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Polymerization of styrene with a magnesium-reduced titanium chloride-based catalyst system

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INTRODUCTION

The number of sites active for polymerization in a Ziegler–Natta catalyst system is a quantity whose evident importance has led to repeated attempts to measure it. Since the activity is normally ascribed to the transition metal component it is usual to express the number of active sites as a fraction of the number of transition metal atoms.

There have been a number of methods employed for such measurements: they have been divided into kinetic methods and methods based upon labelling studies, and there are numerous publications, including a recent authoritative review[1], concerned with this area. Unfortunately, until fairly recently the methods available have been laborious (but see ref. 1) or unreliable, and so there have been few attempts either to cover a wide spectrum of catalysts using a consistent methodology or to study the reactivity of a single catalyst with a series of monomers. A notable exception to this is the study[2] of Schnecko *et al.*

We[3] and others[4] have previously reported the high activity of Grignard reagent-reduced titanium tetrachloride-based catalysts in the polymerization of ethylene. In the course of our study, the fraction of titanium atoms active as polymerization centres at 60°C was estimated to be about 60%, and the conclusion was drawn that the high activity was due to this large fraction of active transition metal atoms. Subsequently, we reported work with propylene[5], where a similar estimation yielded a figure of 3% as the fraction of titanium atoms active at 40°C — again this is a fraction greater than commonly found.

We now report our studies on the polymerization of styrene with this catalyst system, emphasizing in particular the estimation of sites active for styrene polymerization.

After an initial trial polymerization using aluminium triethyl as cocatalyst had established that styrene does react appreciably with this catalyst system, a conclusion reinforced by the isolation of an isotactic fraction[7] via solvent extraction, kinetic runs were carried out in magnetically stirred dilatometers, adopting the usual precautions against oxygen and water. Polymers were isolated to check conversions and to give samples for viscometry and gel permeation chromatography, since the active site determination depends upon the variation of molecular weight with conversion.

EXPERIMENTAL

Materials and methods

Styrene was washed with NaOH solution and with water, dried with $CaCl_2$ and with CaH_2 before fractional distillation under vacuum. The distilled styrene was stored (briefly) over CaH_2 before transference to the dilatometers via burettes fitted to a high (10^{-3} torr) vacuum line.

Isooctane (2,2,5-trimethylpentane) was dried by refluxing over Na/K allow before distillation under purified N_2. The distillate was passed under N_2 through a column of molecular sieve (Linde 4A) before storage on the vacuum system.

Aluminium triethyl (Schering AG) was used as supplied.

Catalyst preparation was performed exactly as before, by reducing a solution of $TiCl_4$ in isooctane with a solution of dodecylmagnesium bromide in the same solvent at the ambient temperature.

Dilatometers were thoroughly cleaned, dried at 120°C in an oven and attached hot to the vacuum manifold. They were charged with styrene diluent and catalyst slurry via a rubber seal, and degassed by freeze–thaw cycles before addition of aluminium triethyl, adjustment of volume to a predetermined mark, and sealing under vacuum. A PTFE coated magnetic stirring bar was included in each dilatometer. The sealed dilatometers were placed in a thermostatically controlled (±0.03°C) bath and magnetically stirred during the experiments.

Polymers were isolated by pouring the contents of the opened dilatometer into stirred methanol (2 dm^3) acidified with concentrated HCl (20 cm^3). The dilatometer was washed out several times with toluene to remove all the polymer, and the combined liquids stood overnight to coagulate the polymer. This was filtered off (glass sinter) and dried (at 50°C *in vacuo*) to constant weight.

Viscometry was performed at 25 ±0.03°C in standard Ubbelhode viscometers on *o*-dichlorobenzene solutions.

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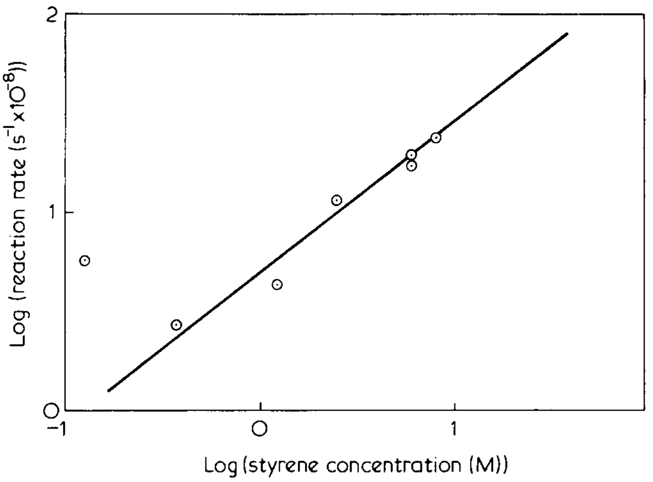

