

# Magnesium alkyl reduced titanium (IV) chloride based polymerization catalysts: materials rich in magnesium chloride††

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Reduction of  $TiCl_4$  with organomagnesiums either in the presence of preformed  $MgCl_2$ , or concurrently with the formation of  $MgCl_2$  from chlorocarbons, yields materials which are active catalysts for the polymerization of propene and ethene. Transformation of these materials to a violet allotrope by heating with  $TiCl_4$  gives materials much more active for propene polymerization, albeit stereoregulation is still not good. Interestingly, these transformed materials show little advantage for ethene polymerization except at high temperatures. Use of a Lewis base does not give high stereoregulation with propene; although some advantage is gained activity is greatly diminished by this.

**Keywords** Ziegler-Natta; catalyst; titanium chloride; magnesium-reduced; magnesium chloride; polypropene

Over the past years the commercial polymerization of ethene and propene by Ziegler-Natta catalysts has become an important industry. Initially, both these polymerizations were carried out using materials prepared by reduction of titanium (IV) chloride with aluminium trialkyls, with aluminium alkyl halides or with aluminium itself<sup>1</sup>. Latterly, other catalysts have come into use, and prominent amongst these are those containing magnesium halides<sup>2</sup> in the place of the aluminium halides previously incorporated. Amongst the most active of such catalysts for propene are those based upon the reaction of titanium halides with the surface of specifically prepared magnesium chlorides. Some of these materials are very active for the polymerization of propene<sup>3</sup>, and give very stereoregular reactions.

In previous reports we have communicated the results of studies using magnesium dialkyls or magnesium alkyl halides as reductants for titanium (IV) chloride. Originally, materials obtained using magnesium alkyl halides as reductants were shown to be very active in the polymerization of ethene<sup>4,5</sup>, and subsequently to be active for propene<sup>6</sup>. The high activities for these two monomers have been shown to be largely a result of high concentrations of active sites in these very disordered materials and this conclusion is supported by the work on a closely allied catalyst system reported by Böhm<sup>7</sup>, who also found that a high proportion of transition metals function as active sites. Later work in our laboratories has concentrated on propene, with efforts being directed to improving both rate and stereospecificity in the polymerization. In this effort the effects of reducing the amount of magnesium in the precipitated catalyst<sup>8</sup> and those of the

allotropic conversion of the catalysts to the violet form<sup>9</sup> have been studied.

We now report on the extension of the work to the study of materials rich in magnesium chloride. These have been prepared both by coprecipitation of the magnesium chloride with the titanium chloride during the reduction and, alternatively, by preprecipitation of magnesium chloride, followed by reduction of titanium (IV) chloride to precipitate the usual catalyst phase onto the preformed magnesium chloride. In both cases the chlorides were kept in the solvent, without drying or exposure to air, in order to achieve and keep high surface areas in the precipitated catalyst materials.

In those cases where the precipitated catalysts proved to have good activities for propene polymerization, and in some others, they were treated with titanium tetrachloride in an attempt to convert them to a layer lattice (violet) form. In many cases this greatly increased the activity of the catalyst, in combination with aluminium trialkyl co-catalysts, for propene polymerization. These materials have also been tested as ethene polymerization catalysts.

## EXPERIMENTAL

Catalyst preparations were carried out under purified nitrogen in apparatus similar to that described before<sup>7</sup>. In reactions designed to produce preformed magnesium chloride, a number of techniques were employed. Typically, HCl was bubbled through a solution of *n*-octylmagnesium chloride in *n*-heptane/tetrahydrofuran to precipitate  $MgCl_2$ . Excess HCl was then purged from the apparatus with  $N_2$  before adding a second aliquot of *n*-octylmagnesium chloride solution to the stirred slurry: the molar ratio of  $MgCl_2$  to Grignard reagent in this second stage was estimated to be 9:1, based on the quantities of Grignard solution used in the two stages. A solution of  $TiCl_4$  in *n*-heptane (1:1 molar ratio with the

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Table 1 Supported catalysts prepared from RMgCl/MgCl<sub>2</sub>\*/TiCl<sub>4</sub>

