Reaction of the Ti–polyethylene bond with carbon monoxide over the bis(cyclopentadienyl)titanium dichloride–methylaluminoxane catalyst system

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The reaction between carbon monoxide and the Ti–polyethylene bond was investigated using a stopped-flow (short-time) polymerization method which provides quasi-living polymers with very low molecular weights. Ethylene polymerization was conducted with a typical homogeneous Cp_2TiCl_2–methylaluminoxane catalyst. The Ti-terminated polymers were introduced into toluene saturated with carbon monoxide or containing ^{13}C-enriched carbon monoxide at −78°C. The mixture was gradually heated up to room temperature, and a small portion of the reaction mixture was taken out at −78°C, 0°C and room temperature to analyse the structure of each polymer by *FT*i.r., gel permeation chromatography, ^1H n.m.r. and ^{13}C n.m.r. It was found from these analyses that carbon monoxide is incorporated into the polymer mainly as a ketone carbonyl.

(Keywords: Cp_2TiCl_2; methylaluminoxane; ethylene polymerization)

INTRODUCTION

Recently, much attention has been paid to homogeneous Kaminsky catalysts owing to their extremely high activity and easy control of stereoregularity[1–5]. Such a high activity may result from a large propagation rate constant as well as a high efficiency of the active species. Tsutsui and Kashiwa[6] and Tait *et al.*[7] have reported that all the Zr atoms involved in the bis(η-cyclopentadienyl)zirconium dichloride–methylaluminoxane (MAO) catalyst system are active for ethylene polymerization, based on the results obtained from kinetic and radio-tagging methods using ^{14}C-labelled carbon monoxide (^{14}CO).

The ^{14}CO-quenching method is widely used to determine the number of active centres ([C*]) in Ziegler–Natta catalysts[8–13]. However, the incorporation mechanism of ^{14}CO into the polymer chain is still open to discussion.

The reactions between transition metal–carbon bonds and carbon monoxide have been investigated in some homogeneous catalyst systems. Fachinetti *et al.*[14] showed that bis(η-cyclopentadienyl)haloalkyltitanium, i.e. $Cp_2TiX(R)$, reacts with CO to give the acyl derivative $Cp_2TiX(COR)$. Grigoryan and Gyulumyan[15] investigated the reaction of CO with a mixture of bis(η-cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) and $Al(CH_3)_2Cl$ in the absence of monomer and found that CO is converted to formaldehyde and ketene. It is necessary, however, to check whether such reactions between Ti–alkyl bonds and CO are affected by olefin monomers or not.

In the work described herein, we conducted ethylene polymerization with a Cp_2TiCl_2–MAO catalyst system using a stopped-flow method, which supplies Ti-terminated polymers with very low molecular weights, and investigated the insertion mechanism of CO into the Ti–polymer bond.

EXPERIMENTAL

Materials

Ethylene (Sumitomo Seika Co.) was purified by passing through columns of $CaCl_2$, P_2O_5 and 3A molecular seives. Cp_2TiCl_2 (Kanto Kagaku Co.) was purified by recrystallization from chloroform. MAO (Tosoh Akzo Chemical Co.) was used without further purification. Argon (Nippon Sanso Co., 99.9995%), CO (Takatiho Kagakukogyo Co., 99.95%) and ^{13}C-enriched CO (Isotec Inc., 99.2 at% ^{13}C containing 16.2 at% ^{18}O) were used without further purification. Research grade toluene (commercially obtained) was dried over calcium hydride under reflux for 24 h and distilled before use.

Polymerization of ethylene

The polymerization apparatus used in this study was similar to the one previously used by Keii *et al.*[16]. A catalyst solution ([Ti] = 0.25 mmol dm^{-3}) and a MAO

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solution (125 mmol dm^{-3}) in 200 cm^3 of toluene, both saturated with ethylene at 20°C under atmospheric pressure (ca. 0.13 mol dm^{-3}), were forced to flow out simultaneously at about 10 cm^3 s^{-1} through a glass tube of 3.2 mm inner diameter, 5 to 20 cm in length. When the solutions met at a three-necked joint, polymerization started and the polymerization mixture was introduced into 1 dm^3 of hydrochloric acid solution in ethanol. In order to avoid significant changes in the monomer concentration and temperature of polymerization, the polymerization conditions were adjusted to hold monomer conversions in the tube below 10%. The precipitated polymer was filtered with a glass-paper filter, washed with plenty of ethanol, and dried under vacuum at 60°C for 8 h.

