

Ethylene Insertion with Soluble Ziegler Catalysts: Direct Insight into the Reaction Using Enriched $^{13}\text{C}_2\text{H}_4$ and ^{13}C NMR Spectroscopy

II. The System $\text{Cp}_2\text{TiMeCl}/\text{AlMeCl}_2/^{13}\text{C}_2\text{H}_4^*$

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Dedicated to Professor Dr. Dr. h. c. mult. Günther Wilke on the occasion of his 60th birthday

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Ziegler Catalysis, Ethylene Insertion, ^{13}C NMR Spectra

The elementary processes involved in the polymerization of ethylene by soluble Ziegler catalysts of the type $\text{Cp}_2\text{TiMeCl}/\text{AlMeCl}_2$ have been studied by ^{13}C NMR spectroscopy. Using ^{13}C -enriched ethylene, detailed information was obtained directly on the system in the course of the polymerization. No spectroscopic evidence was found for precoordination of the monomer. The development of the oligomer distribution, which could be followed spectroscopically, proves that the mechanism proposed by Olivé cannot be correct. These experiments show conclusively that the ethylene is inserted into the titanium-carbon bond.

Introduction

Ziegler-Polymerization is poorly understood at the molecular level since the nature of the active species is still unknown. Accordingly, the central theme of our investigations in the field of soluble Ziegler catalysts is the quantitative elucidation and formulation of all elementary reactions down to the elementary steps in catalytic action. A major objective in these studies is the measurement of precise and pertinent experimental data. One suitable method for obtaining information on catalytically active systems without disturbing the reaction is ^{13}C NMR spectroscopy.

In an earlier publication [1] we reported our studies on the polymerization of ^{13}C -enriched ethylene using the soluble $\text{Cp}_2\text{TiEtCl}/\text{AlEtCl}_2$ catalyst in an NMR sample tube. Experiments using a batch reactor have shown that this Ti–Et system is a much more active polymerization catalyst than Ti–Me systems (see Fig. 1). The lowest curve (solid line) is for the $\text{Cp}_2\text{TiMeCl}/\text{AlMeCl}_2$ catalyst system, with which the polymerization proceeds much more slowly. This catalyst is ideally suitable for the ^{13}C NMR investigations reported here, and with the right choice of experimental parameters it has proved possible to learn more about details of the insertion reaction mechanism.

The Application of ^{13}C -enriched Ethylene

In these experiments we used ethylene enriched to over 90 atom-% in ^{13}C . Besides providing a considerable gain in sensitivity over ethylene with ^{13}C at natural abundance (1.1%), this allows the carbons in the polymer chain derived from ^{13}C -enriched ethylene to be distinguished from those from the Ti–Me or Al–Me carbons on the basis of their signal intensities. Whereas ^{13}C – ^{13}C spin-spin couplings are observed in natural abundance ^{13}C NMR spectra only as very weak satellites, in enriched samples they may cause the signals to appear as multiplets. The proton-decoupled spectrum of enriched free ethylene in solution is a singlet because the two ^{13}C nuclei are magnetically equivalent. Once incorporated into a chain, these carbons are no longer chemically equivalent and the coupling between neighbouring ^{13}C nuclei is observed. In alkyl chains $^1J_{\text{CC}}$ lies in the range 30–35 Hz; coupling to geminal and vicinal carbons is much smaller ($^2J_{\text{CC}} < 1$ Hz, $^3J_{\text{CC}} \sim 4$ Hz) [3] and is not resolved in the experiments reported here.

Table I summarizes the multiplet structures expected for a Ti-alkyl chain formed by the repeated insertion of ethylene enriched to 91 atom-% in ^{13}C at both carbons starting with a Ti-methyl at the natural isotopic abundance. For molecules containing ^{13}C in the α -position there is a probability of 91% that the β -carbon will also be ^{13}C , and the α -carbon signal will therefore be split into a doublet due to $^1J_{\text{C}\alpha\text{C}\beta}$. The remaining 9% of the molecules have ^{12}C β -neighbours and show no coupling. The α -carbon signal is

* For I see ref. [1].