Catalyst (Type) (m mol)	Co-catalyst (m mol)	Polymer field		Diluent-insol- uble polymer (%)
		(g/3 h)	(Kg/g Ti)	
(A) 0.5	10	21	0.88	52
0.5	10	21	0.88	53
1.0	10	36	0.75	53
1.0	10	35	0.73	54
1.7	17	45	0.55	52
1.7	17	42	0.51	52
(B) 1.0	10	68	1.41	39
(C) 1.0	10	167	3.48	45

Polymerization conditions: Co-catalyst TiBA; temperature 40°C; time 3 hours; diluent 1 dm<sup>3</sup> Isopar C

\* Produced by reaction of the Grignard reagent with HCl, see text

second aliquot of Grignard) was then added to the well-stirred slurry, and the resultant slurry used as a catalyst without further treatment—catalyst A. In a second procedure, an ether-free solution of di-n/s-butyl magnesium was added dropwise through an HCl atmosphere to a stirred solution of TiCl<sub>4</sub>. The resultant solid was filtered and washed before being reslurried and used—catalyst B. A portion of the dried solid was also treated with TiCl<sub>4</sub> at 120°C, and transformed to a violet powder, which was tested—catalyst C.

Attempts to coprecipitate MgCl<sub>2</sub> and TiCl<sub>3</sub> were made by placing a mixture of TiCl<sub>4</sub> (30 cm<sup>3</sup>) and CCl<sub>4</sub> (usually 30 cm<sup>3</sup>) in the apparatus, and adding by syringe 25 cm<sup>3</sup> of a 0.63 Molar solution of di-n/s-butyl magnesium. This addition was done fast enough to reflux the liquids (CARE!). The resultant solids were filtered and washed with n-heptane (3 × 100 cm<sup>3</sup>) before a portion was reslurried in n-heptane (100 cm<sup>3</sup>)—catalyst type D. The remaining dried powder was treated with TiCl<sub>4</sub> and converted to a violet form—catalyst type E. Variants on this procedure have been tried, using other chlorinating agents. Polymerizations were carried out exactly as described before the ethene<sup>5</sup> and propene<sup>6</sup>, and the soluble fraction of the latter polymer estimated as in ref 8. Viscometry was performed in decalin, at 135°, using suspended level Ubbelohde viscometers. Intrinsic viscosities were estimated using a one point method due to Elliot *et al.*<sup>10</sup>, and the molecular weights calculated from the equation given by Parrini *et al.*,  $[\eta] = 0.917 \times 10^{-4} M_n^{0.80}$ <sup>11</sup>

Elemental analyses of catalysts were carried out at ICI Plastics Division; titanium contents were also estimated spectrophotometrically.

## RESULTS

These catalyst systems represent an approach to one of the extreme possibilities available in a sequence starting with pure TiCl<sub>3</sub>, passing through phases with more and more MgCl<sub>2</sub> in them, until finally there are materials which are MgCl<sub>2</sub> either 'doped' or coated with TiCl<sub>3</sub>. In our previous studies it transpired that varying the ratio of magnesium to titanium in the catalyst phase between about 0.5 and about 1 made only small differences to the catalytic activity for propene, and that the stereoregulation remains poor over all that range even after transformation of the material to a violet form; it is therefore logical, given the very good results obtained in

certain other related systems, to proceed towards much larger values of this ratio.

Initially, attempts were made to preform MgCl<sub>2</sub> by precipitation, and to coat this material with precipitated 'TiCl<sub>3</sub>'. This would, of course, be expected to lead to materials either coated with a TiCl<sub>3</sub> lattice or slightly doped on the surface with Ti. In either case, the majority of the transition metal atoms ought to be available for reaction. Magnesium chloride was produced both by reaction of a Grignard reagent with HCl, bubbled through the solution and by reaction of drops of magnesium alkyl solution with HCl gas above a solution of titanium tetrachloride. In the latter case, a catalyst was produced directly, whereas in the former case a separate precipitation reaction was required, using additional Grignard reagent followed by titanium chloride solution.