Reaction of the Ti–polymer bond with CO

The polymerization of ethylene was conducted according to the procedure described above and the reaction mixture was directly introduced into 100 cm^3 of toluene, saturated with CO (1 atm) or containing 100 cm^3 (25°C, 1 atm) of ^{13}CO, which was cooled to −78°C under an argon atmosphere. The mixture was stirred at −78°C for 1 h and part of the mixture was added to acidic ethanol. During the residual reaction the mixture was gradually warmed up to room temperature, and part of the reaction mixture was taken at 0°C. Approximately half of the mixture was then poured into acidic ethanol, and the rest was quenched by adding a deuterium chloride solution in ethanol-*O*-d (ca. 1 N, 20 cm^3). The polymers obtained were purified according to the procedure described above.

The Ti content in each fractionated reaction mixture was calculated from the volume of the mixture and the Ti concentration, and then used to obtain the polymer yield per mol Ti.

Analytical procedures

^{1}H and ^{13}C n.m.r. spectra of the samples were recorded on a JEOL GX-500 spectrometer operating at 500.00 MHz and 125.65 MHz, respectively, in the pulsed Fourier transform mode. The spectra were obtained at 120°C in 1,1,2,2-tetrachloroethane-d_2 solution. The peaks of tetrachloroethane and tetrachloroethane-d_2 were used as internal references for ^{1}H n.m.r. (5.90 ppm) and ^{13}C n.m.r. (74.47 ppm), respectively. The pulse angle was 45° for a 9 s pulse repetition. About 1000 scans were accumulated for ^{1}H n.m.r. and about 30 000 scans for ^{13}C n.m.r. I.r. spectra of the polymers were recorded on a JASCO FT-IR 3. Around 200 scans were accumulated to obtain the i.r. spectra.

Molecular mass distributions of the polymers were recorded on a Waters 150 C equipped with a Shodex 80M/S column at 140°C using *o*-dichlorobenzene as the solvent.

RESULTS AND DISCUSSION

Ethylene polymerization

The stopped-flow polymerizations with different contact times were quenched by hydrochloric acid solution in ethanol, the results of which are summarized in *Table 1*. The yield and number average molecular weight $\bar{M}_n$ are plotted against polymerization time in *Figures 1* and *2*, respectively.

Both the polymer yield and $\bar{M}_n$ increased linearly after a very short induction period. On the other hand, the number of polymer chains increased gradually with increasing polymerization time to reach a saturated value of 1 mol of polymer chain per mol of Ti (*Figure 3*). Therefore, the polymerization in the initial short period

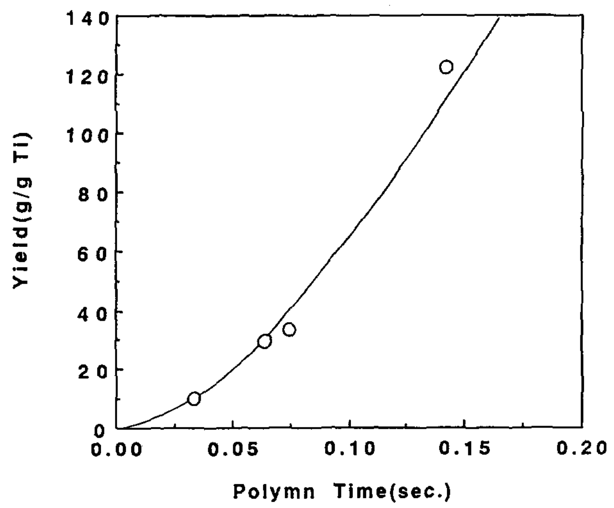


Figure 1 Relationship between polymer yield and polymerization time

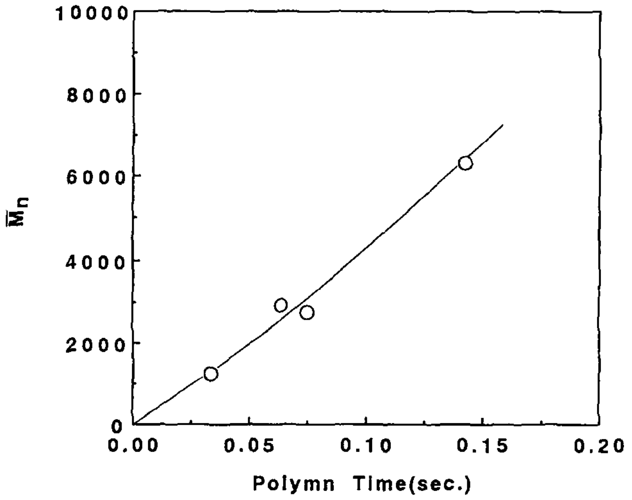


Figure 2 Relationship between number average molecular weight and polymerization time

