slurrying in n-heptane, in which it is insoluble. In some cases (see text) this material was repeatedly washed with heptane to remove residual materials before analysis and use. The slurries were standardized by back-titration of a mixture of EtOH and 1 M HCl (25 cm^3), to which the slurry (10 cm^3) had been added, against NaOH, using phenolphthalein.

Magnesium octyl chloride was made as a solution in n-heptane from n-octyl chloride, precisely as previously detailed for the bromide[1].

Organomagnesium/aluminium complexes[5] — di-n-butyl magnesium was prepared and then treated with $AlEt_3$(95°C) or Al (i-butyl)$_3$ (20°C). The slurred dialkyl magnesiums dissolved, and after analysis the clear solutions were used in catalyst preparations. These so-

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lutions were assayed for Mg (EDTA at pH 10, Erichrome black T, using triethanolamine to mask the Al) and Al (EDTA at pH 4.5, Dithizone, back titration using $ZnSO_4$) as well as for alkyl groups by gas evolution on hydrolysis.

Di-(n + s) butyl magnesium and the complex of di-n-butyl magnesium and tri-iso butyl aluminium (Mg:Ti 2.2) were supplied as hydrocarbon solutions (Lithium Corp.) and used as received.

Catalyst Preparation

'Forward addition' was carried out as before[1,3,4]. 'Reverse addition' was carried out in the apparatus shown in *Figure 1*, which allows for removal of the excess $TiCl_4$ and washing of the solids with further quantities of heptane whilst maintaining the N_2 blanket. In a typical reverse addition reaction the oven dried (110°, overnight) glassware was assembled hot and purged (N_2), whilst cooling to the ambient temperature, before charging the vessel with $TiCl_4$(30 cm^3). To this was added, over 1 min with stirring, a solution of the reducing agent, in this case $[(n+s)\ butyl]_2$ Mg (0.63M, 10 cm^3), via a syringe needle through the rubber seal. The mixture was stirred for 30 min, before the solid product was filtered from the $TiCl_4$ hydrocarbon mixture, and then washed with n-heptane (3 x 100 cm^3), before slurrying in fresh heptane (200 cm^3). This slurry contained ~ 3 mg Ti/cm^3 and was used directly for polymerization after estimation of Ti content by the method given in ref 7.

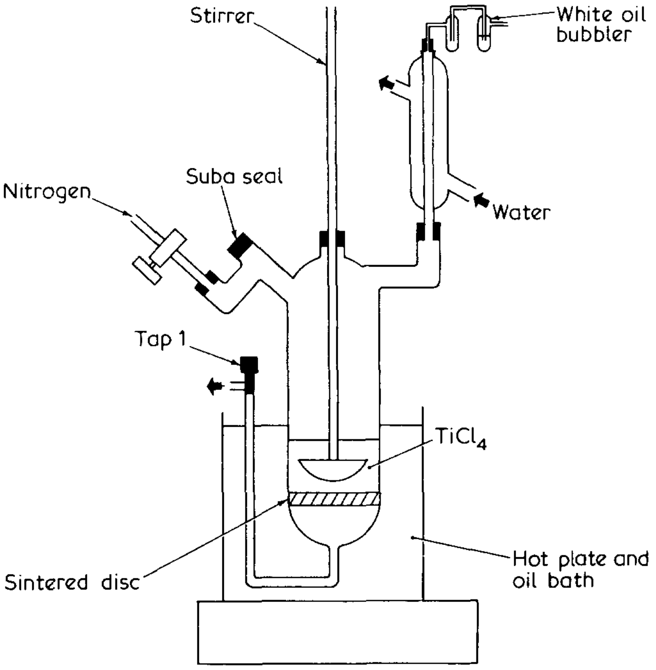


Figure 1 Apparatus for reverse addition

Polymerizations were carried out, in isopar C, exactly as before, rates being measured with a wet gas meter.

Estimation of the hydrocarbon-soluble fraction of the polymer was achieved by removal of a sample of the diluent after it had settled. A sample of the insoluble material was also removed for later study.

