

Organomagnesium-reduced vanadium (IV) based catalysts for olefin polymerization

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Ethene has been polymerized using organomagnesium-reduced vanadium tetrachloride based catalyst systems. When used with aluminium alkyls as activators these materials give moderate activities, mostly in the range 10–30 kg polymer (g V)⁻¹, at 1 atm (10⁵ Pa) pressure over 2 h. The activities have been studied over the temperature range 30–80°C. These materials are only very poor catalysts for propene. Attempts to measure the concentrations of active sites in these materials by two different methods indicate that between 8 and 30% of the transition metal atoms function as active sites.

(Keywords: catalysis; olefin polymerization; vanadium (IV))

INTRODUCTION

The most useful and industrially significant Ziegler–Natta catalysts for the polymerization of olefins have been those based upon titanium and vanadium. In mechanistic studies titanium has assumed pre-eminent importance because, in addition to its technical and industrial importance, it has proved possible to isolate, identify, and study true catalytic precursors, such as α -TiCl₃. Solid VCl₃, like α -TiCl₃¹, has structural layers corresponding to hexagonal close packing of chlorine atoms, and might thus show some useful similarities to titanium catalysts in areas where crystal form is significant.

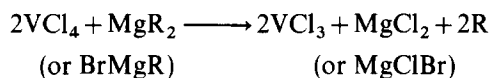
In analogy with titanium chemistry, Lehr², and Henrici-Olive and Olive³ have carried out studies using various vanadium species with aluminium alkyls as reductants/activators, and they concluded that the oxidation state for good activity is probably III, although it is difficult to be certain of this. More recently, Tait and co-workers^{4–6} have used vanadium trichloride activated with aluminium tri-isobutyl in an extensive and careful kinetic study of the polymerization of 4-methyl pentene.

Previous studies⁷ in these laboratories have shown, as have a number of other studies⁶, that catalysts formed by reduction, under a variety of conditions, of titanium tetrachloride with organomagnesium compounds have high activities for the polymerization of ethene and propene. These high activities have been attributed to the very disordered state of the precipitated materials, which led in turn to high concentrations of active sites.

We now report on our initial attempts to extend these studies to other transition metals; because vanadium was known¹⁰ to exhibit a reasonably extensive halogen chemistry it was chosen for the first foray in this field. Vanadium is known to give some activity for ethene polymerization (as well as possessing extensive and

various activities for dienes), and crucially it has a liquid tetrachloride, so that our standard types of reaction could be used straightforwardly for the production of vanadium catalysts.

These initial studies have concentrated mainly on the polymerization of ethene, using the general reaction



which is entirely similar to the reactions used in our earlier work.

EXPERIMENTAL

Materials

Propene was a gift from ICI Plastics Division, and other gases were supplied by BOC Ltd; all were dried and purified as previously described¹¹. Liquid diluents were purified by refluxing under N₂ overnight (at least) over either Na/K alloy or LiAlH₄. The main diluent used was Isopar C (Esso), an aromatic- and olefin-free hydrocarbon mixture boiling between 98 and 100°C. CCl₄ was dried over molecular sieves before use, and vanadium tetrachloride¹² was freshly prepared as required from vanadium metal and chlorine. Grignard solutions were synthesized as described previously⁷; the solution of magnesium (n+s)butyl in Isopar E (Texas Alkyls) was a gift from ICI, and the aluminium alkyls used were either gifts from ICI or supplied by Schering AG.

Catalyst preparations

The catalyst equations fall into three main groups: those in which solutions of the vanadium compound were reacted with magnesium alkyl solutions alone, those in which the VCl₄ was premixed with CCl₄ and this mixture reacted with solutions of magnesium alkyls, and those in

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which preformed MgCl_2 (from MgR_2 and CCl_4) was used as a support for VCl_4 .

All the preparations were carried out under N_2 in vessels having internal provision for washing and filtering the precipitated material. In the first case, catalysts were made by rapid addition of freshly prepared VCl_4 to a vessel containing a stirred solution of the reductant; this was followed by washing (three times) with n-heptane. Finally, the precipitate was reslurried in n-heptane and transferred by syringe to an N_2 filled storage vessel. In the second and third cases, the reductant solution was added by syringe to the reaction vessel; clearly, the preforming of MgCl_2 required subsequent addition of the VCl_4 to the reaction product from this step.

All the final catalyst slurries were analysed for V by a photometric method¹³ before use.