Table 1 Results of ethylene polymerization[a] with the Cp_2TiCl_2– methylaluminoxane catalyst system

Run	Polymerization time (s)	Yield (mg)	Yield (g polymer per mol Ti)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	0.033	24.2	484	1200	1.9
2	0.064	71.4	1430	2900	1.7
3	0.075	79.9	1600	2700	1.9
4	0.143	292.6	5840	6300	1.5

[a] Polymerization conditions: [Ti] = 0.25 mmol dm^{-3}; [Al] = 125 mmol dm^{-3}; [ethylene] = 0.13 mol dm^{-3}; 400 cm^3 of toluene as solvent; 20°C

may be analysed as a slow initiation system without any chain transfer and termination reactions using the following equations

$$N=[C^*]=\frac{Y}{\bar{M}_n}=[C_s^*][1-\exp(-k_i t)] \qquad (1)$$

$$\begin{aligned} Y &= 28\int_0^t k_p[C^*][M]\,dt \\ &= 28k_p[M]\int_0^t [C_s^*][1-\exp(-k_i t)]\,dt \\ &= 28k_p[M][C_s^*]\left\{t+\frac{1}{k_i}[\exp(-k_i t)-1]\right\} \qquad (2) \end{aligned}$$

$$\begin{aligned} \bar{M}_n &= \frac{Y}{[C^*]} \\ &= \frac{28\int_0^t k_p[C^*][M]\,dt}{[C^*]} \\ &= 28k_p[M]\left\{\frac{t}{[1-\exp(-k_i t)]}-\frac{1}{k_i}\right\} \qquad (3) \end{aligned}$$

where N, Y, t, $[C^*]$, $[C_s^*]$, $[M]$, k_i and k_p are, respectively, number of polymer chains and weight of polymerized ethylene (g) per mol of Ti, polymerization time, numbers of active centres at time t and at the steady state, monomer concentration, and rate constants of initiation (pseudo first order) and propagation.

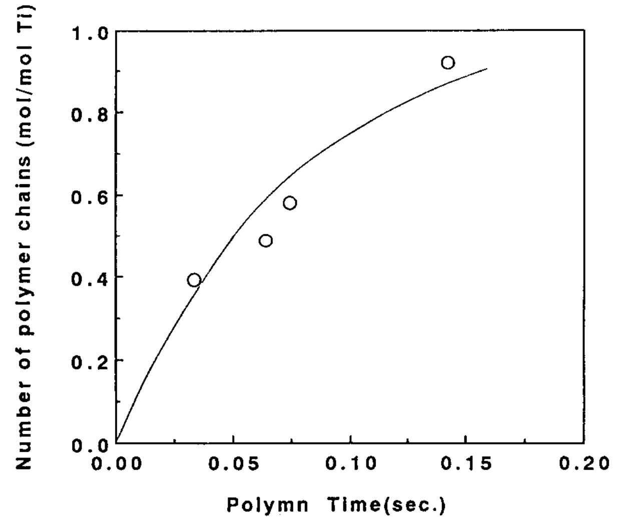


Figure 3 Relationship between number of polymer chains and polymerization time

It may be plausible to approximate $[C_s^*]$ to unity from the results shown in *Figure 3*, and equations (1) and (2) can be simplified

$$k_i=-\frac{\ln(1-N)}{t} \qquad (4)$$

$$k_p=\frac{Yk_i}{28[M][k_i t-1+\exp(-k_i t)]}=\frac{\bar{M}_n N}{28[M][1+N/\ln(1-N)]t} \qquad (5)$$

From the data indicated in *Table 1*, the average values of k_i and k_p are calculated to be $14\,s^{-1}$ and $19\,000\,dm^3\,mol^{-1}\,s^{-1}$, respectively. The time dependences of Y, $\bar{M}_n$ and N can be calculated by use of these values and equations (1) to (3). The calculated values are shown by solid lines in *Figures 1* to *3*, and they are in good agreement with the experimental values. It seems that the k_p value obtained here is not so different from that obtained with the $MgCl_2$-supported $TiCl_4$ catalyst system ($5\times10^4\,dm^3\,mol^{-1}\,s^{-1}$ at 20°C).[17,18].

