Isomerisation on the $CrCp_2/SiO_2$ catalyst during polymerisation of ethylene: pressure dependence

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Abstract

Ethylene polymerisations have been carried out with the $CrCp_2/SiO_2$ catalyst at ethylene pressures from 6 to 20 bar. End-group analyses show that the formation of methyl side branches and transvinylene fragments are strongly dependent on the ethylene pressure used. Such fragments can be formed from an isomerised active site. From a selected reaction scheme a set of relative rate constants has been estimated. The strong dependence of the activity on the ethylene pressure for this catalyst is suggested to be due to a shift in the relative number of potentially active sites towards less active isomerised sites at low ethylene pressures. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polyethylene; Chromocene catalyst; Isomerisation; Kinetics

1. Introduction

The catalyst based on chromocene, $CrCp_2$, reacted with calcined silica, is a very active catalyst for polymerisation of ethylene [1]. Karol et al. [2] at Union Carbide have studied the kinetics of the catalyst when polymerising ethylene alone and in the presence of hydrogen as chain transfer agent. One peculiar property of the catalyst is its ability to produce methyl side branches as well as transvinylene fragments when homopolymerising ethylene. Karol et al. studied the formation of methyl side branches in a qualitative and indirect way, by relating the number of branches to the density of the poly-

mer [3]. In the present paper we have studied the formation of methyl side chains as a function of the ethylene pressure used in the polymerisation. The number of methyl branches as well as transvinylene and vinyl fragments has been measured by spectroscopic methods, thus allowing quantitative kinetic relations to be estimated. A qualitative partial explanation of the strong pressure dependence of the activity is also given.

2. Experimental

2.1. Chemicals and general considerations

$CrCp_2$ (99%) was purchased from Strem Chemicals and used without further purification.

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All solvents used were purified by standard techniques. The silica powder used was EP10 from Crosfield Silicas. All precursors and catalysts were handled and stored under an inert atmosphere, either on a Schlenk line or in a glove box.

2.2. Catalyst preparation

The silica was calcined in a fluidised bed reactor in dry air at 800°C for 16 h, then cooled to ambient temperature in dry nitrogen. When preparing the catalyst, typically 5.0 g calcined silica was transferred to a 50-ml flask in the glove box. Then, 45.0 g mineral oil was added together with a magnetic stirrer. The mixture was stirred to give a homogeneous slurry before a 10 wt.% toluene solution of $CrCp_2$ was added by using a syringe to give 1.0 wt% Cr on the silica. The slurry was stirred for approximately 1 h before it was sealed.

2.3. Polymerisation

Homopolymerisation of ethylene was carried out in a 1-l stainless steel autoclave equipped with a magnadrive stirring system. Batch, slurry polymerisations were performed at 95°C by using 0.5 l of isobutane as diluent. The temperature in the autoclave was kept constant to within ± 0.5°C by an external thermostated bath. The total pressure was kept constant by adding ethylene. After each polymerisation the pressure was released, the autoclave opened, and the polymer collected. The effective partial pressure of ethylene was estimated from the total pressure by using a computer program based on the Peng–Robinson equation of state.

2.4. Polymer characterisation

The polyethylene product was characterised by ^{13}C-NMR and infrared spectroscopy. Our main incentive was to estimate the amount of vinyl, transvinylene and methyl side branches (Me_b). Vinyl and transvinylene fragments were determined as explained in Ref. [4], while the total methyl content was estimated according to ASTM standard D 2238. Methyl side branches give a specific peak at 1150 cm^{-1} in the infrared spectrum. The extinction coefficient of this absorption was estimated from quantitative ^{13}C-NMR measurements for one polymer sample. The NMR experiments were carried out by dissolving a certain amount of polyethylene in 1,2-dichlorobenzene in a 5-mm NMR tube. The air in the tube was removed under reduced pressure before the tube was sealed. The ^{13}C-NMR spectra were recorded at 130°C by using a 16° pulse and 30 s between each pulse. Infrared spectra were recorded on approximately 0.5 mm polymer plates made by pressing the polymer powder in a die between two brass plates at 170°C. The number of methyl side branches per 1000 C for the polymer produced in Exp #6 in Table 1 was estimated by measuring the ratio between the area under the peak at $\delta 20.0$ (specific for methyl side branches [5]) relative to sum of the areas under the other peaks stemming from polyethylene in the spectrum. From