Polymerizations

The polymerizations were carried out in two different types of apparatus. Apparatus 1 was a 2.0 dm^3 mechanically stirred glass pressure vessel which could be run at up to approximately 8 atm^* . Gas consumption was measured with an inlet rotameter. Apparatus 2 was a mechanically stirred 1 dm^3 round-bottomed flask, suitable only for atmospheric pressure studies. Rates in this case were measured using a pressure transducer arrangement. Both set-ups were demand fed with monomer, and were checked for significant mass-transfer effects under the normal conditions of use. Normally, apparatus 1 was run with 1.5 dm^3 of diluent, while apparatus 2 was run with 0.5 dm^3 .

DISCUSSION

Initial studies on the catalysts formed by simple interaction of organomagnesiums with VCl_4 gave the results summarized in Table 1. There appears to be no significant difference between the results obtained using magnesium octyl bromide as reductant and those obtained using di(n+s)butyl magnesium; consequently these are not distinguished in the table.

Under these conditions, using triethyl aluminium (TEA) as cocatalyst, these materials are clearly catalysts of moderate activity for ethene, apparently showing their highest activities between 40 and 60°C and Al/V ratios of 10 – 20 . (In none of the trials we made was any significant activity found with propene.) However, the

catalytic yield was not well reproducible between successive catalysts, probably owing to rapid dying-off of some of the activity in the polymerization, which we attribute to over-reduction of the transition metal in the very early stages (Figure 1) of the reaction, as is often the case (but see, for example, reference 14) with TEA promoted reactions. The usual form of the rate-time curve is of the decay type, plus an apparently constant rate element which is responsible for most of the yield over 3 h. Thus, for the three rate-time curves shown in Figure 1, the percentages of the overall yield after 3 h represented by the constant rate portions of the curves (extrapolated back to the start of the reactions) are 68, 59, and 90% respectively, going from the most to the least active catalyst.

To check that this was not due to non-reproducibility of the polymerization conditions, and to check on mass-transfer effects, the experiments shown in Table 2 were carried out at constant TEA concentration. These show⁷ (see Figure 2) that for a given alkyl concentration, and using the particular catalyst, first that mass transfer

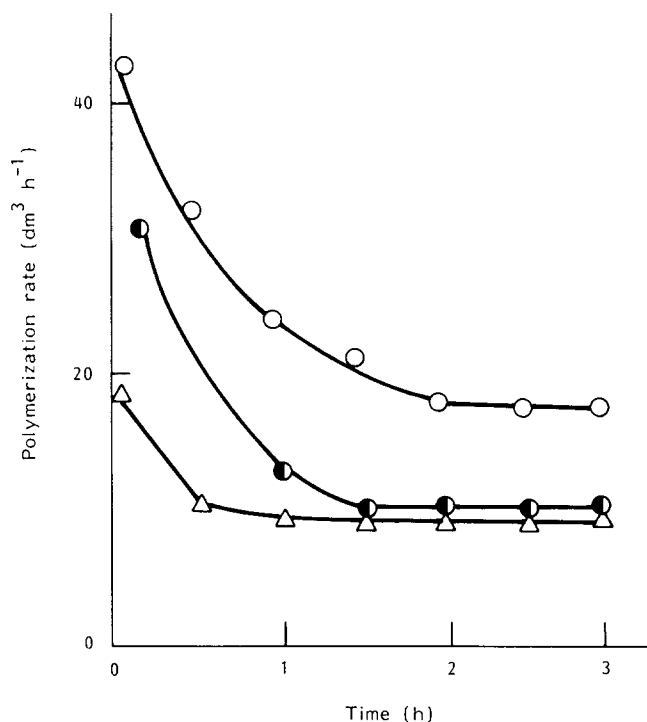


Figure 1 Typical rate versus time curves for straightforward catalysts: \circ , catalyst 1; \bullet , catalyst 4; \triangle , catalyst 7. Polymerization conditions and catalyst reference numbers are given in Table 1

* $1 \text{ atm} \approx 10^5 \text{ Pa}$

Table 1 Results obtained from a series of catalysts prepared by the 'straightforward' method