Reaction of the Ti–polymer bond with CO

As described in the previous section, the experimental time dependences of the polymer yield, $\bar{M}_n$ and N coincide well with the calculated lines based on a model of slow initiation without any transfer or termination reactions. This result suggests that every polyethylene chain has a Ti–carbon bond at the end. The reaction between the Ti–polymer bond and CO was investigated according to the procedure described in the Experimental. The polymerization was quenched at −78°C with a saturated toluene solution of CO at atmospheric pressure. The mixture was gradually heated up to room temperature (25°C), during which small portions of the reaction mixture were taken out at −78°C, 0°C and 25°C and quenched with acidic ethanol. The analytical results for the polymers are summarized in *Table 2*.

Both the polymer yield and $\bar{M}_n$ remained almost unchanged with increasing temperature. The $\bar{M}_n$ values of CO-quenched polymers (6200–6700 at $t=0.13$ s) are in good agreement with that of a methanol-quenched polymer obtained under similar conditions (6300 at $t=0.14$ s). These results suggest that the polymerization is quickly terminated by CO.

To check the incorporation of CO into the polymer, *FT*i.r. spectra were measured on typical CO-quenched polymers. The spectra in the carbonyl region are shown in *Figure 4*, which displays the C=O stretching band at

Table 2 Reaction between the Ti–polyethylene bond and CO[a]

Run	Reaction temperature (°C)	Reaction time (h)	Yield (g polymer per mol Ti)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	N[b] (mol per mol Ti)
CO5	−78	1	2750	6700	1.3	0.41
CO6	0	1	2760	6300	1.4	0.44
CO7	25	1	2460	6200	1.4	0.40
CO8[c]	25	1	2630	6400	1.4	0.41

[a] Polymerization conditions as shown in *Table 1*; polymerization time = 0.13 s; quenched by $100\,cm^3$ of toluene saturated with carbon monoxide at atmospheric pressure and −78°C