Analyses of catalysts were performed on solutions prepared as follows: 10 cm^3 of catalyst slurry was hydrolysed with H_2SO_4 (3 M) and the volume of acid made up to 100 cm^3. This extract was then analysed, at ICI Plastics Division, for Ti, Mg, Cl and (if required) Al. Some catalysts were also assayed at Birmingham using the methods in the references: total Ti,[7] Ti^{II} and Ti^{III},[8] Mg,[9] and Cl[10].

Viscometry was performed on decalin solutions of polymers at 135°C, using Ubbelohde viscometers; molecular weights were estimated, using a one point method, as previously described[3].

RESULTS AND DISCUSSION

An initial objective was to assess the possible importance of the bromide ion in the Grignard-reduced catalysts previously studied[1,3]: it was possible that the bromide would enhance activity by disrupting the '$TiCl_3$' crystal lattice more than by simple inclusion of magnesium ions. Such an enhancement would presumably result in lower stereoregulation. A magnesium alkyl chloride was used as reductant to give magnesium chloride as the only by-product, and was investigated via catalysts prepared by reducing $TiCl_4$ with octyl magnesium chloride, using forward addition. Their apparent reactivity increased as the concentration of titanium in the polymerization reaction decreased (*Table 1*). This was puzzling, as the obvious explanation for this was that at the higher concentrations studied the reaction was limited by the transfer rate of monomer into solution. However, this was ruled out by earlier studies[3] on the same apparatus. Because the solvent had been changed, however, this was checked using catalysts reduced with didodecyl magnesium, which did not show increased activity at low concentrations (see later), both at constant activator concentration and at constant Ti:Al ratio (1:10). (Both were undertaken because it is not clear which is the better test). The results (see ref 11 for details) (*Figures 2* and *3*) support our earlier conclusion that the transfer rate of monomer into the diluent is large enough for the rate of the polymerization to be unaffected by this. Present studies gave a higher value (~500 g h^{-1}) than the previous one (~100 g h^{-1}) for the transfer rate. Some

Table 1 Octyl magnesium chloride-reduced catalysts

Catalyst (mmol)	Co-catalyst (mmol)	Polymer yield			Diluent-insoluble polymer		Soluble polymer	
		(g/3 h)	(g/g Ti)	(%)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)
0.85	8.5	35	965	41	2.605	4.2	0.590	0.59
1.71	17.1	62	850	40	2.839	4.7	0.524	0.50
1.71	17.1	54	741	40	2.689	4.3	0.560	0.55
1.71	17.1	50	687	40	2.526	4.0	0.588	0.59
1.71	17.1	53	727	40	2.617	4.2	0.616	0.62

Polymerization conditions: Co-catalyst TiBA [(i-butyl)$_3$Al] ; temperature 40°C; diluent 1 dm^3; time 3 h other explanation must be found for the definite increase in measured activity at low $TiCl_3$ concentrations. The increase in activity cannot be due to decreasing chain transfer to metal alkyl because the effect is not found with all the catalysts.

Initial studies using dialkyl magnesium reductants were carried out using our previous procedure, the only difference being the use of a slurry of didodecyl magnesium, to which was added a solution of titanium tetrachloride. After preliminary experiments, a ratio of 2:1 ($TiCl_4$:R_2Mg) was shown to be adequate for total reduction of the titanium and to give the best activity (*Table 2*). The catalysts obtained by this means were shown on analysis to have a Ti:Mg ratio close to the expected 2:1, but they showed no signs of crystallinity in X-ray studies. Neither did any of a number of heat treatments effect a change to a violet form.

These catalysts showed noticeably higher activities for propene polymerization (vis-a-vis Grignard reduced materials) at 40°C, using tri-isobutyl aluminium as activator, but the stereospecificity of the reaction was not greatly improved.