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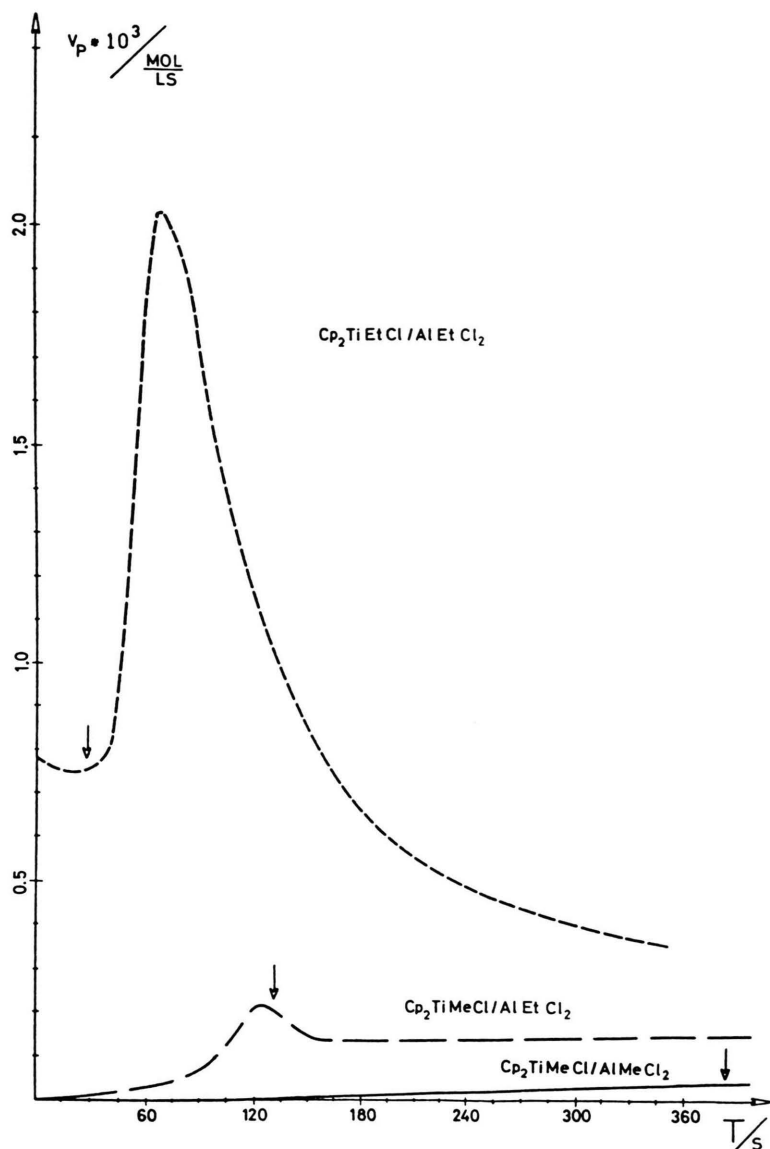


Fig. 1. Overall polymerization rate of ethylene versus time for various Ti/Al catalysts determined in a batch reactor by following the rate of consumption of ethylene. (For experimental method see ref. [2].) Al/Ti = 4; [Ti] = 3.10^{-3} mol/l; $[C_2H_4]$ = 0.089 mol/l; solvent toluene; T = 283 K.

Table I. Multiplet structures expected for a Ti-alkyl chain formed by the repeated insertion of ethylene enriched to 91 atom-% ^{13}C at both carbons starting with a Ti-methyl at the natural isotopic abundance.

	$ \begin{array}{c} \alpha \quad \quad \quad \omega-2 \quad \quad \omega \\ \text{Ti} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \quad \quad \quad \beta \quad \quad \quad \omega-1 \end{array} $				
	α	$\beta-(\omega-2)$	$(\omega-1)$	ω	Multiplet structure
Rel. Intensity	0.91	0.91	0.91	0.011	—
Fraction with 0	9.0	0.8	8.9	9.0	s
with 1	91.0	16.4	90.1	91.0	d
with 2	—	82.8	1.0	—	t
^{13}C neighbours (%)					

Ethylene: 91 Atom-% ^{13}C .

thus observed to be a doublet superimposed on a small singlet slightly shifted off-centre as a result of isotope shifts. The β -carbon has a probability of 82.8% that both the α - and γ -carbons are ^{13}C , and a triplet will be observed, while those isotopomers with only the α - or only the γ -carbon ^{13}C (combined probability 16.4%) will give a doublet. Only 0.8% of the β -carbons have both neighbours ^{12}C and appear as a singlet. For the $(\omega-1)$ -carbon the probabilities differ slightly from those for the α -carbon because of the presence of the ω -carbon with ^{13}C at natural abundance.

Inspection of the ^{13}C chemical shifts of the n -alkanes shows that the α -, β - and γ -carbons have

characteristic shift ranges, but that for carbon atoms from the δ -position to the chain centre the environments become too similar to produce any significant differences in their chemical shifts. These carbons in the middle of the chain have resonances at approximately 30 ppm. Similarly, for Ti-alkyls, the presence of the metal substituent on the α -carbon will produce

no significant effect beyond the γ -carbon. Thus a signal at 30 ppm indicates that chains at least eight carbon atoms long are present; the larger its relative intensity the greater the fraction of even longer chains which are present. This peak is labelled in the spectra with the symbol $\cdots\cdots\text{CH}_2\cdots\cdots$.