Figure 1 Dependence of reaction rate on styrene concentration temperature, 50° C; [Al(nOctyl)$_3$], 7.7 x 10^{-3} M; [Ti], 1.4 x 10^{-2} M

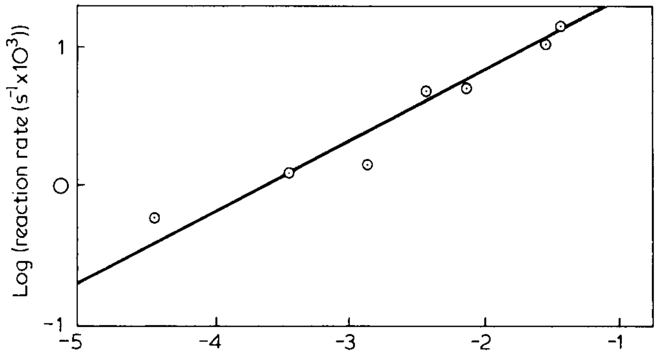

Figure 2 Dependence of reaction rate on titanium concentration temperature, 50° C; [Al(nOctyl)$_3$], 7.7 x 10^{-3} M; [Styrene], 6.2 M

Molecular weights were calculated using parameters from Krigbaum[6].

Gel permeation chromatography (*g.p.c.*) was performed at RAPRA, using tetrahydrofuran (THF) solutions.

DISCUSSION

Although this catalyst system is active for styrene polymerization, it is not an efficient one. The reaction in isooctane solution is slow, and gives strikingly low amounts of stereoregulation (isotactic material), in contrast with commercially-available materials, for example, Stauffer AA grade ($TiCl_3$ 1/3$AlCl_3$), which react much more rapidly[8] and give a highly stereoregular product. (We have confined our study to isooctane solutions in order to maintain comparability with our earlier studies, but of course the styrene itself partly vitiates this).

Kinetic studies at 40°C, employing methods of analysis similar to those of Tait *et al.*[9], yielded the salient results that the reaction order in styrene is appreciably less than unity (0.75 ± 0.15), see *Figure 1*, whilst that in titanium is about 0.5 (0.47 ± 0.05), see *Figure 2*. Studies at various temperatures between 30° and 70°C were aimed at an estimation of the activation energy for the reaction (*Figure 3*). However, as marked on the Figure, it is not clear whether the data are best interpreted as a single activated process or as two, with a breakpoint at about 50°C. For the former interpretation the overall activation energy is calculated to be 64 ± 30 kJ mol^{-1}, whereas in the latter case the two energies are, 100 ± 30 kJ mol^{-1} between 30° and 50°C, and 20 ± 9 kJ mol^{-1} between 50° and 70°C.

The method of estimating the concentration of active sites has been set forth before by us[3,5] and by others[10]. Essentially it consists of using a knowledge of the variation of $\bar{M}_n$ and conversion with time to calculate the variation in the numbers of molecules with time. Extrapolation of this quantity to zero time, or zero conversion, gives the estimate of [C*], and the gradient gives an estimate of the transfer rate. This analysis assumes, of course, that [C*] is actually a constant over the duration of the experiment. We are not clear that this will be so for this system, so our value for [C*] represents a minimum estimate — it may be that sites are continuously created in a system containing appreciable amounts of styrene powerfully adsorbed onto the catalyst surface — and we give no value for the transfer constant. The relevant data are displayed in *Figure 4*, and they lead to the result that the fraction of titanium atoms active for styrene polymerization is 0.1 ± 0.08%. The rather large error arises from both the scatter in our data and the use of a reciprocal plot.

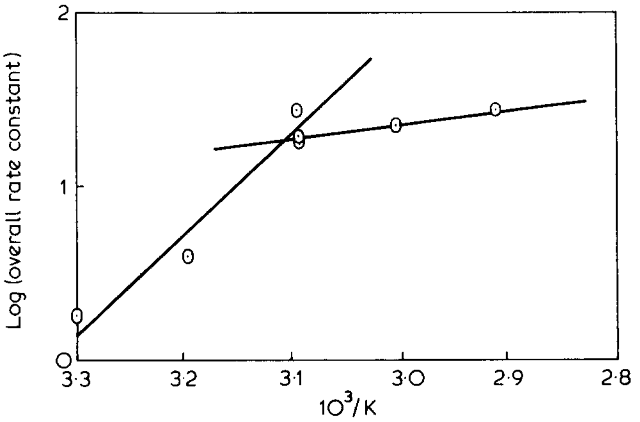

Figure 3 Arrhenius Plot, showing the effect of temperature on reaction rate. [Al(nOctyl)$_3$], 7.7 x 10^{-3} M; [Ti], 1.4 x 10^{-2} M; [Styrene], 6.2 M