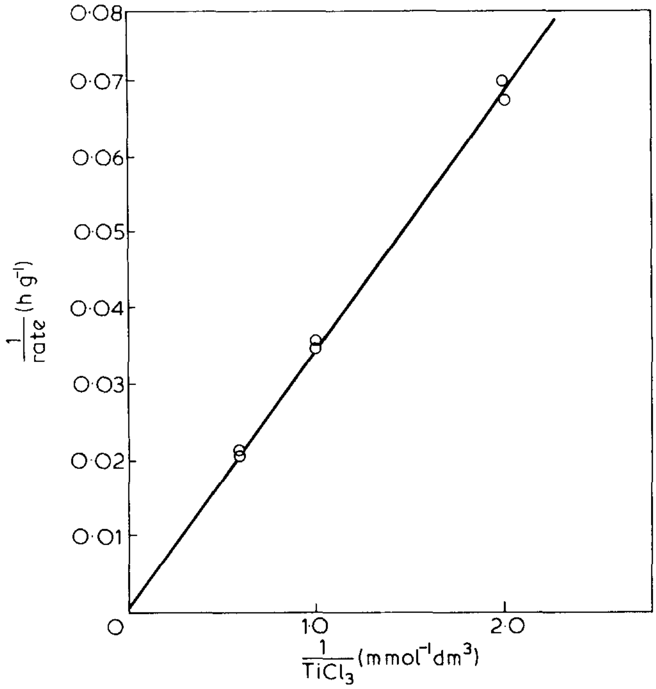


Figure 2 1/rate *versus* 1/$TiCl_3$ (titanium to aluminium ratio constant)

Later experiments, using a commercial solution of mixed magnesium butyls similar to the slurry discussed above, gave similar catalysts. These materials were less active than those prepared from Grignard-reduced catalysts (*Table 3*), and the fraction of polymer insoluble in n-heptane was only very slightly increased from 40 to 42%. Neither the measured activity nor the stereospecificity of these materials varied significantly with catalyst concentration.

Although these results are reproduceable, the differences in activity observed between catalysts produced from soluble and insoluble magnesium alkyls cannot be explained: the results from the liquid reductant are roughly as expected for dialkyl magnesium reduced catalysts, but the insoluble materials do not seem to fit. The precipitation of the '$TiCl_3$' onto the existing solid could be a factor here.

We have investigated the possibility that the effect is due to residual 1,4-dioxan in the magnesium didodecyl by producing catalysts (1) from carefully washed magnesium dialkyl, (2) from purified magnesium dialkyl with added 1,4-dioxan, and (3) from the hydrocarbon solution above 1,4-dioxan-contaminated magnesium alkyl. The results (*Table 4*) show that the ether has a deleterious effect on the activity, with only small effects on stereoregulation and molecular weight. We conclude therefore that the increase in activity vis-a-vis the catalysts produced from soluble magnesium alkyl, is not due to residual ether.

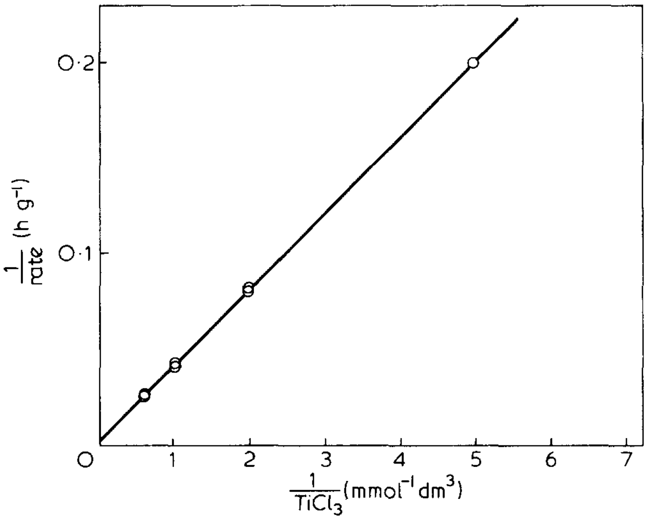


Figure 3 1/rate *versus* 1/$TiCl_3$ (TiBA concentration constant)