The results of these two approaches were disappointing in that no marked improvement over previous materials, either in polymerization activity or in stereoregulation, could be obtained (Table 1): on treating the catalyst from the second method with titanium tetrachloride at 120°C, however, a significantly more active material was obtained, showing also a slightly improved stereoregulation. Analyses of these latter two materials showed ratios of Mg:Ti between 3 and 4 and they thus had substantially more magnesium in the lattice than our earlier materials. However the method, with dropwise addition of organometallic through an atmosphere of hydrogen chloride, was experimentally tricky, and another method was therefore sought.

The next approach tried was to produce the magnesium chloride as nearly as possible simultaneously with reduction so as to produce a precipitate containing both the 'TiCl<sub>3</sub>' and 'MgCl<sub>2</sub>' very intimately mixed. The most straightforward way to do this might have been to saturate a solution of titanium tetrachloride with hydrogen chloride, and to treat this with organomagnesium, but this approach was rejected in favour of mixing the titanium tetrachloride with another liquid chlorinating agent. Since it is known that carbon tetrachloride reacts vigorously with organomagnesiums, this was employed in initial experiments. A series of experiments, using fixed amounts of titanium tetrachloride and of organomagnesium, with varying amounts of carbon tetrachloride, were carried out and the precipitated solids assayed as catalysts, both as produced and after treatment with titanium tetrachloride at 120°. The results of these experiments (Table 2) were to give marked rate enhancements, especially after the treatment with titanium tetrachloride.

As can be seen from Figure 1, the amount of magnesium in the precipitate originally produced is a simple function, if the temperature is held constant by reflux, of the ratio CCl<sub>4</sub>/TiCl<sub>4</sub> in the initial mixture, and an increase in the magnesium titanium ratio in this precipitate produces a modest increase in catalyst activity (the squares in Figure 2). The post treatment with TiCl<sub>4</sub> greatly increases the Mg/Ti ratio in the catalyst, which it does by leaching out about half the titanium, the amount of magnesium in the preparation remaining undiminished. Table 3 shows analyses and approximate composition of the various materials, on the assumption that titanium is trivalent. Chlorine analyses were not sufficiently accurate to determine the titanium valency. Titration with ceric sulphate corresponded to what was expected of trivalency,

Table 2 Supported catalysts prepared from (n/s Bu<sub>2</sub>Mg)/CCl<sub>4</sub>/TiCl<sub>4</sub>

cm <sup>3</sup> of CCl <sub>4</sub> used	Catalyst type (m mol)	Polymer yield			Diluent-insoluble polymer		Soluble polymer	
		(g/3 h)	(kg/g Ti)	(%)	Yield (kg/g Ti)	$\bar{M}_v \times 10^{-5}$	Yield (kg/g Ti)	$\bar{M}_v \times 10^{-5}$
0	D (1.00)	30	0.63	45	0.28	6.5	0.35	0.76
	E (1.00)	60	1.25	50	0.62	6.6	0.63	1.05
10	D (0.15)	31	4.3	33	1.4	6.5	2.9	0.76
	E (0.18)	128	11.8	52	6.1	6.8	5.7	1.03
30	D (0.18)	56	6.5	35	2.3	6.2	4.2	0.72
	E (0.09)	100	23.2	47	10.9	6.2	12.3	1.02
50	D (0.16)	52	6.8	35	2.4	6.6	4.4	0.74
	E (0.07)	156	46.7	45	21.1	6.5	25.6	1.07
100	D (0.15)	51	7.1	34	2.4	6.6	4.7	0.75
	E (0.02)	45	47.3	45	21.3	6.6	26.0	1.05

Polymerization conditions: Co-catalyst 10 m mol TiBA; temperature 40°C; time 3 hours; diluent 1 dm<sup>3</sup> Isopar C

