The microstructure of propylene homo- and copolymers obtained with a Cp_2ZrCl_2 and methylaluminoxane catalyst system

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The microstructure of propylene homopolymer and ethylene–propylene copolymer obtained using a bis-(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) and methylaluminoxane catalyst was investigated by ^{13}C nuclear magnetic resonance. The homopolymer had the following features: meso (*m*) and racemic (*r*) arrangements of propylene units are present with almost equal probability; the chains of propylene units are joined head-to-tail; and the polymer chain end groups are isopropenyl and n-propyl. In the copolymer, the structure of the polymer chain ends was almost entirely based on propylene units, such as isopropenyl and n-propyl, in spite of a high ethylene content (60 mol%), suggesting that the chain transfer reaction is most probably caused by propylene monomer when the propagating chain end is a propylene unit.

(Keywords: Cp_2ZrCl_2; methylaluminoxane; microstructure; polypropylene; propylene–ethylene copolymer)

INTRODUCTION

The soluble catalyst system comprising a bis(cyclopentadienyl)zirconium compound and methylaluminoxane has been reported to exhibit high activity in ethylene and/or α-olefin polymerization and to produce atactic polymers in α-olefin polymerization[1–4]. Furthermore, the kinetics[5–7] and the effects of ligands around the zirconium atom[8–10] in olefin polymerization have also been investigated. However, there has been less information published on the microstructure of the polymer, especially the polymer chain ends, in Zr catalyst systems.

In this paper, the characteristics of the microstructure of propylene homopolymer (PP) and ethylene–propylene copolymer (EP) obtained with a Cp_2ZrCl_2 and methylaluminoxane catalyst system, especially the structure of the polymer chain ends, were investigated by ^{13}C n.m.r. Moreover, on the basis of the ^{13}C n.m.r. analytical data, the chain transfer reaction and the initiation reaction were also discussed.

EXPERIMENTAL

Polymerization of propylene

In a 1 litre glass reactor equipped with a stirrer was placed 500 ml of toluene, and the system was fed with propylene. Methylaluminoxane[7] (5.0 mmol, as Al atom) and Cp_2ZrCl_2 (0.01 mmol) were added at 20°C in this order. Polymerization was carried out under atmospheric pressure at 20°C for 1 h and terminated by the addition of a small amount of methanol. The polymer solution was washed several times with water and 16.8 g of PP was separated as a viscous liquid polymer by evaporating off the toluene. The resulting polymer had $\bar{M}_n = 2400$ and $\bar{M}_w/\bar{M}_n = 2.0$ (by g.p.c.).

Short-time polymerization was also carried out by a similar method as described above except for using CD_3OD (10 ml) as a terminating agent for the polymerization under the following conditions: Al = 10 mmol; Zr = 0.05 mmol; toluene, 1 litre; polymerization time, 5 s.

Copolymerization of propylene with ethylene

Copolymerization was carried out in a similar manner as for polymerization of propylene except for feeding a gas mixture of propylene and ethylene at 80 l h^{-1} and 20 l h^{-1} respectively, under the following conditions: Al = 2.5 mmol; Zr = 2.5×10^{-3} mmol; toluene, 250 ml; polymerization temperature, 45°C; polymerization time, 1 h. The resulting copolymer (9.2 g) was a viscous liquid, like the propylene homopolymer, with $\bar{M}_n = 2100$ and $\bar{M}_w/\bar{M}_n = 2.1$ (by g.p.c.).

^{13}C n.m.r. analysis

The polymer solution was prepared by dissolving ~250 mg of the polymer sample in ~0.6 ml of deuteriochloroform. ^{13}C n.m.r. spectra were recorded on a JEOL GX-500 spectrometer operating at 125.8 MHz under proton noise decoupling in Fourier-transform mode. Instrument conditions were as follows: pulse angle, 45°; pulse repetition, 4.6 s; spectral width, 20 000 Hz; number of pulses, 3000–5000; temperature, 40–50°C; data points, 64 000.

RESULTS AND DISCUSSION

All of the polymers obtained (three samples) were viscous liquids, indicating that the chain transfer reaction took place frequently in polymerization with a catalyst system comprising Cp_2ZrCl_2 and methylaluminoxane.

Microstructure of polypropylene

The microstructure of a homopolypropylene (PP) prepared by 1 h polymerization was investigated by ^{13}C n.m.r.