Table 1
Results from polymerisation with $CrCp_2/SiO_2$ catalyst

Exp. #	$[E]$ (bar)	Yield (g)	Activity (kg$_{PE}$/g$_{Cr}$ h)	Vinyl/1000 C	Transvinylene/1000 C	Me_b/1000 C	Total Me/1000 C
1	6.2	13.6	4.6	0.121	0.48	20.3	18.6
2	6.2	18.7	3.0	0.115	0.48	17.1	18.3
3	13.2	66.0	47.5	0.118	0.17	6.6	7.8
4	13.2	62.1	43.9	0.117	0.16	6.9	7.3
5	20.1	92.0	139.0	0.119	0.11	4.7	5.4
6	20.1	69.7	128.0	0.109	0.09	4.3	5.1

All polymerisations were performed at 95.0°C. Approximately 160 mg catalyst was used in each run.

the known value of $Me_b/1000$ C and the absorbance of the peak at 1150 cm^{-1} in the IR spectrum, an extinction coefficient was estimated to $1.2 \cdot 10^8$ cm^2/mol. This extinction coefficient was then used to determine the number of methyl side branches for the other polymer samples.

Nonlinear least-squares fitting of constants in curve equations from the data was carried out with the Excel spreadsheet, using the Solver tool.

3. Results and discussion

Ethylene polymerisations were carried out at ethylene pressures in the range 6 to 20 bar with

a $CrCp_2/SiO_2$ catalyst containing 1.0 wt.% Cr. The polymerisation conditions and the activity data are given in Table 1 together with the results from end-group analyses by infrared spectroscopy.

There is a strong dependence of ethylene pressure on the activity, as have been shown earlier [1]. We believe this is caused by a pressure dependence on the number of exposed active sites, and not a higher than first order dependence in the ethylene pressure of the rate equation.

By adopting the reaction schemes developed by Karol et al., we can, in the absence of hydrogen, set up the reactions shown in Scheme 1. We have included both chain transfer to monomer (k_M) and hydride transfer to chromium

Scheme 1.
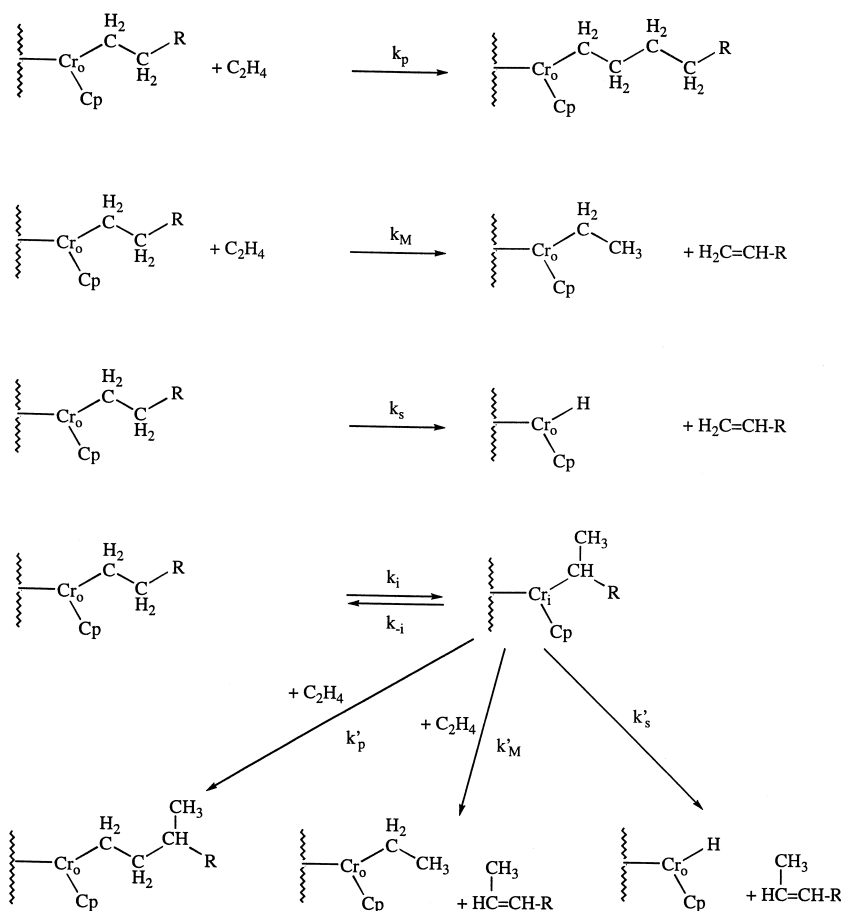
(k_s) on the polymerisation active Cr_o site. Isomerisation on the active site (k_i) forms a chromium site denoted Cr_i. Three reactions can proceed from the Cr_i site: propagation under formation of methyl side branches (k'_p), chain transfer to ethylene (k'_M) and hydride transfer to chromium (k'_s).

