Titanium chloride–alkylmagnesium polymerization catalysts: effects of transformation to violet allotropes

John A. Licchelli, Robert N. Haward and Ian W. Parsons*
Department of Chemistry, University of Birmingham, P.O. Box 363, *Birmingham B*15 2*TT, UK*

and Anthony D. Caunt
Imperial Chemical Industries Ltd, Plastics Division, P.O. Box No. 6, *Bessemer Road, Welwyn Garden City, Hertfordshire AL*7 1*HD, UK*
(*Received* 29 *January* 1981)

Titanium (III) chloride catalysts, prepared by reduction of titanium (IV) chloride with magnesium octyl chloride and with dialkyl magnesiums, have been transformed to violet forms by treatment with titanium (IV) chloride, either in hydrocarbon solution or neat, at elevated temperatures. These materials show some increase in activity towards propene polymerization, but remain poorly stereoregulating catalysts.

INTRODUCTION

We have recently reported[1] our latest results on the catalytic activity of organomagnesium-reduced titanium chlorides, prepared in various ways, towards propene. This work followed on our previous studies of related materials as catalysis for ethene[2] and styrene[3], as well as our initial studies on propene[4]. In all these previous studies and despite various attempts, with a single exception, none of the materials made were, or could be converted to, the violet structure favoured in commercial $TiCl_3.\frac{1}{3}AlCl_3$ catalysts for propene polymerization, all the materials being of the brown type.

However, it is known that in other catalyst systems the transformation to a violet material confers substantial benefits upon the activity of the catalyst towards the propene, increasing both stereo-regulating ability and, often, reaction rate vis-a-vis the untransformed material. Accordingly we have made extensive and systematic attempts to procure this transformation, and we now report on the results of these experiments.

EXPERIMENTAL

Catalyst preparation

The reduction of $TiCl_4$ using alkyl magnesium compounds was carried out as described before, using the previously described apparatus for reverse addition. Subsequent treatments with liquid reagents were carried out by filtration of the material on the sinter, drying by prolonged passage of purified N_2 through it, and addition, by syringe, of the reagent to the residual solid, with constant stirring, via the rubber seal. The lower portion of the apparatus could be immersed in an oil bath for temperature regulation.

Polymerizations. Polymerizations were carried out exactly as described previously in Isopar C, which is an aromatic-free hydrocarbon diluent.

Viscometry was performed in decalin solutions using Ubbelhode viscometers. A one point method, due to Elliot[5], was employed to estimate $[\eta]$. Viscosity-average molecular weights, $\bar{M}_v$, were derived using the expression $[\eta]=1.4\times10^{-4}\ (\bar{M}_v)^{0.76}$, given by Boor[6].

RESULTS AND DISCUSSION

Initially, it was by no means certain that the transformation to a layer lattice could be achieved with these materials, since the early work of Haward and Roper[7] had shown that the materials were amorphous with no apparent (to X-rays) crystallinity. This was ascribed to the difficulty of Mg^{2+} and Ti^{3+} co-existing in a common lattice, and of course the transformation sought here presumably depends on the establishment of at least short-range and possibly medium range order in the material, to give a significant difference between the two structural types. Nevertheless, the isolated observation[1] of a violet material in our previous work gave cause for hope.

Methods used in the past on 'standard'-catalysts to produce the transformation fall essentially into two groups; those dependent on simple temperature control, including heating or cooling during the reduction stage and subsequent heating of the brown catalyst; and those utilizing a chemical reagent of some sort, such as $TiCl_4$, to assist in the change.