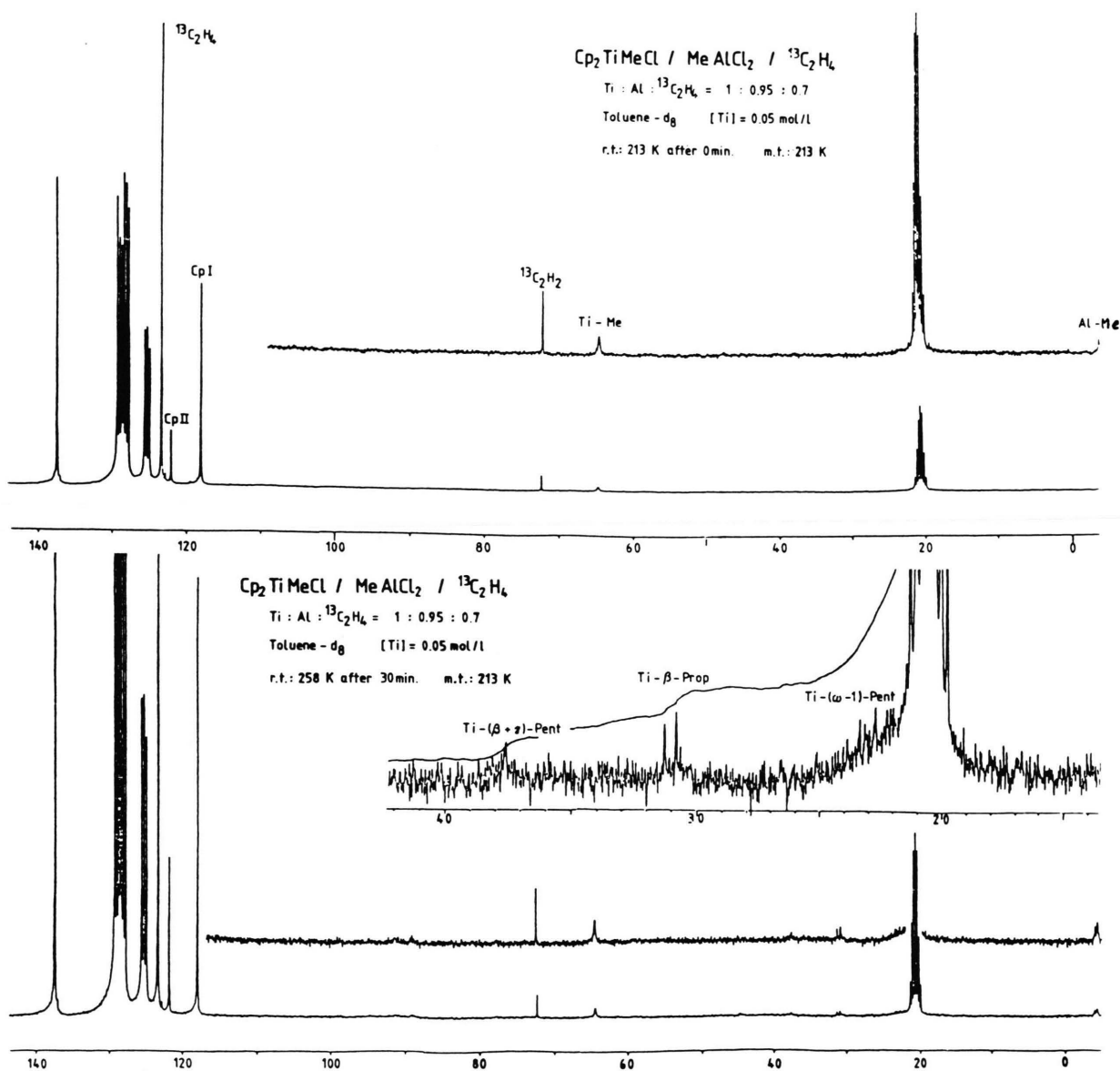


Fig. 2. 75.5 MHz ^{13}C NMR spectra of the system $\text{Cp}_2\text{TiMeCl}/\text{AlMeCl}_2$ reacting with $^{13}\text{C}_2\text{H}_4$ in toluene-d_8 recorded at 213 K; $[\text{Cp}_2\text{TiMeCl}] = 0.05 \text{ mol/l}$; $[\text{Ti}]:[\text{Al}]:[^{13}\text{C}_2\text{H}_4] = 1:0.95:0.7$. Upper spectrum: at start of reaction (0 minutes). Lower spectrum: after the sample had reacted for 30 min at 258 K and then been cooled rapidly to 213 K.

Polymerization

Fig. 2 illustrates the first of a series of ^{13}C NMR spectra of the system reacting with ethylene. The upper spectrum was recorded at 213 K before the start of the reaction. The lower spectrum was measured after the sample had been kept at 258 K for 30 min and shows that the first insertion steps

have occurred as indicated by the small peaks of the β -carbons of Ti-propyl and Ti-pentyl. The ethylene signal at 123 ppm remains a sharp singlet and is unshifted, demonstrating that even at the chosen ratio $\text{Ti}:\text{Al}:\text{C}_2\text{H}_4 = 1.0:0.95:0.7$ no interaction with the catalyst is detectable. Thus pre-coordination of the monomer to the primary complex (for instance, the