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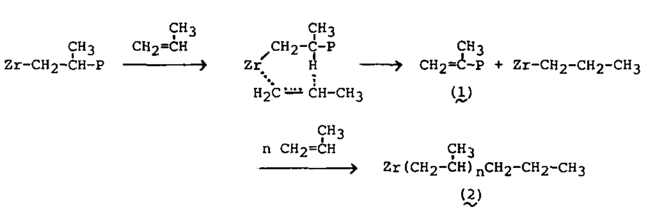
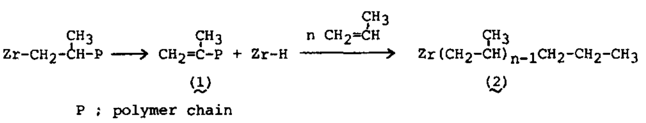
First, in order to distinguish the types of carbon species (CH, CH_2, CH_3), the ^{13}C n.m.r. spectrum was measured by the DEPT (distortionless enhancement by polarization transfer) method. The result is shown in *Figure 1*. On the basis of the results of DEPT and previous papers[11–13], peaks were assigned as shown in *Figure 2*.

From the peaks based on the side-chain methyl groups in the range 19–22 ppm, the *mm* (meso–meso) triad sequence content was determined to be 22 %, very close to the theoretical value (25 %) for pure atactic PP. In *Figure 2* were also observed the peaks based on isopropenyl and n-propyl groups having almost the same intensity. This observation can be explained by assuming that the chain transfer reaction in the investigated propylene polymerization takes place by monomer and/or hydride β-elimination[14,15], as shown in the following reaction schemes:

Chain transfer by monomer



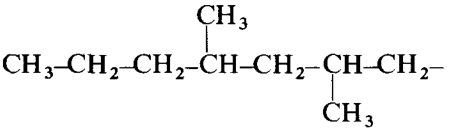
Chain transfer by hydride β-elimination



Chain transfer by monomer takes place by simultaneous hydride β-elimination and propylene monomer insertion at the active centre without forming Zr–H bonds. According to the above schemes, isopropenyl (**1**) and n-propyl (**2**) groups are present at either end of the polymer chain.

Moreover, in *Figure 2*, there was no peak that is attributable to propylene unit inversion (head-to-head or tail-to-tail structure). This fact and the presence of isopropenyl or n-propyl groups indicate that propylene polymerization proceeds only by primary insertion of propylene monomer at the active centre.

Next, the peak which splits into two bands at ~14.5 ppm based on the methyl carbon of the n-propyl group at the polymer chain end is considered to be due to the following two different stereochemical environments:



$$\mathrm{CH_3{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2{-}\underset{\underset{CH_3}{}}{\underset{|}{C}}H{-}CH_2{-}} \qquad \text{(r)}$$

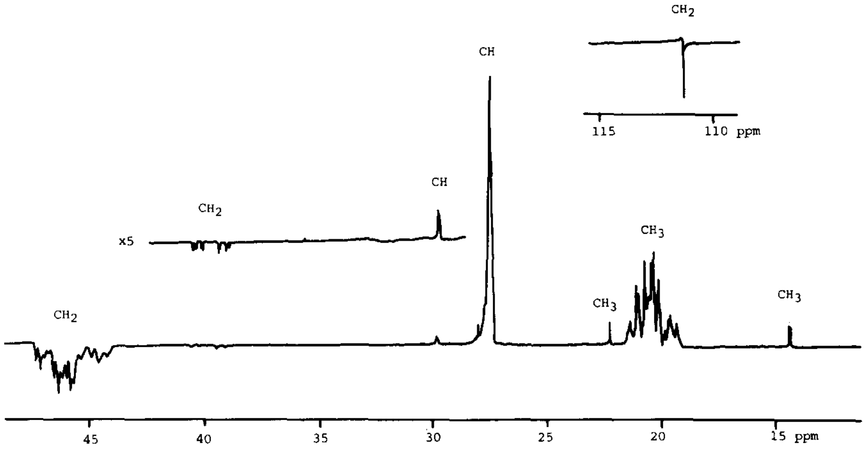


Figure 1 ^{13}C n.m.r. spectrum of PP produced by 1 h polymerization by DEPT method