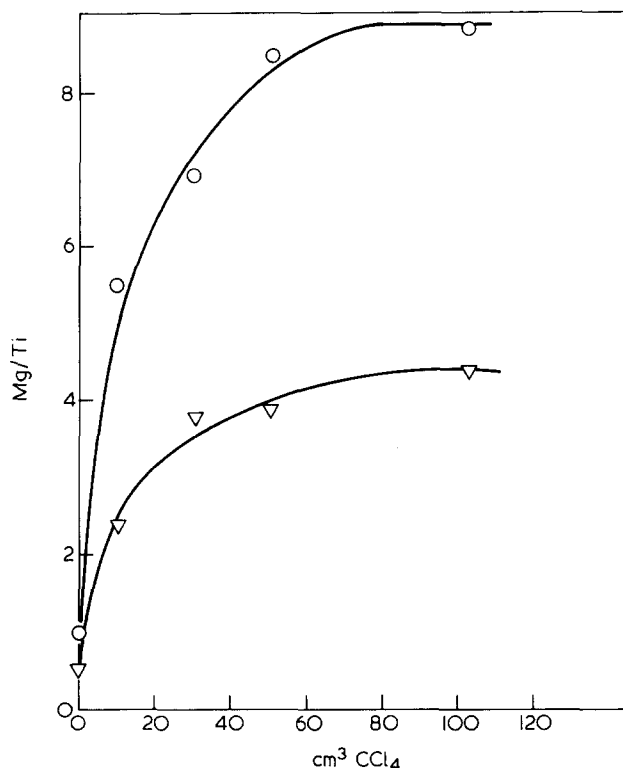


Figure 1 Effect of variations in the quantity of CCl<sub>4</sub> in initial catalyst preparation on the Mg/Ti ratio in the final catalysts. Catalysts are types D and E (see text). (Δ) Type D; (○) type E

and attempts to titrate divalent titanium by the method of Martin and Stedefeder<sup>1,2</sup> failed to show significant amounts of Ti<sup>II</sup>. The effect of treatment is seen in Figure 2 (circles) as being to bring about a considerable gain in activity.

Some other chlorinating agents have also been employed, in attempts to find one giving materials more reactive than those prepared from carbon tetrachloride, but none has yet been found. The results, for instance, with silicon tetrachloride (Table 4) suggest that the relative rate of reaction is likely to be important, since the Mg/Ti ratios thus produced were not high. It is interesting also, that in this case little titanium was leached out in the post treatment.

We have also investigated some methods of improving stereoregulation with these high activity formulations (Table 5). We report here only two approaches; changing

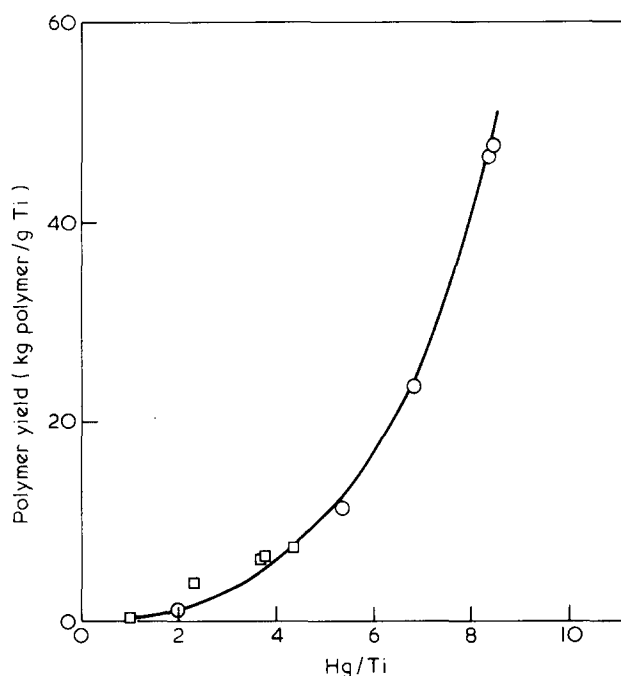


Figure 2 Relationship between Mg/Ti ratio in catalysts and polymer yield. (□) Type D; (○) type E