Table 2 Didodecylmagnesium-reduced catalysts prepared at varying $R_2Mg:TiCl_4$

Mg/Ti used in catalyst preparation	Polymer yield (g/3 h)	Polymer yield (g/gTi)	Polymer yield (%)	Diluent-insoluble polymer (I.V. 100 cm^3/g)	Diluent-insoluble polymer ($\bar{M}_v \times 10^{-5}$)	Soluble polymer (I.V. 100 cm^3/g)	Soluble polymer ($\bar{M}_v \times 10^{-5}$)
0.50	43	1781	40	3.997	7.3	1.057	1.3
0.50	44	1823	40	3.900	7.1	1.002	1.2
0.50	44	1823	39	4.100	7.6	1.100	1.3
0.75	38	1577	39	3.995	7.3	0.990	1.2
0.75	39	1618	38	4.048	7.4	1.058	1.3
0.75	40	1660	39	4.000	7.3	1.020	1.2
1.00	37	1535	38	4.058	7.4	1.058	1.3
1.00	38	1577	38	3.990	7.3	1.100	1.3
1.00	38	1577	40	4.000	7.3	1.000	1.2

Polymerization conditions: catalyst 0.5 mmol; catalyst 5 mmol TiBA; temperature 40°C; time 3 h

Table 3 Di-n/s-butylmagnesium-reduced catalysts

Catalyst (mmol)	Co-catalyst (mmol)	Polymer yield			Diluent-insoluble polymer		Soluble polymer	
		(g/3 h)	(g/gTi)	(%)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)
0.5	5	11	457	42	3.637	6.4	0.894	1.00
0.5	5	11	457	43	3.591	6.3	0.840	0.94
0.5	5	12	499	40	3.599	6.4	0.885	1.00
1.0	10	23	477	41	3.613	6.4	0.842	0.94
1.7	17	36	438	43	3.500	6.1	0.820	0.91
1.7	17	38	464	43	3.602	6.4	0.860	0.97

Polymerization conditions: co-catalyst TiBA; temperature 40°C; time 3 h; diluent 1 dm^3

Table 4 Effect of washing didodecylmagnesium before catalyst preparation and of other treatments on reactivity

Reductant used in catalyst preparation	Polymer yield			Diluent-insoluble polymer		Soluble polymer	
	(g/3 h)	(g/gTi)	(%)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)
Slurry of unwashed	41	1702	38	3.476	6.1	0.890	1.01
R_2Mg	43	1785	40	3.501	6.1	0.903	1.03
n-Heptane from	8	333	36	3.233	5.5	0.854	0.96
unwashed slurry	9	374	38	3.361	5.8	0.911	1.04
Slurry of	56	2322	39	3.347	5.8	0.871	0.98
washed R_2Mg	52	2156	39	3.406	5.9	0.860	0.97
Slurry washed and then	17	704	40	3.256	5.6	0.808	0.89
10% 1,4-dioxan added	19	787	39	3.500	6.1	0.812	0.90

Polymerization conditions: catalyst 0.5 mmol; co-catalyst 5 mmol TiBA; temperature 40°C; time 3 h; diluent 1 dm^3

Table 5 Didodecylmagnesium-reduced catalysts used with different co-catalysts prepared at Mg/Ti ratio 0.5

Co-catalyst	Temp (°C)	Polymer yield			Diluent-insoluble polymer		Soluble polymer	
		(g/3 h)	(g/gTi)	(%)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)
TiBA	40	43	1785	39	3.991	7.3	1.001	1.18
TiBA	60	32	1327	39	3.900	7.1	1.010	1.19
TnOA	40	42	1743	38	3.989	7.3	1.054	1.26
TnOA	60	37	1535	40	4.056	7.4	1.054	1.26
TEA	40	25	1036	41	2.914	4.8	0.616	0.62
TEA	60	12	499	41	2.599	4.1	0.520	0.50

Polymerization conditions: catalyst 0.5 mmol TnOA = (n-octyl)$_3$Al; diluent 1 dm^3 TEA = (ethyl)$_3$Al; time 3 h

Having established reasonable catalyst formulations, the effects of temperature and of different cocatalysts were studied briefly. The catalysts ('TiCl$_3$') were prepared from magnesium didodecyl, as above, at a ratio Mg:Ti of 0.5:1. The results are shown in *Table 5*. We also show (*Figure 4*) the types of rate curve obtained for the different aluminium alkyls at 40°C, to illustrate the dramatic 'dying-off' of the aluminium triethyl activated reactions, presumably owing to over-reduction of the titanium. It was concluded that acceptable results could be obtained using aluminium tri-isobutyl at 40 or 60°C.