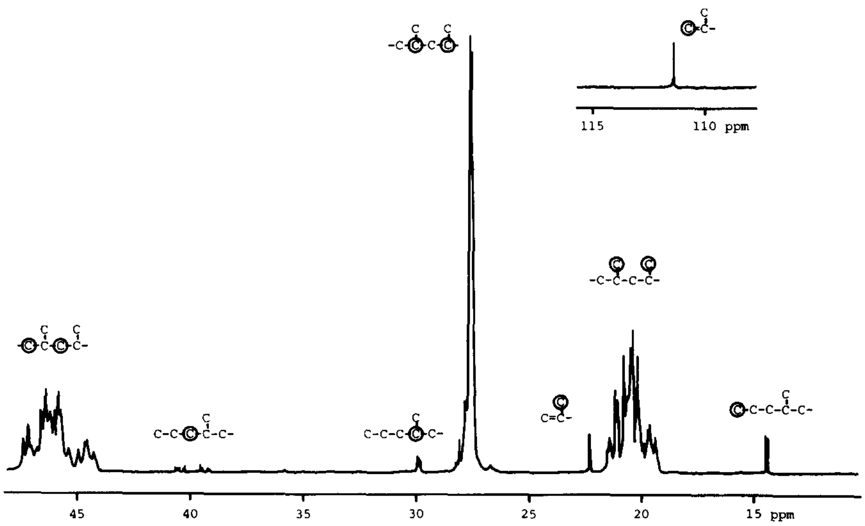
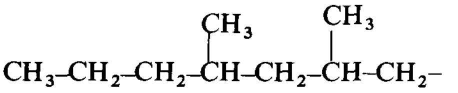
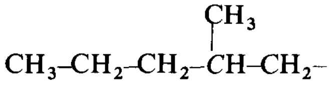


Figure 2 ^{13}C n.m.r. spectrum of PP (the same sample as in *Figure 1*)

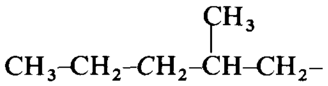

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-} \qquad (m)$$

According to the *r* shift and the RIS model of PP[16], the peak at higher magnetic field would be assigned to the (*r*) structure, while the other peak would be the (*m*) structure. From the peak intensity, the (*m*)/(*r*) ratio was found to be 1.10, indicating that (*r*) and (*m*) structures were formed with the same frequency.

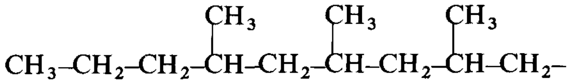
Moreover, it is to be noted that the peaks based on the methyne carbon for

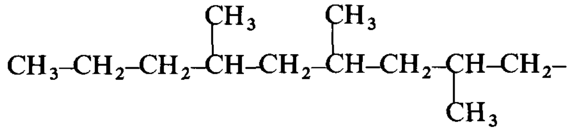

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}$$

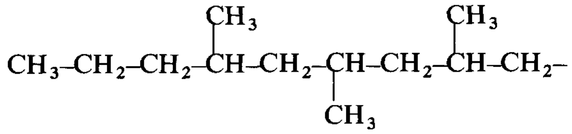
near 30 ppm and the methylene carbon for

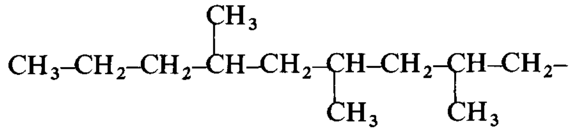

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}$$

at 40.3–41.3 ppm split into four bands with equal intensity, respectively. These findings lead to the conclusion that the investigated polymer is a mixture of the following four types of polymer chains having different stereochemical structures with the same concentration:


$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}$$


$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}$$


$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}$$

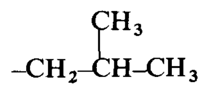

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}$$

Therefore, one can conclude that the stereochemical structure of PP examined is regulated with statistical randomness.

Initiation reaction in polymerization

Very short-time polymerization of propylene was performed in order to investigate the initiation reaction in polymerization.

The ^{13}C n.m.r. spectrum of PP prepared by 5 s polymerization is shown in *Figure 3*. The spectrum exhibited a number of peaks at 25.4, 23.2–23.8 and 22.2–22.7 ppm which were not observed in the spectrum of PP with 1 h polymerization in *Figure 2*. These peaks were assigned to be the methyne and two methyl carbons of


$$\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_3$$

structure (I) at the polymer chain end.

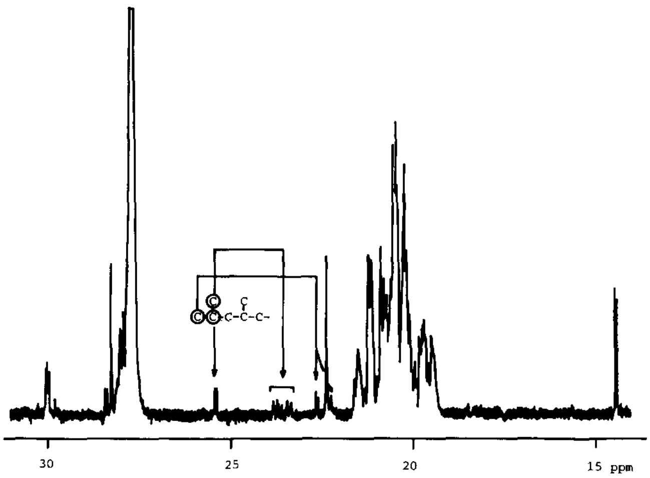
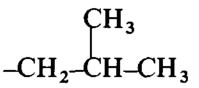


Figure 3 ^{13}C n.m.r. spectrum of PP produced by 5 s polymerization

Structure (I) will not form by the termination reaction because CD_3OD is used to terminate polymerization in this experiment.