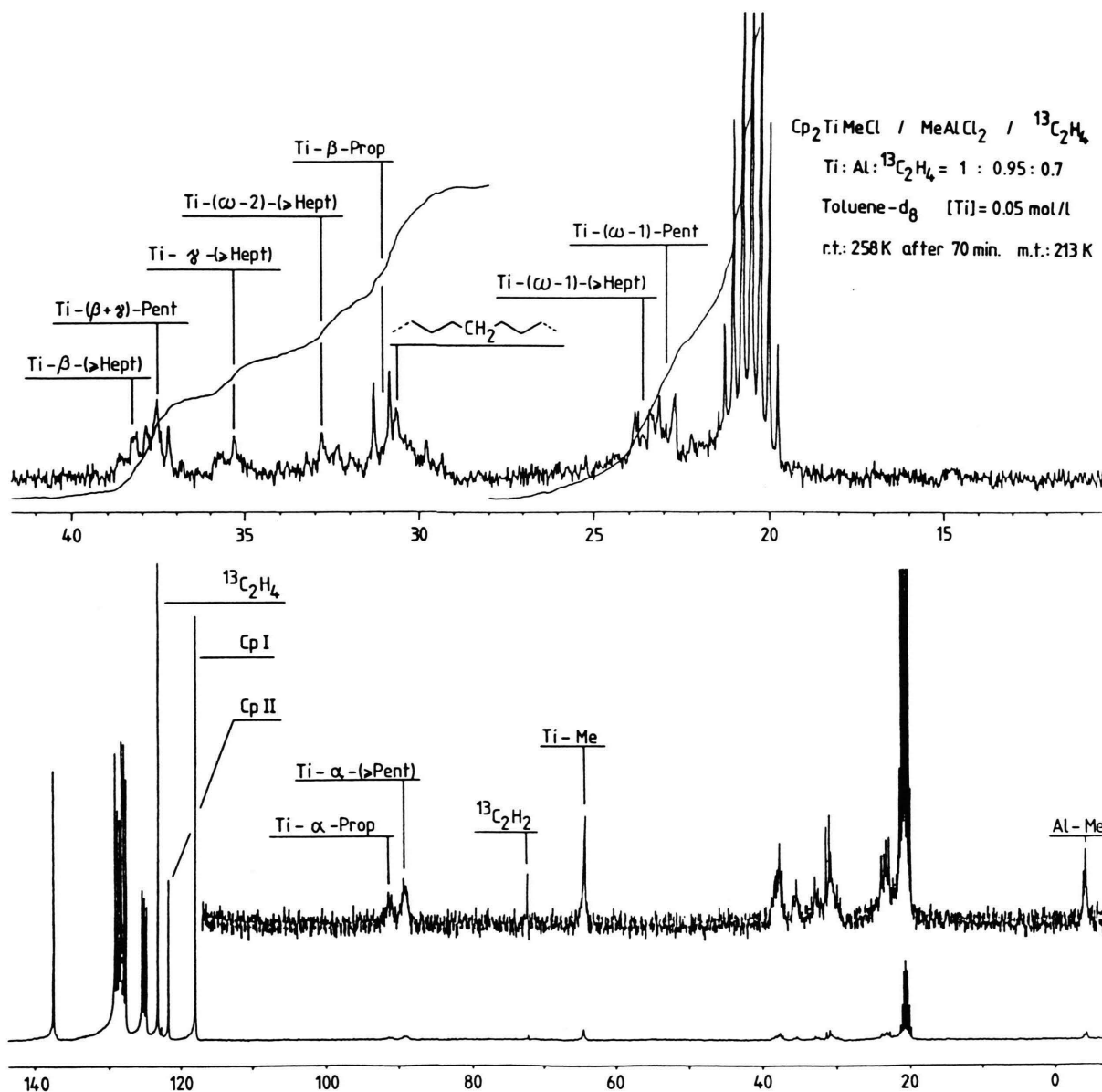


Fig. 3. As for Fig. 2, but after a total reaction time of 70 min at 258 K.

π -complex of Cossée and Olivé [4]) is not observed and can be present only to a very minor extent. If there is exchange of the olefin, then the fraction of pre-coordination complex is too small to broaden and shift the signal of the free ethylene. If the coordinated ethylene does not exchange with the free olefin, the signals of such a pre-coordination complex lie below the noise level. It should be emphasized here that according to the polymerization mechanism proposed by Henrici-Olivé and Olivé [4], all the

titanium added initially should be polymerization active.

In Fig. 3, after a reaction time of 70 min, the α , β , γ , ω -2 and ω -1 signals of the different chains up to Ti-heptyl are to be discerned. In addition, the presence of a small peak at 30.7 ppm due to central CH_2 -groups indicates that chains with a least 9 carbon atoms are present. Fig. 4 shows the situation after 110 min. The signals reveal the developing oligomer distribution and the size of the peak of the central