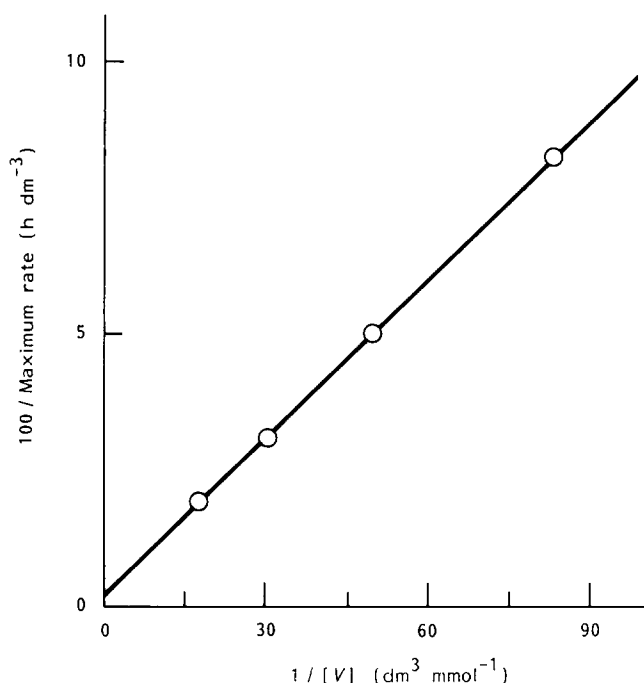
Ref. no.	Catalyst conc. (mmol dm^{-3})	Cocatalyst conc. (mmol dm^{-3})	Monomer pressure (atm)	Yield over 2 h ($\text{kg polymer (g V)}^{-1}$)
1	0.15	2.5	1.0	4
2	0.13	2.5	1.0	6
3	0.13	2.5	1.0	6
4	0.12	2.5	1.2	8
5	0.02	0.48	1.0	7
6	0.02	0.99	1.0	9
7	0.03	0.5	1.2	12
8	0.03	0.5	1.2	13
9	0.04	2.5	1.2	15
10	0.02	14.6	1.0	5

Catalyst preparation: typically $\text{Mg}(\text{octyl})\text{Br}$ (0.0425 mol) reacted with VCl_4 (2 cm^3), washed (three times) with n-heptane (100 cm^3)
 Polymerization conditions: 50°C ; AlEt_3 as cocatalyst; 2 h run; monomer pressure = total pressure

Table 2 Investigation of the effect of catalyst concentration on yield

Catalyst conc. (mmol dm ⁻³)	Max. rate (dm ³ h ⁻¹)	Average rate (dm ³ h ⁻¹)	Al/V	Yield (kg (g V) ⁻¹)
0.057	53	13.6	5.7	9.27
0.033	32	10.6	10	12.8
0.020	20	7.0	16	13.7
0.012	12	4.3	27	13.5

Polymerization conditions: C₂H₄ at 1.2 atm; temperature 50°C; 3 h run; [AlEt₃] = 0.32 mmol dm⁻³

**Figure 2** The linear relationship between the reciprocal of the maximum rate and the reciprocal of the vanadium concentration (data in Table 2)

is not an important limitation in our system (which can transfer ethene at 100 g h⁻¹); and second that the overall yield on catalyst is sensibly independent of catalyst concentration below about 0.05 mmol. Above this concentration there does seem to be a problem with the initial surge, since the measured maximum rate in the first run was approximately 50 g h⁻¹. This may be a significant fraction of the limiting transfer rate, thus this may have had some effect upon the measured yield, although the different Al/V ratio may be significant here too. Also, the viscosity of the diluent plus polymer suspension may be important in imposing transport limits here.

The effect of changing alkyl concentration has been separately assessed (Table 3) using both TEA and tri-n-octyl aluminium (TNOA) at 50°C. As the table shows, low concentrations of alkyl are beneficial with TEA but not with TNOA. We interpret this as showing slower over-reduction of the active vanadium species by TEA at lower concentrations, rather than superior complexing power of the TEA more severely inhibiting monomer access to the surface.

This is supported by our studies of the effects of temperature on the reaction. This has been checked with three different aluminium alkyls, TEA, TNOA and

diethyl aluminium chloride (DEAC). As is shown in Table 4, the temperature profiles vary, with the yield from TNOA increasing over the whole range studied, while TEA and DEAC, as is more commonly found, show a decrease in activity at 80°C compared with 50°C. The view that this is evidence for over-reduction by TEA, rather than for competitive absorption (between monomer and alkyl), is reinforced by the higher concentrations of TNOA and DEAC used, and by the reduced solubility of ethene in the medium at higher temperatures.