As described before, polymerization proceeds only by primary insertion of propylene monomer. Therefore, the detection of

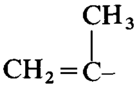

$$\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_3$$

suggests that the first propagation step would be propylene primary insertion at the Zr–CH_3 active centre arising from the methylation of Zr by methylaluminoxane used as co-catalyst.

The negligibly small concentration of polymer chain ends having structure (I) in PP with 1 h polymerization is attributable to the presence of quite a large amount of

$$\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

and


$$CH_2{=}\overset{CH_3}{C}\text{-}$$

chain ends produced by the very frequent repetition of the chain transfer reaction.

Microstructure of copolymer with ethylene

Copolymerization of propylene and ethylene (80 and 20 l h^{-1} of supply, respectively) was carried out with the same catalyst system as propylene homopolymerization to obtain further information about the features of this catalyst system.

Figure 4 shows the ^{13}C n.m.r. spectrum of the copolymer. As shown, the peaks based on propylene unit inversion, which resonate at ~34 ppm ($S_{\alpha\beta}$) and ~28 ppm ($S_{\beta\gamma}$) according to previous papers[17–19], were not found as in the homopolymer. Kaminsky *et al.* have also reported that there is no peak due to sequences with head-to-head propylene units in the ^{13}C n.m.r. spectra of ethylene–propylene copolymer and ethylene–propylene–diene terpolymer with a similar Zr catalyst system[4].

In *Figure 4*, strong peaks of isopropenyl and n-propyl groups based on the propylene unit were observed at 22.3

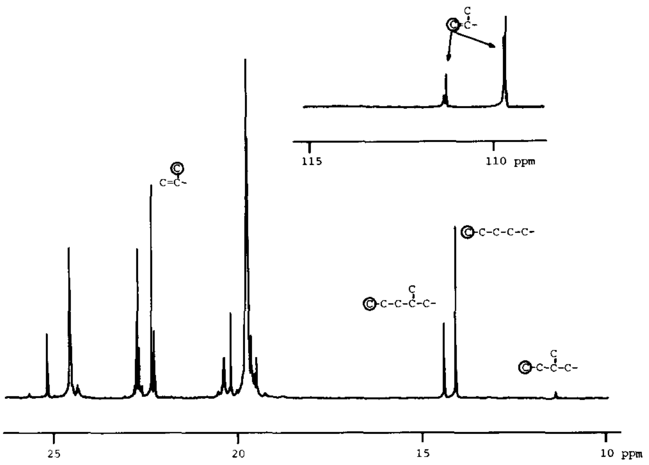


Figure 4 ^{13}C n.m.r. spectrum of copolymer of propylene with ethylene

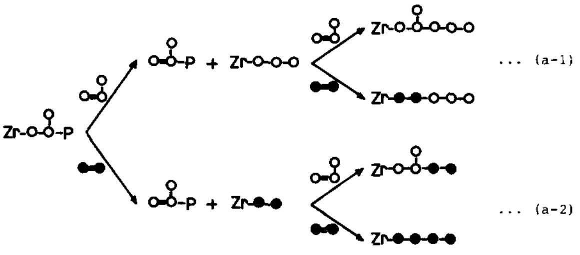
and 14.4 ppm, respectively, and the peak at 14.1 ppm was determined to be the n-pentyl group

$$-(CH_2-CH_2)-(CH_2-CH_2-CH_3)$$

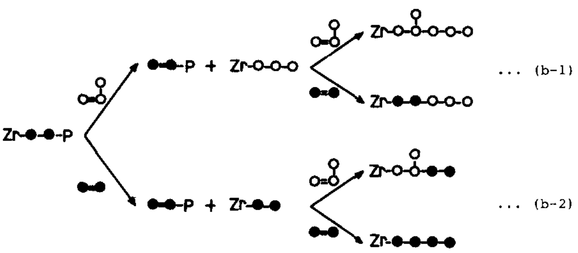
On the other hand, those of vinyl (~114 ppm) and ethyl groups (11.4 ppm) based on the ethylene unit could not be found or were detected at negligibly small levels.