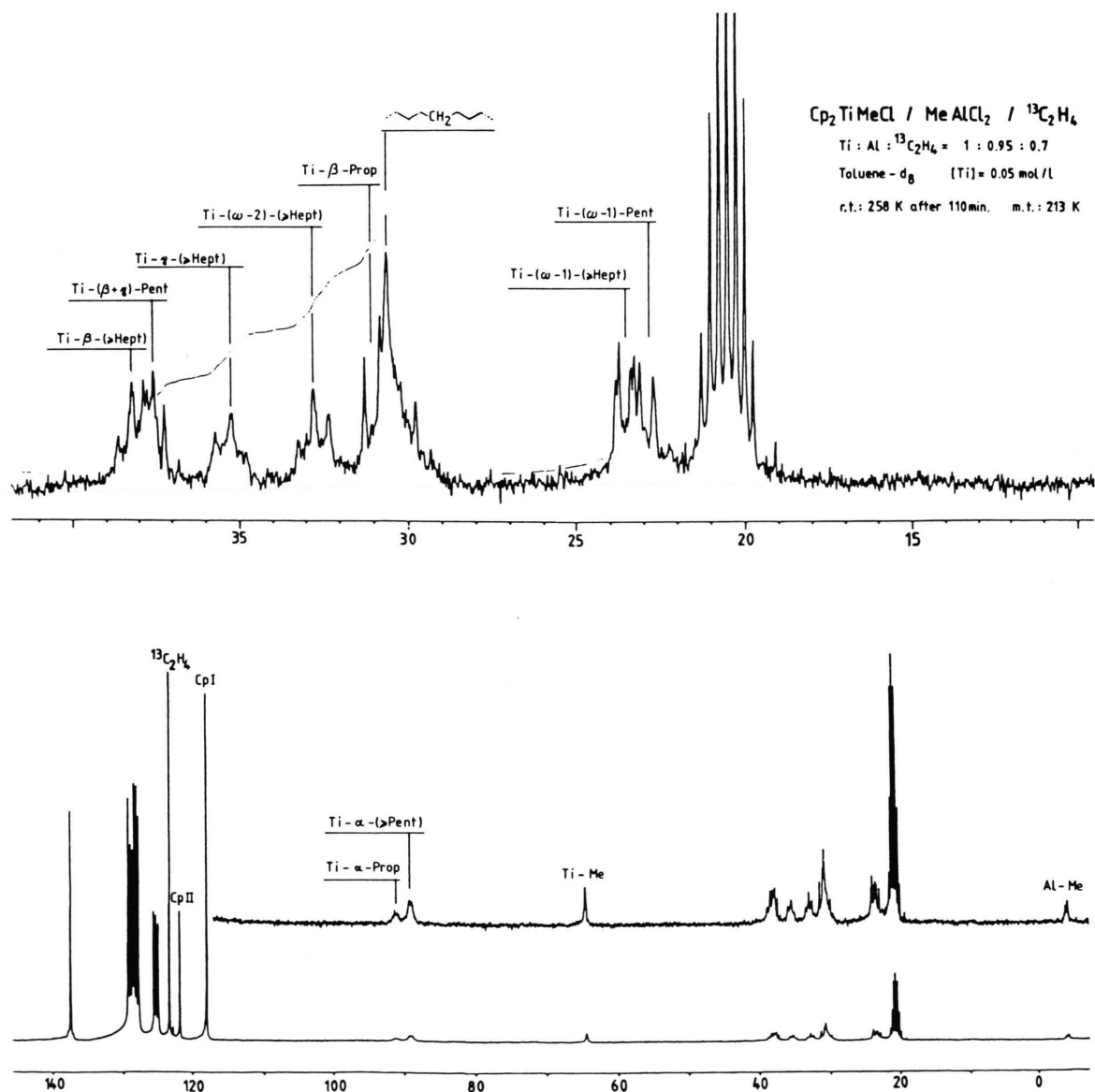


Fig. 4. As for Fig. 2, but after a total reaction time of 110 min at 258 K.

CH_2 -groups has increased considerably. By the time that the reaction has been proceeding for approximately 3 h (Fig. 5) this peak has become the major feature of the oligomer spectrum, showing that most chains are longer than Ti-nonyl.

Let us now consider how this result could arise when the initial concentration ratio $\text{Ti}:\text{C}_2\text{H}_4$ was 1.0:0.7. If *all* the initially added Ti had been active then at the end of the reaction on average less than *one* ethylene per $\text{Ti}-\text{CH}_3$ would have undergone insertion. In this case we would find mostly Ti-propyl

chains and possibly a small quantity of Ti-pentyl chains. It is assumed that all the ethylene has been consumed, but as can be seen in Fig. 5, there are much longer oligomer chains present even though there is a considerable amount of unreacted ethylene left.

The observation that longer oligomer chains have been formed is very important since it proves that not all the Ti has been able to undergo insertion. A large amount of $\text{Ti}-\text{CH}_3$ groups must therefore still be present. This is confirmed by the corresponding