We have extended this study to supported versions of this system, using two separate procedures: coprecipitation of the reduced vanadium species with MgCl₂ by simultaneous reaction of the magnesium butyl with tetrachloromethane and VCl₄ (the 'premixed' catalyst); and preparation of MgCl₂ by the reaction of magnesium butyl with tetrachloromethane followed by treatment with VCl₄ (the 'preformed' catalyst). The results from these catalysts (Tables 5 and 6) are clearly superior to the straightforwardly made catalyst.

A priori it might be thought that the preformed catalyst would be superior (in terms of activity per gram of transition metal), since by the method of preparation the transition metal is likely to be distributed over the surface of the support, rather than occluded within it, and thus needs little or no disruption of the catalyst structure to achieve high activity. This is generally found to be the case, although the difference is perhaps not as marked as might be expected except for the not very active systems involving TEA and DEAC, where the preformed material seems to be up to four times more active.

It is, however, very noticeable that the optimum activity here is attained using TNOA as cocatalyst: we attribute this superiority to its poorly reducing behaviour,

Table 3 Effects of different aluminium alkyls on yield at 50°C for the straightforward catalyst

Catalyst conc. (mmol dm ⁻³)	Cocatalyst conc. (mmol dm ⁻³)	Al/V	Yield (kg (g V) ⁻¹)
0.01	AlEt ₃ 0.49	50	14
	2.47	250	7
	4.86	490	6
0.02	Al(n-octyl) ₃ 0.73	36	9
	1.45	72	10
	5.81	290	12

Table 4 Effects of temperature on polymerization yield for the straightforward catalyst

Catalyst conc. (mmol dm ⁻³)	Cocatalyst conc. (mmol dm ⁻³)	Al/V	Temp. (°C)	Yield (kg (g V) ⁻¹)
0.02	AlEt ₃ 0.49	25	30	8
			50	14
			80	3
0.02	AlEt ₂ Cl 1.07	53	30	7
			50	9
			80	6
0.02	Al(n-octyl) ₃ 1.45	72	30	5
			50	10
			80	15

All polymerizations conducted at 1 atm

Table 5 Results obtained for the 'premixed' catalyst using different polymerization temperatures and cocatalysts

Cocatalyst conc. (mmol dm ⁻³)	Catalyst conc. (mmol V dm ⁻³)	Temp. (°C)	Activity over 2 h (kg polymer (g V) ⁻¹)
TEA 4.0	0.098	40	5.8
		50	7.3
		60	7.1
		75	3.8
DEAC 6.0	0.098	40	5.4
		50	7.1
		60	6.8
		75	5.7
TIBA 4.0	0.098	40	4.7
		50	7.4
		60	9.0
		75	6.0
TNOA 8.8	0.088	40	13.0
		50	22.4
		60	24.9
		75	18.0

Catalyst preparation: CCl₄ (310 mmol) and VCl₄ (4.7 mmol) were mixed at room temperature and then MgBut₂ in hexane (14 mmol) was added. The washed solids were used as a slurry in heptane
All the rate curves were of the decay type

Table 6 Results obtained for the 'preformed' catalyst using different polymerization temperatures and cocatalysts

Cocatalyst conc. (mmol dm ⁻³)	Catalyst conc. (mmol V dm ⁻³)	Temp. (°C)	Activity over 2 h (kg polymer (g V) ⁻¹)
TEA 6.0	0.064	40	23.9
		50	20.6
		60	16.1
		75	8.5
DEAC 6.0	0.064	40	8.5
		50	21.3
		60	22.5
		75	13.7
TIBA 6.0	0.064	40	10.8
		50	14.3
		60	14.1
		75	13.3
TNOA 16.5	0.064	40	10.0
		50	23.4
		60	36.1
		75	17.6

Catalyst preparation: CCl₄ (310 mmol) and MgBut₂ in hexane (14 mmol) were reacted at room temperature and then VCl₄ (4.7 mmol) was added. The washed solids were used as a slurry in heptane
All the rate curves were of the decay type, except for the 40°C run with TIBA, which showed a constant rate

and have explored the effect of changing the alkyl concentration for the preformed catalyst (Table 7). At 50°C increasing the TNOA concentration increases overall yield over the whole range studied, whereas tri-isobutyl aluminium (TIBA) gives a constant yield at concentrations above about 12 mmol dm⁻³, and DEAC (presumed, on the basis of the results from the straightforward catalyst, to be similar to TEA) also increases the yield over the range to 50 mmol dm⁻³. Indeed, for this temperature the highest yield we have is attained using DEAC.