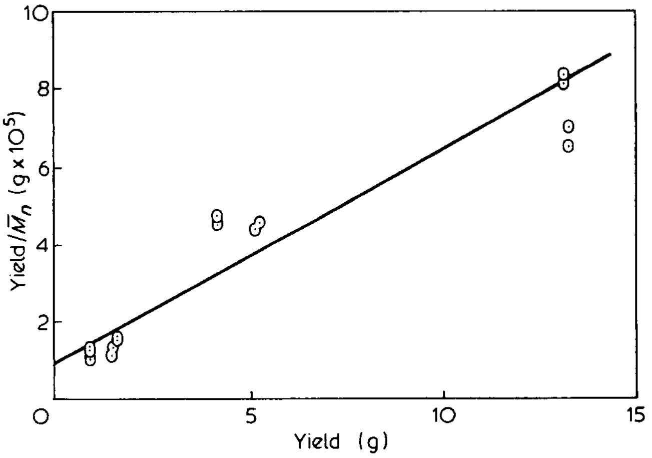

Figure 4 Determination of active site concentration 50°C, [Ti] = 1.4 x 10^{-2} M; [Al(nOctyl)$_3$], 7.7 x 10^{-3} M, [Styrene], 6.2 M

The large difference in the number of active sites for styrene (0.1%) and ethene (60% of titanium atoms) found with this catalyst strongly suggests that the reactivity with ethene must depend heavily upon the breaking-up of the performed catalyst particles into very small pieces indeed. Only thus can the very high site concentration be generated for ethene, and the lower site counts for other monomers may be explained on the basis that encapsulation of catalyst particles within growing polymer particles is faster than diffusion - with concomitant disruption of the inorganic matrix — of these larger molecules into the catalyst particles.

A Referee suggests that, alternatively, it may be that the different monomers are directly involved somehow in the formation of active sites, other than by their simple consumption, and that this involvement causes the different numbers of active sites via differing reactivities of monomers. We cannot, however, see how to distinguish these possibilities with presently available data.

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^{13}C nuclear magnetic resonance spectroscopy of polyvinylferrocene

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INTRODUCTION

Many studies have shown that ^{13}C n.m.r. is a useful tool for detecting and measuring the distributions of stereochemical configurations that can occur in polymers. Monomer placement assignments (triad, tetrad, pentad, etc.) are generally made after observing a close conformity of a methylene or methine intensity distribution with either Markovian or Bernoullian statistics.

We report in this note the stereochemical configuration of polyvinylferrocene by means of a ^{13}C n.m.r. study showing the assignment of the peaks arising from tetrad and hexad configurations.

EXPERIMENTAL

Polyvinylferrocene was prepared with butyllithium in tetrahydrofuran at 20°C[1-2]. The ^{13}C n.m.r. spectra were recorded at 25.033 MHz at approximately 120°C on a Jeol J NM PS 100. The polyvinylferrocene sample was dissolved in *ortho*(1,2-)dichlorobenzene and mono-bromo-perdeuterobenzene was added to the mixture to maintain a lock signal at 120°C.

Polyvinylferrocene spectra were accumulated with pulse spacings of 0.82 s. The spectra were ^{1}H noise decoupled and obtained after accumulation of 20000 transients.

RESULTS AND DISCUSSION

The point of most interest is the methylene carbon resonance (*Figure 1*) in which nine methylene resonances are present.

This observation is in itself interesting since a ^{13}C n.m.r. sensitivity to just tetrad sequences would have produced six resonances while a complete hexad sensitivity would have produced twenty resonances. Combinations of tetrad and hexad resonances are possible that will produce

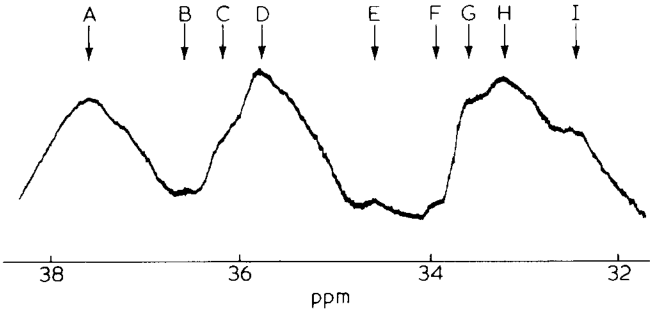

Figure 1 The methylene region of a ^{13}C n.m.r. spectrum for polyvinylferrocence at 25.033 MHz and 120°C. The ppm values are relative to TMS

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