Table 3 Approximate compositions (by elemental analysis)<sup>a</sup>

cm <sup>3</sup> of CCl <sub>4</sub> in preparation	Catalyst D	Catalyst E
0	TiCl <sub>3</sub> . 0.5 MgCl <sub>2</sub>	
10	TiCl <sub>3</sub> . 2.3 MgCl <sub>2</sub> <sup>b</sup>	TiCl <sub>3</sub> . 5.4 MgCl <sub>2</sub> <sup>b</sup>
30	TiCl <sub>3</sub> . 3.7 MgCl <sub>2</sub> <sup>b</sup>	TiCl <sub>3</sub> . 6.8 MgCl <sub>2</sub> <sup>b</sup>
50	TiCl <sub>3</sub> . 3.8 MgCl <sub>2</sub> <sup>b</sup>	TiCl <sub>3</sub> . 8.4 MgCl <sub>2</sub> <sup>b</sup>
100	TiCl <sub>3</sub> . 4.4 MgCl <sub>2</sub> <sup>b</sup>	TiCl <sub>3</sub> . 8.7 MgCl <sub>2</sub> <sup>b</sup>

<sup>a</sup> The valency of Ti is assumed to be 3

<sup>b</sup> These materials were deficient in chlorine, according to the elemental analyses: these deficiencies have been overlooked in calculating the formulae shown

the aluminium alkyl used as cocatalyst, and pre-reaction of the alkyl with a Lewis base. For the alkyl, we knew already that aluminium triethyl was likely<sup>13</sup> to prove better in terms of stereoregulation: this has been substantiated. Further, we have used a Lewis base, ethyl anisate, a reagent which has found use<sup>14</sup> elsewhere.

Table 4 Supported catalysts prepared from (n/s Bu<sub>2</sub>Mg)/SiCl<sub>4</sub>/TiCl<sub>4</sub>

Catalyst (colour)	Cm <sup>3</sup> of SiCl <sub>4</sub> used	Mg/Cl	Polymer yield		Diluent-insoluble polymer		Soluble polymer
			(g/3 h)	(kg/g Ti)	(%)	$\bar{M}_v \times 10^{-5}$	$\bar{M}_v \times 10^{-5}$
Untreated (brown)	10	0.57	25	1.0	43	6.5	0.81
	100	0.57	23	0.96	39	6.2	0.74
Treated (violet)	10	0.83	54	2.3	46	6.6	0.74
	100	0.81	48	2.0	48	6.6	0.76

Polymerization conditions: catalyst 0.5 m mol, Co-catalyst 10 m mol TiBA; temperature 40°C; time 3 hours; diluent 1 dm<sup>3</sup> Isopar C

 Table 5 Treated catalysts from (n/s Bu<sub>2</sub>Mg)/100 cm<sup>3</sup> CCl<sub>4</sub>/TiCl<sub>4</sub> with EtOAn

m mol of EtOAn added to TEA	Catalyst (m mol)	Polymer yield			Diluent-insoluble polymer		Soluble polymer	
		(g/3 h)	(kg/g Ti)	(%)	Yield (kg/g Ti)	$M_v \times 10^{-5}$	Yield (kg/g Ti)	$M_v \times 10^{-5}$
0	0.02	15	15.6	65	10.1	6.7	5.5	0.73
1.5	0.10	58	12.1	81	9.8	6.8	2.3	0.74
1.5	0.03	18	12.5	82	10.2	6.7	2.3	0.71
3.0	0.10	41	8.6	93	8.0	6.8	0.6	0.76
3.0	0.05	20	8.3	93	7.7	6.6	0.5	0.75
3.5	0.20	18	1.9	95	1.8	6.6	0.1	0.75

Polymerization conditions: Co-catalyst 8 m mol TEA stirred with ethyl anisate (EtOAn); temperature 60°C; time 3 hours; diluent 1 dm<sup>3</sup> Isopar C

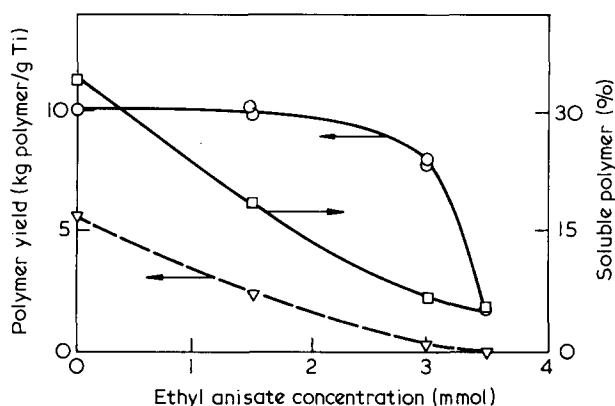


Figure 3 Effect of ethyl anisate concentration on the polymerization characteristics of a treated catalyst. (O) Insoluble polymer; (□) % soluble in total polymer; (Δ) soluble polymer