We note here also two further points of interest: first, the rate *versus* time curves for many of these reactions show (Figure 1) a very fast initial decay, followed by a very flat portion with no significant decay, suggesting

that a very stable catalytic system may be possible with vanadium. Second, we note that activities are of the same order in systems using TEA and systems using DEAC as cocatalysts. This contrasts with the analogous titanium systems, where TEA is a much better cocatalyst than DEAC. This observation leads us to speculate upon the nature of the active sites in the two types of catalyst.

Nielsen¹⁵, in a discussion of Solvay ether treated titanium/aluminium chloride catalysts, has suggested that there will be at least two types of active sites, which require to be activated in different ways, giving different results with the two types of alkyl. Briefly, his thesis is that sites of type II (see Scheme 1) may be activated by either alkyl type, whereas type I sites will only be activated by non-halogenated alkyls, since both bridging groups in the intermediate complex formed with, e.g., DEAC will be chlorine and thus the alkyl group transfer required to initiate the polymerization will be suppressed.

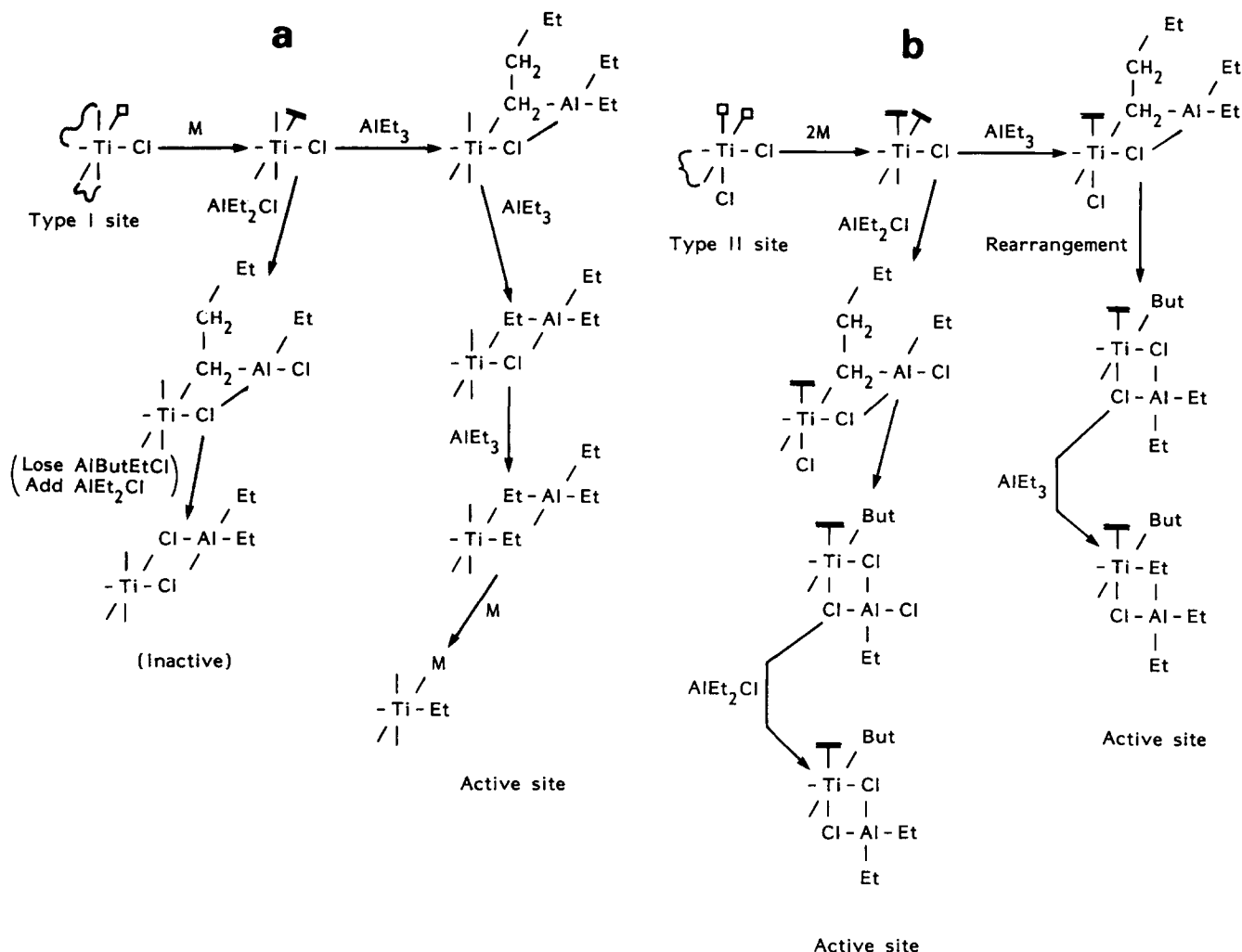
It seems, therefore, that in the titanium catalysts there is a preponderance of type I sites, which cannot be activated by DEAC, whereas in the vanadium equivalents the main contributors to the catalytic activity are of type II. Nielsen's original theory describes a further two types of site, generated by consideration of epitaxial adsorption of TiCl₄ onto the sites shown, but they are not germane here. It is not clear how much of the original argument, which applies to Solvay-type titanium-aluminium systems, is relevant to systems based upon vanadium or titanium species supported upon magnesium chloride, but it is plausible that the main structural features of the active centres will be similar, and that the bulk of Nielsen's argument will apply. We speculate that the difference between the vanadium and titanium systems may originate in the precipitation of the TiCl₃, which occurs in the β form, whose analogue is not known for vanadium.