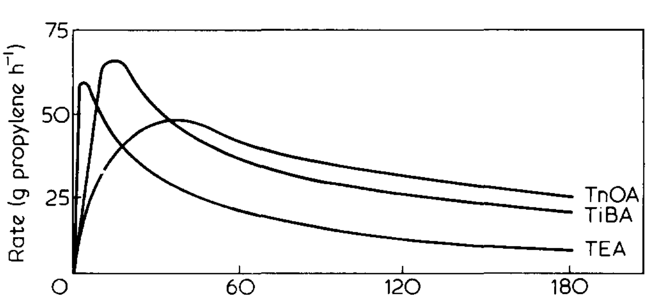


Figure 4 Effect of different co-catalysts on polymerization rates at 40°C, 0.5 mmol TiCl$_3$, 5.0 mmol co-catalyst

The preparation of catalysts by addition of a solution/slurry of magnesium alkyl to an excess of titanium tetrachloride (reverse addition) was assayed, and gave encouraging results *Table 6*. On the molecular scale this procedure is quite different from forward addition because (1) there is an appreciable temperature increase (~20–30°C) and (2) the incoming reducing agent is in a situation where there is a large excess of titanium tetrachloride, and thus no serious danger of transient over-reduction, as may well be the case for forward addition. The increase in catalyst activity was ~30% for soluble and 48% for insoluble reductants, but interestingly the stereoregulation of the catalysts moved in different directions with the soluble-alkyl derived ma-

Table 6 Dialkyl catalysts prepared by reverse addition prepared at Mg/Ti = 0.5

Catalyst (mmol)	Co-catalyst (mmol)	Polymer yield			Diluent-insoluble polymer		Soluble polymer	
		(g/3 h)	(g/gTi)	(%)	(I.V. 100 cm^3/g)	($\bar{M}_w \times 10^{-5}$)	(I.V. 100 cm^3/g)	($\bar{M}_v \times 10^{-5}$)
A 1.0	10	30	624	45	3.667	6.5	0.714	0.76
A 1.0	10	28	582	45	3.675	6.5	0.882	1.00
A 1.0	10	30	624	44	3.680	6.5	0.884	1.00
B 0.5	5	63	2613	34	3.529	6.2	0.883	1.00
B 0.5	5	65	2696	34	3.806	6.8	0.773	0.84
B 1.0	10	128	2655	33	3.453	6.0	0.880	1.00

Polymerization conditions: co-catalyst TiBA; temperature 40° C; diluent 1 dm^3; time 3 h
Catalysts A – prepared using di-n/s-butyl-magnesium to reduce $TiCl_4$
Catalysts B – prepared using didodecylmagnesium to reduce $TiCl_4$

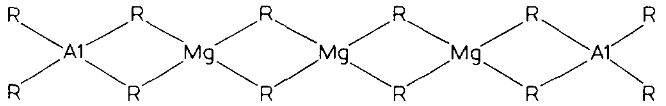
Table 7 Comparison of catalysts

Reducing alkyl	Forward addition		Reverse addition		Composition		
	3-h yield (g/gTi)	% solubles	3-h yield (g/gTi)	% solubles	$TiCl_3$	$MgCl_2$	$AlCl_3$
$(C_{12}H_{25})_2Mg$ (insoluble)	1800	40	2650	34	1	0.5	0
″ (washed)	2200	39	–	–	1	0.5	0
$C_8H_{17}MgCl$	750	40			1	1	0
$(^nC_4H_9)(^sC_4H_9)Mg$	470	42	610	45	1	0.5	0
$Et_3Al:4(C_{12}H_{25})_2Mg$	–	–	(~2600)	34	11	4	1
$i\text{-}Bu_3Al:2$ to $4\ (^nC_4H_9)(^sC_4H_9)Mg$	–	–			7/11	2/4	1
$Et_3Al:2$ to $6(^nC_4H_9)_2Mg$	–	–	(610	45)			
$i\text{-}Bu_3Al:2.2(^nC_4H_9)_2Mg$	–	–					
$Et_3Al:0.5(^nC_4H_9)_2Mg$*	–	–	960	65	9.5	1	2.5

* Catalysts turned violet

terials giving slightly improved stereoregulation whereas the insoluble alkyl derived material gave poorer stereoregulation. There again appears to be little effect on molecular weight.