Under primary insertion, the following four types of chain transfer reactions are possible in copolymerization:

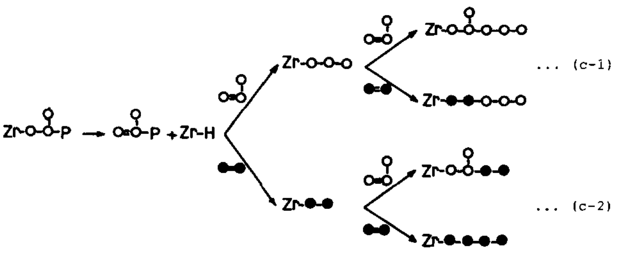
a) Chain transfer by monomer at propylene unit end



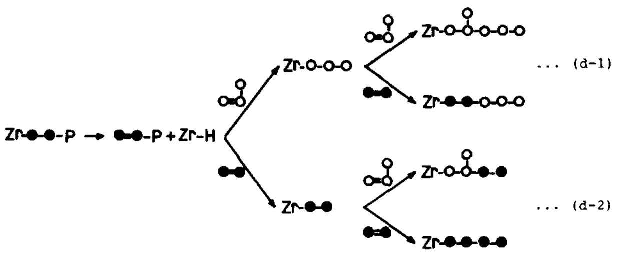
b) Chain transfer by monomer at ethylene unit end



c) Chain transfer by hydride β-elimination at propylene unit end



d) Chain transfer by hydride β-elimination at ethylene unit end



P ; polymer chain ○ ; propylene carbon ● ; ethylene carbon

Cases (b) and (d) can be excluded owing to the absence of the vinyl group. The negligible amount of ethyl groups in spite of the large content (60 mol %) of ethylene units in the copolymer suggests that the chain transfer reaction would almost exclusively take place through case (a) rather than case (c), because Zr–H active centres arising from case (c) would necessarily form ethyl groups at the polymer chain end. Furthermore, the fact that most of the polymer chain ends were isopropenyl, n-propyl and n-pentyl groups implies that case (a-1) is the most plausible as the chain transfer reaction.

Therefore, one can conclude that the chain transfer reaction is most probably induced by propylene monomer when the propagating chain end is a propylene unit.

REFERENCES

1 Sinn, H. and Kaminsky, W. *Adv. Organomet. Chem.* 1980, **18**, 99
2 Kaminsky, W. 'Transition Metal Catalyzed Polymerizations' Vol. 4, 'Alkenes and Dienes' (Ed. R. P. Quirk), Harwood, New York, 1983, p. 225
3 Kaminsky, W., Miri, M., Sinn, H. and Woldt, R. *Makromol. Chem., Rapid Commun.* 1983, **4**, 417
4 Kaminsky, W. and Miri, M. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 2151
5 Kaminsky, W., Külper, K. and Niedoba, S. *Makromol. Chem., Macromol. Symp.* 1986, **3**, 377
6 Kaminsky, W. and Schlobolm, M. *Makromol. Chem., Macromol Symp.* 1986, **4**, 103
7 Tsutsui, T. and Kashiwa, N. *Polym. Commun.* 1988, **29**, 180
8 Kaminsky, W. *Angew. Makromol. Chem.* 1986, **145/146**, 149
9 Giannetti, E., Nicoletti, G. M. and Mazzocchi, R. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 2117
10 Miya, S., Harada, M., Mise, T. and Yamazaki, H. *Polym. Prepr. Japan* 1987, **36**, 189
11 Lindeman, L. P. and Adams, J. Q. *Anal. Chem.* 1971, **43**, 1245
12 Ammendola, P., Oliva, L., Gianotti, G. and Zambelli, A. *Macromolecules* 1985, **18**, 1407
13 Zambelli, A., Locatelli, P. and Bajo, G. *Macromolecules* 1979, **12**, 154
14 Zucchini, U. and Cecchin, G. *Adv. Polym. Sci.* 1983, **51**, 101
15 Boor, J., Jr. 'Ziegler–Natta Catalysts and Polymerizations', Academic Press, New York, 1979, pp. 258, 259
16 Suter, U. W. and Flory, P. J. *Macromolecules* 1975, **8**, 765
17 Carman, C. J., Harrington, R. A. and Wilkes, C. E. *Macromolecules* 1977, **10**, 536
18 Ray, G. J., John, P. E. and Knox, J. R. *Macromolecules* 1977, **10**, 773
19 Delfini, M., Segre, A. L. and Conti, F. *Macromolecules* 1973, **6**, 456