We have, as part of our initial studies, attempted various methods belonging to the first group, on magnesium reduced titanium catalysts, with uniformly poor success. Thus straightforward heating of the catalysts either dry to 250°C or in solvents gave only reduced activities, vis-a-vis the 'original' materials, and indeed, although the materials did darken in colour, they did not turn violet. We also prepared catalysts by adding slowly $TiCl_4$ to molten didodecylmagnesium at about

---

* To whom communications should be addressed

0032–3861/81/111558–03$02.00

Table 1 Comparison of didodecylmagnesium-reduced catalysts prepared at room temperature and 200°C. Polymerization conditions Cocatalyst TIBAL (triisobutylaluminal), temperature 40°C, diluent 1 dm^3 Isopar C, time 3 h, 1 atmosphere pressure of propene

Preparation temperature (°C)	Catalyst (mmol)	Co catalyst (mmol)	Polymer yield (g/gTi)	Mean activity (g/mmol h)	Insoluble polymer $\bar{M}_v \times 10^{-5}$	Soluble polymer %	Soluble polymer $\bar{M}_v \times 10^{-5}$
Ambient	0.5	5	2083	29	7.2	62.5	1.25
	1.0	10	2035	28	7.35	60.5	1.3
200	0.5	5	1097	17	7.3	62	1.19
	1.0	10	1128	18	7.2	61	1.18

Table 2 Treatment of didodecylmagnesium-reduced catalysts with 40% TiCl$_4$. Polymerization conditions as in *Table 1* using 0.5 mmol catalyst and 5 mmol TIBAL

Treatment of TiCl$_4$ treatment (°C)	Polymer yield (g/gTi)	Mean activity (g/mmol h)	Insoluble polymer $\bar{M}_v \times 10^{-5}$	Soluble polymers %	Soluble polymers $\bar{M}_v \times 10^{-5}$
Ambient	2152	34	5.35	60	1.03
40	2235	36	5.0	66	0.96
60	2738	44	4.05	65.5	0.91
80	4890	78	3.5	66	0.66
100	3447	55	3.55	64	0.64

200°C, the mol ratio of Mg to Ti being 0.5. The resulting product was dark brown rather than violet and showed diminished activity compared with catalysts prepared at ambient temperature. *Table 1* shows these rather disappointing results.

The activities of catalysts made using didodecylmagnesium were improved a little by washing the didodecylmagnesium, which is a solid, with heptane. A small loss of alkyl was found which was thought to be due to solubilizing by residual dioxan left from its preparation.

Attempts to induce transformation to violet catalysts were made using group 2 methods. Heating catalysts prepared from washed didodecylmagnesium with 40 volume percent of TiCl$_4$ in heptane, followed by removal of TiCl$_4$ with heptane washing gave significantly increased activity, although in no case were the catalysts turned violet (*Table 2*). The activity reached a peak with treatment at 80°C (*Figure 1*), but the stereoregulation was poor. The molecular weight of polymers decreased as the treatment temperature was increased.

The increase in mean activity of catalysts treated at 80°C was partly due to a change in the shape of the polymerization curve (*Figure 2*), there being less of a fall-off in rate after the maximum is reached. After the 80°C treatment, the maximum rate is also much higher. This may be connected with the interesting observation that the analysis of catalysts had changed from TiCl$_3$.0.5MgCl$_2$ before treatment to TiCl$_3$MgCl$_2$ after. This came about by loss of some TiCl$_3$ which had solubilized as a clear red solution in the TiCl$_4$/heptane solvent. No measurable amount of MgCl$_2$ had dissolved.

Similar treatments with 40% TiCl$_4$ in heptane at 80°C were carried out with catalysts prepared from a solution of dibutylmagnesium in heptane (equimolar primary and secondary butyls) or a solution of the Grignard reagent n-C$_8$H$_{17}$MgCl.THF in heptane. In no case was an activity increase observed nor any significant change in stereospecificity or colour. These catalysts were less active than those prepared from the insoluble didodecylmagnesium.