As displayed in Table 5, the use of aluminium triethyl does yield a more stereoregular polymer, but at reduced activity, (largely due to a rapid fall off in rate with time), whilst from Figure 3 it is seen that the ethyl anisate greatly improved the stereoregulation, by uniformly lowering yields of soluble polymer, but at high concentration yields of solid polymer are also reduced. Interestingly, it is likely from Table 5 that the only effect of the ethyl anisate in this system is to suppress active sites rather than to change their nature, since the molecular weights of the two fractions remain essentially unaltered with increasing anisate in the reaction.

We also report the use of these latter catalysts, which are highly active for propene, as ethene polymerization catalysts. Although the 'straightforward' reduction of titanium tetrachloride by magnesium alkyls is known to give very high activities<sup>4</sup>, which have been ascribed by use to very high proportions of active sites<sup>5</sup>, a conclusion supported by the closely related studies of Böhm<sup>7</sup>, yet there was clearly room for improvement since only about 50% of the titanium atoms were catalytically active. The technique of supporting the titanium atoms in a matrix of magnesium halide offers a route to this improvement, and

 Table 6 Polymerization of ethene with supported catalysts from Di (n + s) butyl magnesium/CCl<sub>4</sub>/TiCl<sub>4</sub>

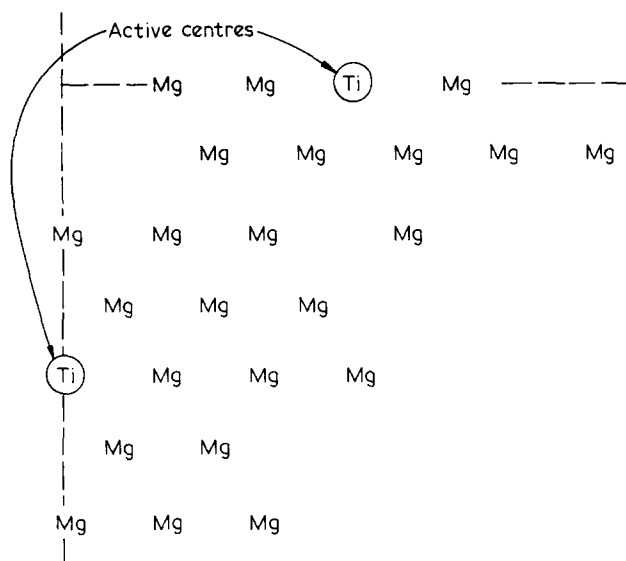
Temperature	Catalyst D (brown) Polymer yield (kg/g Ti)	Catalyst E (violet) Polymer yield (kg/g Ti)
50	170	200
55	140	170
65	170	170
70	170	200
75	200	250
80	200	230
85	170	200

so the type of catalyst prepared by precipitation from carbon tetrachloride/titanium tetrachloride was studied both before and after the TiCl<sub>4</sub> treatment.

Our initial studies were carried out at two atmospheres pressure, and under these conditions the two types of catalyst both worked well, giving good activities (Table 6). Surprisingly, there was little difference between the activities measured for the two catalysts at various temperatures (Figure 3) and so it must be concluded that with ethene as monomer, comparatively little is gained by the post treatment. This is readily understood if it is postulated that one function of the post treatment is to increase the surface order of the solid; in the polymerization of ethene it is most likely that a wholly disordered matrix is desirable since, probably, only access of monomer to the surface is of importance here.

## DISCUSSION

In the cases where it substantially increased activity, the effect of the titanium tetrachloride post treatment is interesting. Clearly, the major effect is to abstract titanium from the solid, and it seems that the material removed is probably not significantly catalytically active in any way, or at least not very active, since the activity per titanium remaining goes up as the titanium content goes down.