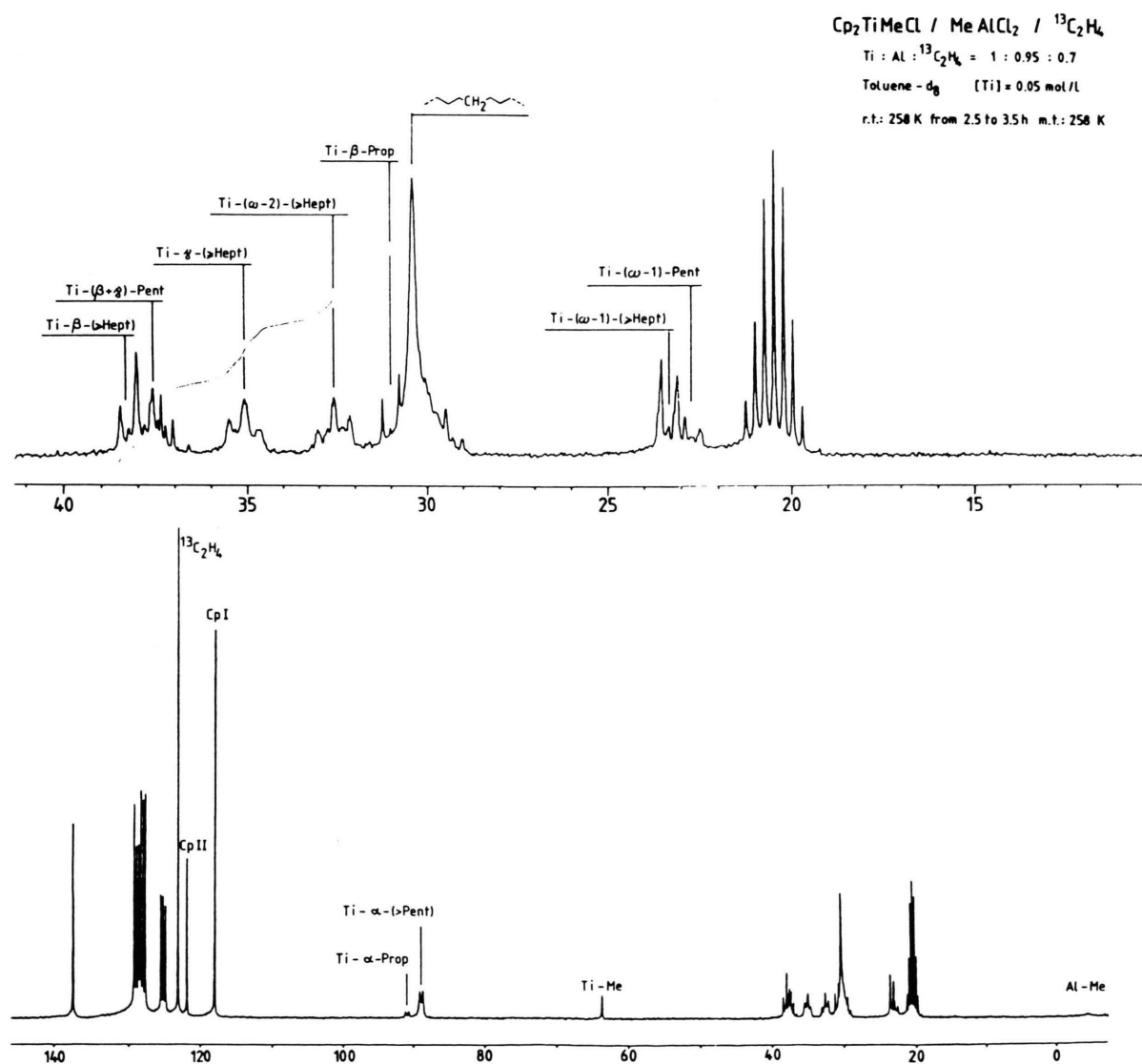


Fig. 5. ^{13}C NMR spectrum of the system $\text{Cp}_2\text{TiMeCl}/\text{AlMeCl}_2$ reacting with $^{13}\text{C}_2\text{H}_4$ in toluene- d_8 at 258 K. $[\text{Cp}_2\text{TiMeCl}] = 0.05 \text{ mol/l}$; $[\text{Ti}]:[\text{Al}]:[^{13}\text{C}_2\text{H}_4] = 1:0.05:0.7$. Spectrum recorded at 258 K at between 2.5 and 3.5 h of reaction time.

signal at 64 ppm, which represents a considerable concentration of Ti-methyl groups because the methyl group has *natural* ^{13}C abundance.

This is further evidence that the mechanism of Olivé cannot be correct. Fig. 6 gives a brief synopsis of the reaction scheme which has been deduced from our previous experiments [2, 5, 6] and which is confirmed by the experiments in this paper. The most important component of this reaction scheme for soluble Ziegler catalyst systems is the formation of the active species in two successive equilibrium steps. The first equilibrium lies well to the right, the second well to the left. Consequently at low ratios Al/Ti there is only a very small concentration of active species C^* . A further consequence is that the propagation process itself is then an intermittent process which causes the molecular weight distribution to undergo a particular type of development [5, 6].

The ^{13}C NMR spectrum recorded towards the end of the reaction (after 14.5 h at 258 K) is illustrated in Fig. 7. In addition to the oligomer distribution and the strong "polyethylene" peak, the following features should be noted:

(I) Comparing the intensities of all Ti- α -peaks (*i.e.*, Ti- α -propyl, Ti- α -($\geq$ pentyl)) at 90 ppm with the intensity of the Ti-methyl peak at 64 ppm and taking into account the ^{13}C abundances of 91% and 1.1%, respectively, one obtains the true concentration ratio of about 0.1:1.0. This indicates that only 10% of the initial Ti-methyl compound has been involved in insertion reactions. This is to be expected from the location of the successive equilibria at the chosen ratio of Ti/Al = 1:1.

(II) The signal of the ω -carbon at approximately 14 ppm is very weak since it is at the natural abundance of ^{13}C .

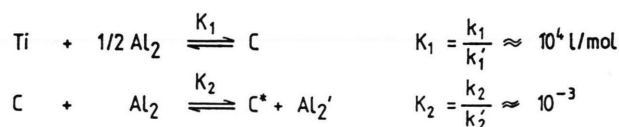
(III) The (ω -1) peak for Ti-heptyl and longer chains is clearly a doublet, produced by coupling with only *one* adjacent ^{13}C nucleus (see Table I).