[b] Calculated from the polymer yield and the number average molecular weight

[c] The reaction mixture was quenched with $10\,cm^3$ of ethanol-*O*-d

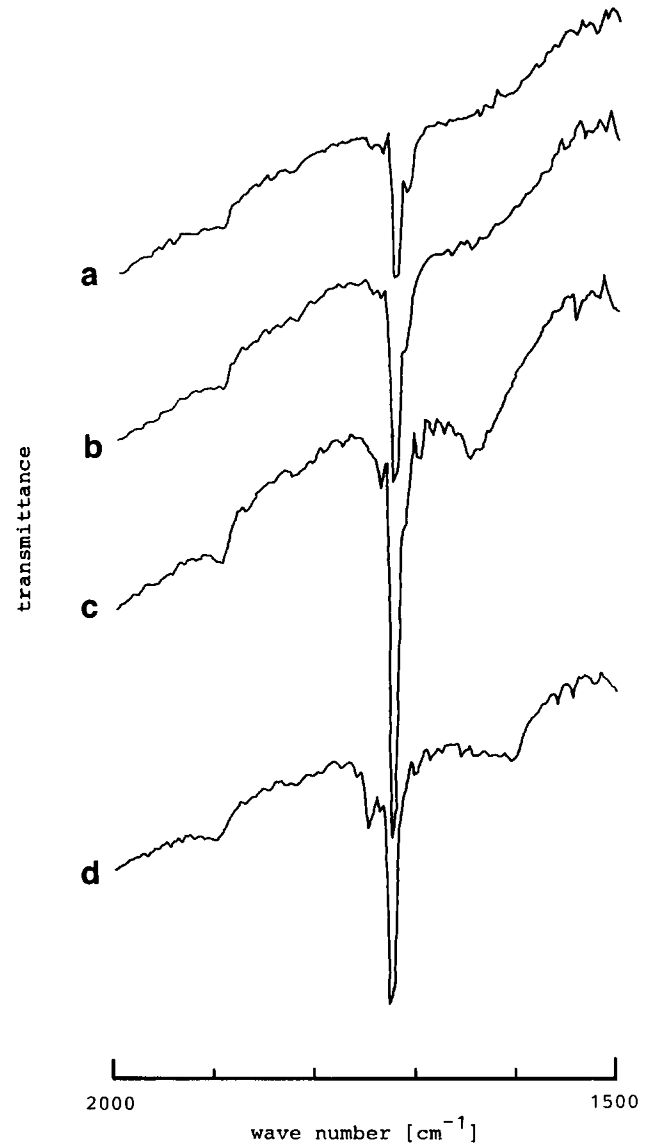


Figure 4 I.r. spectra of polyethylenes quenched with CO: (a) run CO8, hydrolysed with ethanol-*O*-d; (b) run CO7; (c) run CO6; (d) run CO5

around 1720 cm^{-1}. The amount of CO incorporated into the polymer was estimated from the ratio of the signal intensities at 720 cm^{-1} and 1720 cm^{-1} as follows. The relationship between the molar ratio of CH_2/CO (X) and the relative absorbances of the signals at 720 cm^{-1} and 1720 cm^{-1} was obtained by using mixtures of 2-undecanone ($\nu_{C=O} = 1720$ cm^{-1}) and decane. The amount of incorporated CO per mol of Ti (CO/Ti) can be calculated from X and the polymer yield per Ti (Y; g polymer per mol Ti) from

$$CO/Ti = (Y/14)/X \text{ (mol CO per mol Ti)}$$

The analytical data thus obtained are shown in *Table 3*. The CO/Ti values for the polymers obtained at low temperatures agree well with the N values (*Table 2*) calculated from the polymer yield and $\bar{M}_n$. However, the CO/Ti value decreased slightly with increasing temperature, which might result from a further reduction of the carbonyl group.

The ^{1}H n.m.r. spectra of the CO-quenched polymers were also measured to get information about the mechanism of CO incorporation. The ^{1}H n.m.r. spectrum of run CO5 is illustrated in *Figure 5*, which does not show any resonance attributable to an aldehyde proton (around 9.5 ppm) but does display several weak resonances at higher magnetic fields besides a strong resonance due to the methylene protons in the main chain.

Table 3 Content of CO in polyethylene

Run	A_{720}/A_{1720}	CH_2/CO[a] (mol mol^{-1})	CO content[b] (mol per mol Ti)
CO5	3.3	500	0.39
CO6	3.5	510	0.39
CO7	4.5	650	0.27
CO8	5.2	750	0.25

[a] Based on the calibration curve for mixtures of n-decane and 2-undecanone

[b] Calculated from the polymer yields and the value of CH_2/CO

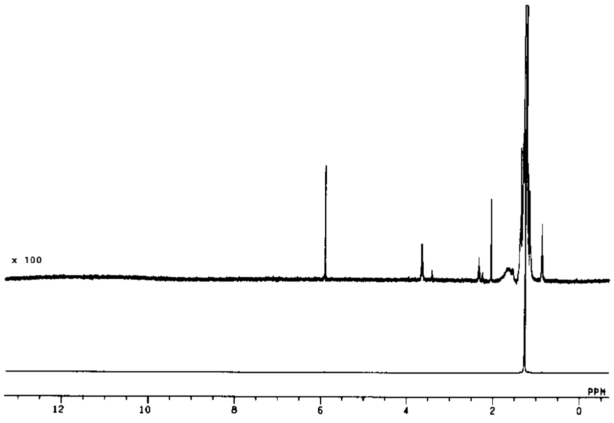


Figure 5 ^{1}H n.m.r. spectrum of polyethylene quenched with CO (run CO5)

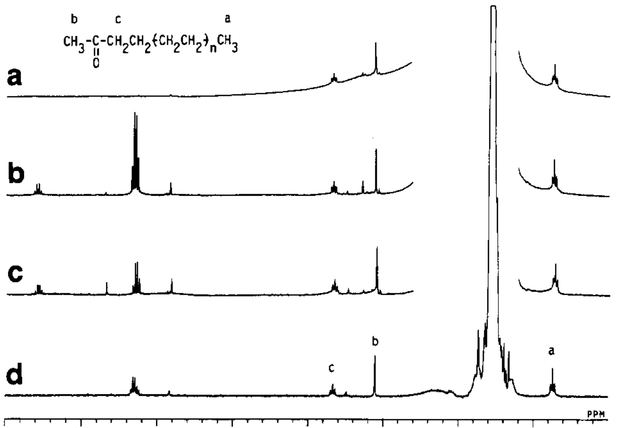
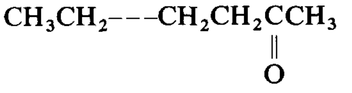