By assuming that all reactions are of first order and that propagation from Cr_i sites is negligible compared to propagation from Cr_o sites, the rate of polymerisation can be written:

$$\frac{d[P]}{dt} = k_p[Cr_o][E] \tag{1}$$

where $[Cr_o]$ denotes the concentration of active sites that have not carried out an isomerisation (k_i) as the last step. $[E]$ is the partial pressure of ethylene. In a similar way, the rate of formation of vinyl chain ends, *trans*-2-butyl chain ends (here called transvinylene) and methyl side branches can be written:

$$\frac{d(vinyl)}{dt} = (k_M[E] + k_s)[Cr_o], \tag{2}$$

$$\frac{d(transvinylene)}{dt} = (k'_M[E] + k'_s)[Cr_i], \tag{3}$$

$$\frac{d[Me_b]}{dt} = k'_p[Cr_i][E]. \tag{4}$$

An expression for the number of vinyl formed relative to the number of propagation steps can be obtained from Eqs. (1) and (2):

$$\frac{d(vinyl)}{d[P]} = \frac{(k_M[E] + k_s)[Cr_o]}{k_p[E][Cr_o]}$$

$$= \frac{k_M}{k_p} + \frac{k_s}{k_p}\frac{1}{[E]}. \tag{5}$$

Fig. 1 shows the number of vinyl fragments expressed in vinyl/1000 C as a function of the inverse partial pressure of ethylene in the reac-
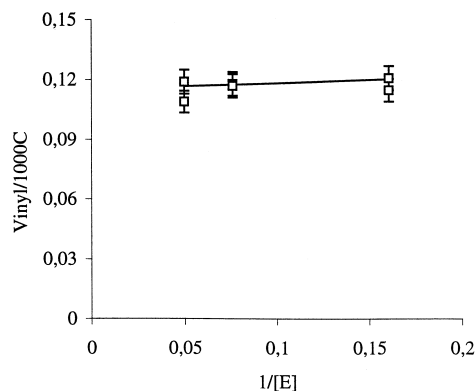

Fig. 1. The number of vinyl groups plotted against the inverse partial pressure of ethylene, $1/[E]$. The line shows the best fit to the experimental points.

tor (data from Table 1). As can be seen, the data form a straight, close to horizontal line with $k_s/k_p = 0.3(3) \cdot 10^{-4}$. A slope not significantly different from zero indicates that termination by hydrogen transfer to monomer is the predominant chain termination mechanism at the conditions used. It is noted that a similar observation has been made for the CrO/SiO_2 catalyst [4]. The k_M/k_p ratio is found to be $1.2(2) \cdot 10^{-4}$, very similar to the value reported by Karol et al. [2] of $1.4 \cdot 10^{-4}$ at 90°C.

In order to develop a similar expression for the number of transvinylene fragments and methyl side branches formed, one can assume that $[Cr_i]$ is at steady state. The following equation can then be written:

$$k_i[Cr_o] = k'_p[Cr_i][E] + k'_M[Cr_i][E] + k'_s[Cr_i]$$
$$+ k_{-i}[Cr_i]. \tag{6}$$

Reorganising with respect to $[Cr_i]$ gives:

$$[Cr_i] = \frac{k_i[Cr_o]}{(k'_p + k'_M)[E] + k'_s + k_{-i}}. \tag{7}$$

For the pressures used here, one may assume to a first approximation that $(k_p + k_M)[E] >> (k_s + k_{-i})$, so the last terms in the denominator may be omitted.