Both (II) and (III) prove that the insertion has occurred into the Ti-carbon bond.

(IV) After the long reaction time of 15.5 h, small quantities of α -olefins are formed as indicated by the weak signals at 114 and 140 ppm. This means that a transfer reaction to the monomer *via* H- β -elimination has occurred.

Formation of active species

For 283 K is valid



$$K_1 = \frac{k_1}{k_1'} \approx 10^4 \text{ l/mol}$$

$$K_2 = \frac{k_2}{k_2'} \approx 10^{-3}$$

$$k_1 \approx 10^{10} \dots 10^{11} \text{ l/mol} \cdot \text{s}$$

$$k_1' \approx 10^6 \dots 10^7 \text{ s}^{-1}$$

$$k_2 \approx k_1$$

$$[\text{C}^*] = f(K_1, K_2, [\text{Ti}]_0, [\text{Al}]_0)$$

Chain propagation



in detail respectively

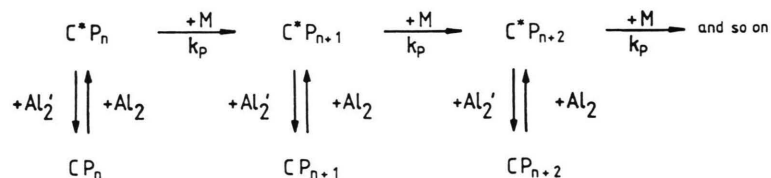


Fig. 6. Reaction scheme of the successive equilibria using *soluble* Ziegler catalysts for ethene polymerization ($\text{Cp}_2\text{TiRCl}/\text{AlR}_x\text{Cl}_y/\text{toluene}$).

The experiment described above has provided general information on the course of the polymerization reaction. We have carried out further investigations aimed at obtaining more details on the chain propagation itself. Fig. 8 illustrates the series of spectra recorded for a sample of $\text{Cp}_2\text{TiMeCl}/\text{AlMe}_2\text{Cl}/^{13}\text{C}_2\text{H}_4$ in the ratio 1:2:2, to increase the concentration of ac-

tive species. The potential of this approach is apparent. Detailed assignment of the NMR spectra and analysis of the signal intensities provides information on the chain length dependency of the propagation constants and the overall rate of formation of the various oligomers. In view of its length, this analysis will be reported separately [7].