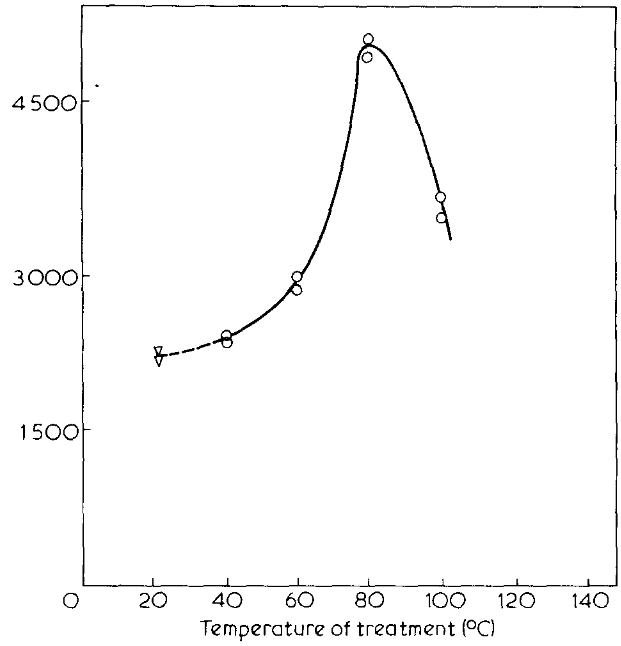

Figure 1 Effect of TiCl$_4$ solution treatment on yield. ▽, Untreated sample; ○, treated samples. Conditions, [Ti] = 0.5 mmol; [TIBAL] = 5.0 mmol

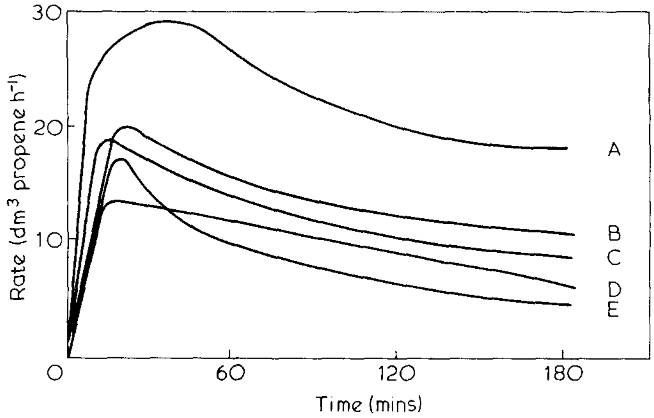

Figure 2 Effect on rate: time curve at 40°C of treating catalysts with a 40% (v/v) solution of TiCl$_4$. Conditions as for *Figure 1*. Temperature of treatment: A, 80°C; B, 100°C; C, 60°C; D, 40°C; E, untreated

However, preparations of didodecylmagnesium-reduced catalysts were found difficult to reproduce. Not all responded to TiCl$_4$ treatment as did the catalysts described in *Table 2* and *Figures 2* and *3*. At one stage it was suspected that an impurity (unidentifed) was

Table 3 Treatment of catalyst prepared from dibutylmagnesium – reduction of $TiCl_4$ with neat $TiCl_4$ after drying. Polymerization conditions as in *Table 1* using 1 mmol catalyst and 10 mmol cocatalyst, (DEAC = diethylaluminium chloride) at 60°C

Catalyst	Cocatalyst	Polymer yield (g/gTi)	Mean activity (g/mmol h)	Insoluble polymer $\bar{M}_v \times 10^{-5}$	Soluble polymer %	Soluble polymer $\bar{M}_v \times 10^{-5}$
Untreated (Brown)	TIBAL	1437	10	6.5	55	0.76
	TEAL	1245	8.7	5.4	50	0.88
	DEAC	144	1	3.5	62	0.75
Treated (Violet)	TIBAL	2874	20	6.6	50	1.05
	TEAL	1341	9.3	5.7	39	0.90
	DEAC	958	6.7	3.5	65	0.72

responsible for the removal of $TiCl_3$ observed with the highly active catalysts. As the stereospecificity remained poor it was decided to leave this problem in favour of further efforts to effect a change of catalyst colour to violet.