In a final series of experiments, reductions were carried out using mixed metal alkyls. These have been reported[5] to be available as soluble materials obtained by the action of aluminium alkyls on the insoluble magnesium dialkyls. They presumably have formulae like:



with the aluminium alkyls end-capping the magnesium alkyl chains and hence reducing their molecular weight; it is reported that various Mg:Al ratios may be made. It was thought that the use of such reducing agents would lead to the incorporation of both magnesium and aluminium ions into the precipitated materials, with the possibility of producing more stereo-specific catalysts.

Initially, attempts were made to synthesize such mixed alkyls from an n-heptane slurry of magnesium didodecyl and triethyl — or tri-isobutyl aluminium. No success was obtained with tri-isobutyl aluminium since owing to facile dealkylation of the aluminium this reaction could not be heated[5] but a soluble material with a magnesium: aluminium ratio of about 4:1 was made using triethyl aluminium and was used to produce, by reverse addition, a catalyst with the approximate composition $(TiCl_3)_{11}(MgCl_2)_4(AlCl_3)$: this catalyst had polymerization properties almost identical to those prepared from didodecyl magnesium using reverse addition. Therefore, it is not necessary to use an insoluble magnesium alkyl to produce a very high activity catalyst. Further catalysts were produced (by reverse addition), using mixed solutions of (n + s) butyl magnesium and aluminium tri-isobutyl as the reductant. Using ratios of magnesium to aluminium between about 2 and 4 gave catalysts with compositions ranging from about $(TiCl_3)_7(MgCl_2)_2(AlCl_3)$ to $(TiCl_3)_{11}(MgCl_2)_4(AlCl_3)$ but again the activites were very similar to those prepared from the magnesium butyl solution by reverse addition, i.e. the aluminium made little difference to the activity.

Further experiments were made with soluble complexes made by reaction of the insoluble di(n-butyl) magnesium with triethyl aluminium. In these complexes the magnesium/aluminium ratio ranged from about 6 to about 2, and again the activities of the catalysts made by reverse addition were similar to those prepared from the soluble magnesium butyl by reverse addition. In one case an alkyl complex was prepared having a Mg/Al ratio of about 0.5. Catalysts prepared from this material turned violet during preparation, and gave, with triethyl aluminium activator at 60°C, about 65% of diluent–insoluble polymer, with a higher yield than other catalysts —about 960 polymer/g titanium as compared with about 600.

A number of catalysts were prepared from a commercial solution of a di(n-butyl)magnesium/aluminium tri-isobutyl complex (Mg/Ti = 2.2). Again, the results here were similar to those obtained from the soluble dibutyl magnesium reductants.

This last group of experiments seems to indicate that small amounts of aluminium in the solid phase do not greatly affect the catalytic activity of the catalyst (or the molecular weight or stereoregularity of the polymer). When there is more aluminium than magnesium an effect is noticed, but again the stereoregulation by this catalyst [empirical formula approximately $(TiCl_3)_{9.5}(MgCl_2)(AlCl_3)_{2.5}$] is not good.

CONCLUSIONS

These studies have shown that reducing the amount of magnesium in fairly active catalyst phases increases their activity by a significant amount, but still leaves them as very non-stereoregulating catalysts. Replacement of some of the magnesium by aluminium has little effect until there is an excess of aluminium. However, the stereoregulation is not good, although the activity is improved.

The change in activity on replacing octylmagnesium chloride as reductant by a dialkylmagnesium seems to depend more on the length of the alkyl group than on a change in the Mg/Ti ratio in the product. Both molecular weight and percentage of insoluble polymer are substantially insensitive to these changes in reductant. This suggests the production of the same range of active sites, and that the same chain transfer mechanisms are important, therefore, this work indicates that the effects of these different catalyst preparation procedures is simply to alter the number of available active sites.

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