A final investigation we have carried out concerns the concentrations of active sites in these materials. This has been estimated using the kinetic method previously employed^{7,11} by us, and by others (for example, reference

Table 7 Results obtained for the 'preformed' catalyst using various concentrations of different cocatalysts

Cocatalyst conc. (mmol dm ⁻³)	Catalyst conc. (mmol V dm ⁻³)	Activity over 2 h (kg polymer (g V) ⁻¹)
DEAC 4.0	0.054	11.9
	0.064	21.3
	0.054	28.5
	0.054	34.8
	0.054	39.9
TIBA 4.0	0.054	3.6
	0.064	14.1
	0.054	32.2
	0.054	32.4
	0.054	33.6
TNOA 8.8	0.064	16.5
	0.054	13.6
	0.064	15.2
	0.054	20.3
	0.054	27.4
	0.054	27.0
	0.054	30.3
	0.027	30.3

Catalyst preparation: CCl₄ (310 mmol) and MgBut₂ in hexane (14 mmol) were reacted at room temperature and then VCl₄ (4.7 mmol) was added. The washed solids were used as a slurry in heptane
Polymerizations: ethene at 1 atm; temperature 50°C



Scheme 1 Reaction of potentially active sites with aluminium alkyls AlEt_3 and AlEt_2Cl : (a) type I site; (b) type II site. Type I sites have one pendant chlorine ligand and one vacancy; the other ligands are chlorines bound into the crystal. Type II sites have two pendant chlorines and two ligands. After Nielsen¹⁵

16), which relies upon the change in \bar{M}_n with time, and using ^{14}C tagging. The former method, which usually gives high values, probably partly due to our use of viscometry data rather than gel permeation chromatography data to estimate M_n , suggests that $30 \pm 10\%$ of the transition metal atoms were active under the conditions employed (straightforward stoichiometric reduction, polymerization at 40°C , AlEt_3 activator). This is a very high number, and previous experience suggests that it will be too high, but it does indicate that a considerable fraction of the transition metal species is active.

The radiotagging method* was employed on a preformed catalyst, using TIBA as activator and a polymerization temperature of 60°C . Polymerization for 1 h, followed by reaction with radioactive CO for 7 min before quenching with methanol gave a polymer whose activity corresponded to 8.2% of the vanadium atoms being active. This is again a high value, suggesting that there is a large number of active sites in these species. A similar experiment with a straightforward catalyst gave a result of 4.2% of the transition metal being active.

* For a discussion of the methods used, see, for example, reference 17. For a discussion of the possible limitations of the method see reference 18

Although these two types of active centre determination give very different answers, they are not necessarily incompatible. Apart from the differences in polymerization temperature and activator, imposed by experimental considerations, the molecular weight method involves extrapolation to zero (yield or time) and so includes any rapidly decaying centres in the count: the rapid fall-off in the rate profiles (Figure 1) suggests that there will be some of these in the present catalysts. The ^{14}C tagging method, however, was applied after 1 h polymerization, when most such centres would be expected to have decayed, and the results may thus represent more nearly than will the results from the other method the time independent activity of the catalyst.

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