**Figure 4** Illustration of the separation of titanium active centres in a magnesium chloride lattice. (1) Only metal atoms are shown. (2) There would actually be significantly more disorder introduced than is shown, since  $\text{Ti}^{III}$  replaces  $\text{Mg}^{II}$

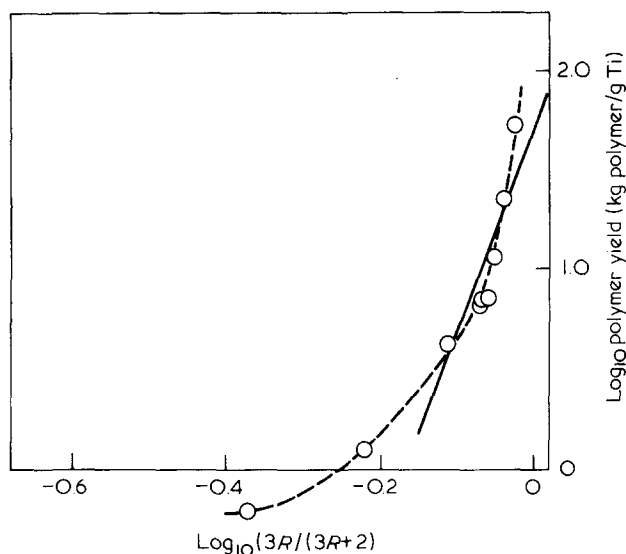
Moreover, the gain in activity cannot be explained simply in terms of loss of inactive titanium as the relative gains in yields of soluble and in particular solid polymer are about 5-fold and 8- to 9-fold, respectively, higher than the relative change in the Ti/Mg ratio. After  $\text{TiCl}_4$  treatment, either active Ti ions must be located in environments which produce an increased propagation rate or, in spite of a lowering of Ti/Mg, more Ti atoms are in the surfaces of the catalysts and so are available for polymerization. Whether either or both possibilities occur cannot be determined without measurement of active centres. There is also a small but consistent improvement of stereospecificity with  $\text{TiCl}_4$  treatment, as indicated by improvement in the percentage solid yield. This is a further indication of a change of environment of active centres.

Obviously, separation of  $\text{Ti}^{+++}$  ions by  $\text{Mg}^{++}$ , as is shown in *Figure 4*, where Ti and Mg ions are assumed to occupy holes in a regular lattice resembling the  $\text{MgCl}_2$  or  $\text{TiCl}_3$  lattices, is such an environmental change. In order to separate a surface Ti atom from its nearest neighbouring Ti atom by more than say 7 to 8 Å some 10 metal positions need to be occupied by Mg only. The chance of this occurring may be calculated assuming Ti and Mg ions are distributed at random in the lattice, and assuming also that a  $\text{Ti}^{3+}$  effectively occupies 3 sites, whereas an  $\text{Mg}^{2+}$  occupies 2, or that sites are occupied in this ratio. This hypothesis leads to the following equation for the chance,  $M$ , of finding an Mg ion in a given lattice position.

$$M = \frac{3[\text{Mg}]}{3[\text{Mg}] + 2[\text{Ti}]}$$

$$= \frac{3R}{3R + 2}$$

where  $[\text{Mg}]$  and  $[\text{Ti}]$  are the Mg and Ti contents of the lattice and  $R = [\text{Mg}]/[\text{Ti}]$ . The chances of configurations such as those shown in *Figure 4* are thus of the order of  $(M)^{10}$ . Indeed a plot of  $\log(\text{yield per g Ti})$  versus  $\log(M)$  (*Figure 5*) does show high order dependence of polymer yield on  $M$ . If it is further assumed that isolated Ti have higher propagation rates, then the rapid increase in activity per titanium with Mg/Ti ratio is explained. This is



**Figure 5** Illustrating the dependence of activity on Mg/Ti ratio (see text). The solid line shown has a gradient of 10. The last points (between -0.1 and 0 on the horizontal axis) lie close to a line of gradient 20, which corresponds to a separation between active sites of ~15 Å

in accord with the suggestion, which has been made elsewhere, that sites less than 5 to 9 Å apart are likely to be restricted in activity by the growing polypropene chain helices<sup>15</sup>. The present catalysts may be instances demonstrating this effect.

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