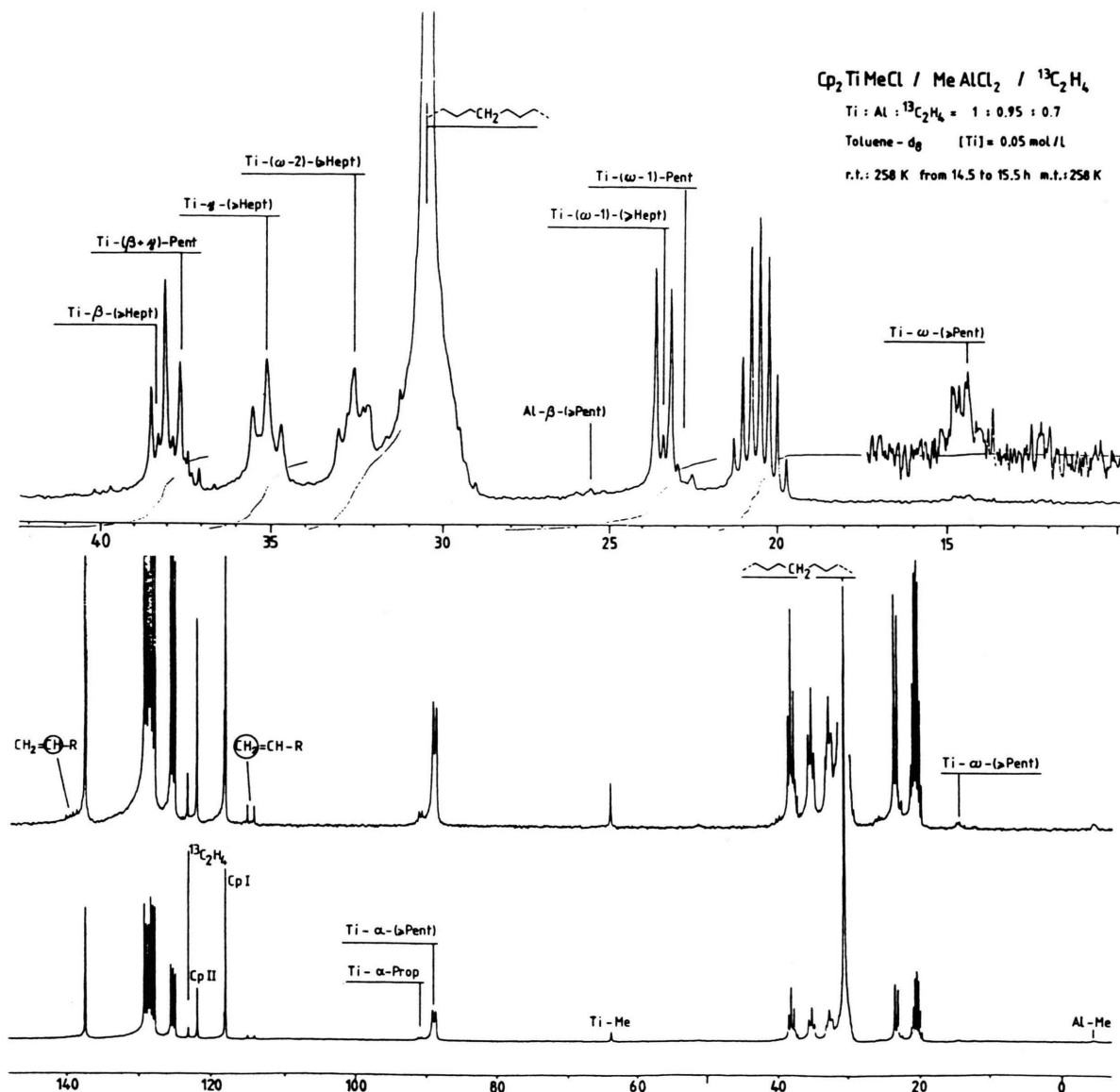


Fig. 8. 75.5 MHz ^{13}C NMR spectra of the system $\text{Cp}_2\text{TiMeCl}/\text{AlMe}_2\text{Cl}$ reacting with $^{13}\text{C}_2\text{H}_4$ in toluene- d_8 at 258 K. Initial $[\text{Cp}_2\text{TiMeCl}] = 0.05 \text{ mol/l}$; $[\text{Ti}]:[\text{Al}]:[^{13}\text{C}_2\text{H}_4] = 1:2:2$. These spectra, each measured over a period of an hour, were recorded successively in order to follow the development in chain growth. The regions depicted are for the Ti- α resonances and for the signals for the β to $\omega-1$ positions.

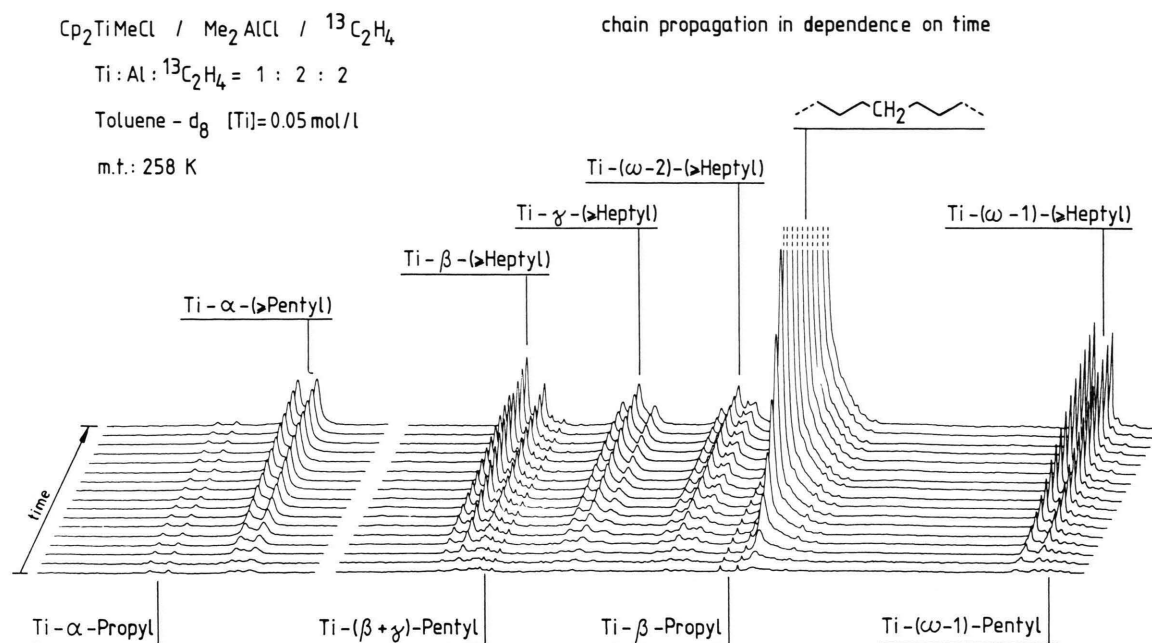


Fig. 7. ^{13}C NMR spectrum of the system $\text{Cp}_2\text{TiMeCl}/\text{AlMeCl}_2$ reacting with $^{13}\text{C}_2\text{H}_4$ in toluene- d_8 at 258 K. $[\text{Cp}_2\text{TiMeCl}] = 0.05 \text{ mol/l}$; $[\text{Ti}]:[\text{Al}]:[^{13}\text{C}_2\text{H}_4] = 1:0.95:0.7$. Reaction time from 14.5 to 15.5 h.

Experimental

NMR measurements

The ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer at a frequency of 75.5 MHz. Samples were measured in 10 mm tubes, dissolved in

D_8 -toluene which had been dried over LiAlH_4 , degassed several times, and distilled *in vacuo*. Chemical shifts were recorded relative to the CD_3 -signal of the D_8 -toluene solvent as internal reference and converted to the TMS scale ($\delta_{\text{CD}_3} = 20.47$ at 258 K).

For preparation of the NMR-samples see ref. [1].

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