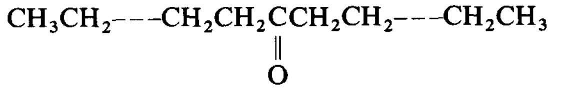
Figure 6 ^{1}H n.m.r. spectra of polyethylenes quenched with CO: (a) run CO8, hydrolysed with ethanol-*O*-d; (b) run CO7; (c) run CO6; (d) run CO5

Therefore, the expanded spectra at higher magnetic fields were taken for the CO-quenched polymers (*Figure 6*), where the signals for the methyl protons at the chain ends and the methylene protons adjacent to the carbonyl group are observed at around 0.88 ppm and 2.34 ppm (triplet), respectively. In addition, a signal for methyl protons adjacent to a carbonyl group is also observed at 2.06 ppm (singlet). These analytical data suggest that the major product is a 'methyl polyethylenyl ketone' (A). However, the signal for the methyl group adjacent to carbonyl is weaker than the signals for the chain-end/methyl group and the methylene protons adjacent to carbonyl, which might be as a result of by-products such as other ketone compounds (B). On the other hand, *Figure 6* also displays two quartets (3.6 and 4.3 ppm) and two singlets (3.4 and 3.8 ppm), the intensities of which become stronger with increasing temperature. These resonances appeared neither in the spectrum of run CO7 after drying nor in the spectrum of run CO8, which is the same as run CO7 except for the hydrolysis by deuterium chloride/ethanol-*O*-d (see Experimental). These resonances are therefore considered to be attributable to some volatile by-products formed in the hydrolysis.



$CH_3CH_2{-}{-}{-}CH_2CH_2\underset{\displaystyle O}{\underset{\|}{C}}CH_3$

A



$CH_3CH_2{-}{-}{-}CH_2CH_2\underset{\displaystyle O}{\underset{\|}{C}}CH_2CH_2{-}{-}{-}CH_2CH_3$

B

To get more information about the polymer structure, the ethylene polymerization was quenched with ^{13}CO. The reaction between the Ti–polymer bond and ^{13}CO was conducted under the same conditions as for the quenching with CO, apart from the lower concentration of ^{13}CO. The polymer yields did not depend on the contact time with ^{13}CO and were almost the same as those of ethanol-quenched polymers for similar polymerization times, which suggests that the polymerization could have been terminated even by a small amount of ^{13}CO (ca. 4 mmol). *Figure 7* illustrates the expanded ^1H n.m.r. spectrum of the ^{13}CO-quenched polymer obtained in the same contact time as that of run CO6. The signal for the methyl protons at the chain end is observed at around 0.88 ppm (triplet). The resonances for methyl and methylene protons adjacent to carbonyl are observed at around 2.06 ppm and 2.4 ppm, respectively. The former splits into a doublet and the latter into a multiplet owing to a nearby ^{13}C-enriched carbon ($|J(^{13}C\text{–}C\text{–}^1H)| = 6.0$ Hz). Traces of other resonances are observed at around 2.15 ppm and 3.65 ppm.

The ^{13}C n.m.r. spectrum of this polymer is illustrated in *Figure 8*, where a strong resonance is observed at 208.5 ppm in addition to two weak resonances at around 212 ppm. The ^{13}C n.m.r. spectra of authentic samples (2-octanone, 3-undecanone and 1-octanal) show their carbonyl carbons at 208.5 ppm, 211.8 ppm and 202.4 ppm, respectively. Therefore, the resonance at 208.5 ppm is assigned to the ^{13}C-enriched carbonyl carbon of ketone A, whereas the resonances at 212 ppm may be assigned to ketone B. From the relative intensities of these carbonyl groups, the molar ratio of A/B was estimated to be approximately 7. In *Figure 8* are also observed weak resonances attributable to the chain-end n-alkyl carbons at 14.3 ppm, 23.0 ppm and 32.3 ppm, as indicated in the figure. The resonance at 44.1 ppm may be assigned to the methylene carbon connected to the carbonyl group. However, other weak resonances cannot be assigned at present.