This expression for $[Cr_i]$ can be introduced into Eq. (3) and by dividing with Eq. (1), one

obtains the following expression for the concentration of transvinylene fragments:

$$\frac{d[transvinylene]}{d[P]} = \frac{k'_M}{k_p}\left(\frac{k_i}{k'_p + k'_M}\right)\frac{1}{[E]}$$
$$+ \frac{k'_s}{k_p}\left(\frac{k_i}{k'_p + k'_M}\right)\frac{1}{[E]^2}. \tag{8}$$

The same procedure can be repeated for the formation of methyl side branches, which gives the following expression:

$$\frac{d[Me_b]}{d[P]} = \frac{k'_p}{k_p}\left(\frac{k_i}{k'_p + k'_M}\right)\frac{1}{[E]}. \tag{9}$$

As these expressions are invariant in the number of active sites, they should hold even if the number of active sites is different at the different pressures. Fig. 2 shows the number of transvinylene fragments plotted against the inverse partial pressure of ethylene. The curve is the best fit of Eq. (8) to the experimental points, yielding the constants 1.5(2) and 10(2) before the first and second order term in Eq. (8), respectively.

Fig. 3 shows the number of methyl side branches against the inverse partial pressure of ethylene. The slope is 0.11(1).
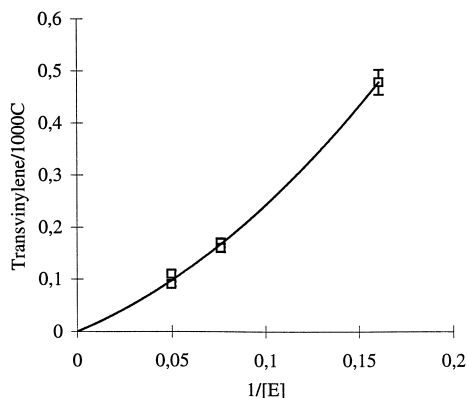

Fig. 2. The number of transvinylene plotted against the inverse partial pressure of ethylene, $1/[E]$. The curve shows the best fit to the experimental points.
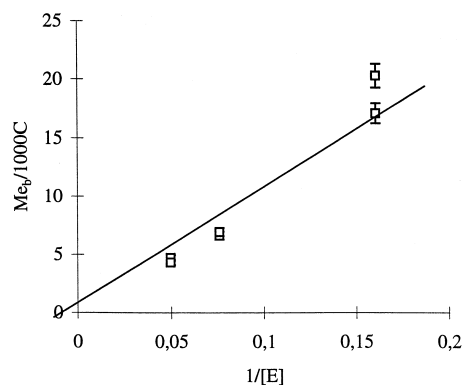

Fig. 3. The measured number of methyl-side branches per 1000 C plotted against the inverse partial pressure of ethylene, $1/[E]$. The line is the best fit to the experimental points (the point at (0.16, 20) was omitted in the least-square analysis).

Noting that the term in the brackets in Eqs. (8) and (9) is identical, the relative magnitude of the three rate constants can be estimated at 10 bar ethylene pressure: $k'_p[E]/k'_M[E]/k'_s = 118/1.6/1$. If instead assuming $k_{-i} = 0$ and carrying out a least-square fit of Eqs. (8) and (9) without the assumption $(k_p + k_M)[E] >> (k_s + k_{-i})$, we obtain the relative rates $115/1.5/1$, which is indistinguishable from the numbers obtained above. In contrast, the k_p/k_M ratio is approximately 8300, which is nearly 100 times greater. The decreased ratio for the isomerised site probably reflects a much lower polymerisation rate constant k'_p as compared to k_p, as k'_M should not be expected to be higher than k_M. This great difference between the rate constants of the regular polymerising site, Cr_o, and the isomerised site, Cr_i, falls in line with the known tendency for Cp_2Cr/SiO_2 not to copolymerise higher 1-alkenes. Also, the relative importance of β-elimination over chain transfer to monomer seems to be greater for the isomerised site, which again could point to some steric hindrance for transfer to monomer at the isomerised site.

Support for the assumption that k_{-i} is small can be obtained by comparing Eq. (6) with the activity at different partial pressures of ethylene. If k_{-i} is large, the last term of the denominator will dominate and the number of Cr_o sites will

show a low dependency on the ethylene pressure. On the other hand, if the last term is small, a first order dependence is expected leading to a pseudo second order dependence in the ethylene pressure on the polymerisation rate, which is close to the observed trend. There is a possibility for most of the active sites to be present in the Cr_i state because of the slow reactions of this site. This may in part explain the strong dependence of activity on ethylene pressure, but is probably not the whole explanation.

4. Conclusions

It is shown that the reactions in Scheme 1 may lead to a good description of the branching and chain terminating reactions in ethylene polymerisations over Cp_2Cr/SiO_2. From end-group analyses, a set of relative rate constants has been estimated. The strong dependence of

the ethylene pressure on the activity may partly be rationalised as most of the potentially active sites being trapped as isomerised sites at low ethylene pressures.

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