X-ray analysis of brown catalysts

X-ray powder studies were carried out on some of the catalysts. No lines could be seen in the photographs obtained from didodecylmagnesium based catalysts before or after treatment with titanium tetrachloride, but a few weak lines were detectable in those from the 40% solution-treated materials prepared from (n+s) butylmagnesium and from octyl magnesium chloride. However, these lines were too weak for useful measurements to be taken, although they definitely did not correspond with the usual magnesium chloride lattice.

Treatment with neat $TiCl_4$

Catalysts prepared by the more reproducible route involving the reduction of $TiCl_4$ with soluble dibutylmagnesium, were treated with neat $TiCl_4$. It was found that only careful drying of the brown solids from heptane by passage of nitrogen for several hours permitted the transformation to occur on treatment of the powder with titanium tetrachloride at temperatures above about 80°C, giving materials which were definitely violet in colour and which were active polymerization catalysts for propene. This treatment did not appear to alter significantly the elemental compositions of the catalysts, which were close to $TiCl_3 0.5(MgCl_2)$ both before and after treatment. This contrasts with the earlier treatment with 40% solutions of titanium tetrachloride, where the successful treatments of the didodecylmagnesium based material all leached out significant amounts of titanium.

These materials have been compared with their untransformed precursors using a variety of temperature/co-catalyst combinations (*Table 3*). The data summarized in the table illustrate the following points:

Firstly, the transformation increases catalyst activity, barely at all for TEAL, but very markedly for DEAC. Activities with DEAC are very poor with the brown catalyst.

Secondly, the hoped for large increase in stereoregulation is not apparent, although with TEAL there is some improvement. This behaviour clearly differentiates these catalysts from catalysts based on violet, layer-lattice $TiCl_3$ crystallites, such as Stauffer-AA, where DEAC produces moderate activity with far better stereospecificity.

Thirdly, it is interesting to note that the viscosity average molecular weights are essentially the same for the brown as for the violet materials. It seems likely therefore that the transformation from brown to violet has increased the number of active centres whilst their local environment and chemistry has remained relatively untouched.

CONCLUSIONS

Reduction of titanium tetrachloride with dialkylmagnesium or alkylmagnesium halide gives brown catalysts showing poor stereospecificity in propene polymerizations. Treatment of catalysts from (insoluble) didodecylmagnesium with dilute $TiCl_4$ can bring about a doubling of the activity, but this effect is difficult to reproduce. No crystal structure has been identified in the brown catalysts. Treatment of catalysts made by the more reproducible route using soluble dibutylmagnesium with neat $TiCl_4$, after drying, can effect a change to a violet, more active form. The stereospecificity is only slightly improved.

ACKNOWLEDGEMENTS

One of us (J. A. Licchelli) thanks the Scientific Research Council and ICI Plastics Division for the award of a CASE studentship. Grateful thanks are also tendered to Dr P. Gavens (ICI) for his assistance in catalyst transformation.

REFERENCES

1 Licchelli, J. A., Caunt, A. D., Haward, R. N. and Parsons, I. W. *Polymer* 1981, **22**, 667

2 Boucher, D. G., Haward, R. N. and Parsons, I. W. *Makromol. Chem.* 1974, **175**, 3461

3 Boucher, D. G. and Parsons, I. W. *Polymer* 1981, **22**, 255

4 Gardner, K., Parsons, I. W. and Haward, R. N. *J. Polym. Sci. Polym. Chem. Edn.* 1978, **16**, 1683

5 Elliott, J. H., Horowitz, K. H. and Hoodcock, T. *J. Appl. Polym. Sci.* 1970, **14**, 2947

6 Boor, J. Jnr. *J. Polym. Sci.* 1963, **C1**, 237

7 Haward, R. N., Roper, A. N. and Fletcher, K. L. *Polymer* 1973, **14**, 365