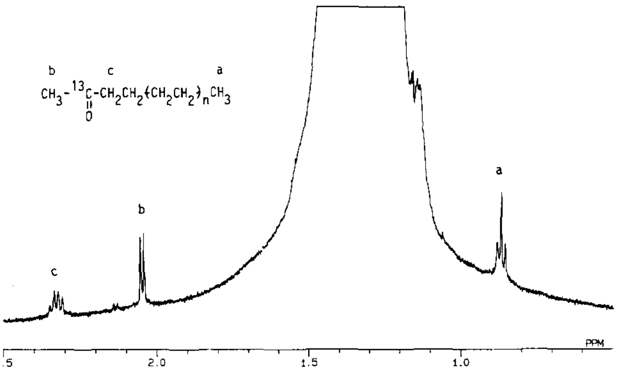


Figure 7 ^1H n.m.r. spectrum of polyethylene quenched with ^{13}CO

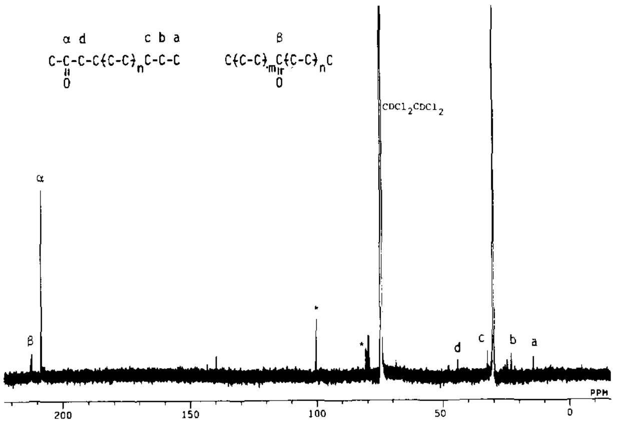
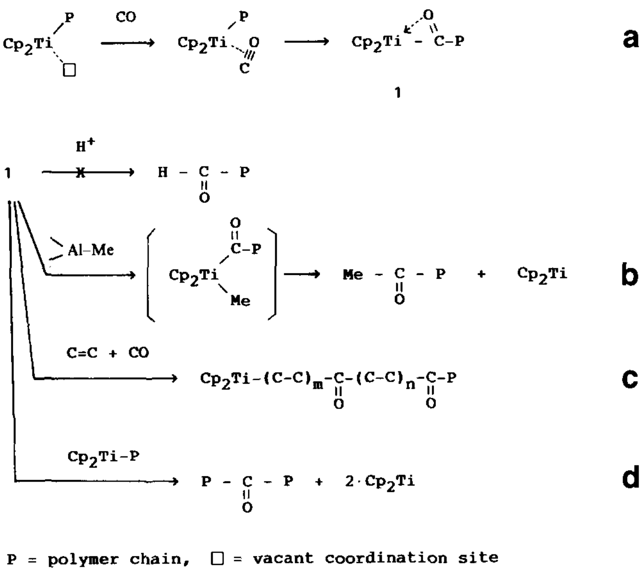


Figure 8 ^{13}C n.m.r. spectrum of polyethylene quenched with ^{13}CO (resonances of impurities in the solvent denoted by *)



Scheme 1 A plausible reaction scheme between the Ti–polymer bond and CO (the active Ti species should be a tetravalent cation, but the valence state has been removed for clarity)

A plausible scheme for the formation of these ketones is illustrated in *Scheme 1*. At first, CO inserts into the Ti–carbon bond to form a Ti-acyl compound **1** (*Scheme 1a*), which reacts with MAO (Al–CH_3 bonds) to give the major product, ketone A (*Scheme 1b*). There are two possibilities for the formation of the minor product, ketone B, i.e. by copolymerization of CO and ethylene (*Scheme 1c*) and by a coupling reaction between **1** and Ti–polymer compounds (*Scheme 1d*). The latter may be more plausible because the amount of CO in the polymer did not increase with increasing reaction time. Further experiments are necessary to elucidate the mechanisms in detail.

In summary, ethylene polymerization was conducted for very short periods with the Cp_2TiCl_2–MAO catalyst system followed by quenching with CO, and the polymers produced were analysed in detail using *FT*i.r., gel permeation chromatography, ^1H n.m.r. and ^{13}C n.m.r. It was found from the analytical data that CO is almost quantitatively incorporated into the Ti–carbon bond and predominantly gives a methyl polyethylenyl ketone.

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