Stereostructure of regioirregular unit of polypropylene obtained with *rac*-ethylenebis(1-indenyl)zirconium dichloride/methylaluminoxane catalyst system studied by $^{13}C-^{1}H$ shift correlation two-dimensional nuclear magnetic resonance spectroscopy

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(Received 13 August 1990; revised 9 November 1990; accepted 20 November 1990)

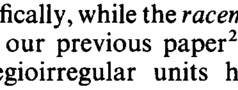
The stereochemical configuration of the regioirregular unit with racemic placement included in isotactic polypropylene, which was prepared with a *rac*-ethylene(1-indenyl)zirconium dichloride/methylaluminoxane catalyst system at 30°C, was studied by $^{13}C-^{1}H$ shift correlation two-dimensional nuclear magnetic resonance spectroscopy. The stereostructure was also studied for the regioirregular unit of propylene copolymer with a small amount of ethylene units. It is concluded that the 2,1-insertion, in addition to the ordinary 1,2-insertion, of propylene monomer is also stereospecifically controlled by the catalyst.

(Keywords: zirconium catalyst; regioirregular structure; racemic placement; isotactic polypropylene; $^{13}C-^{1}H$ two-dimensional nuclear magnetic resonance spectroscopy)

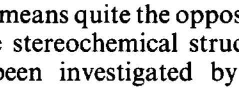
INTRODUCTION

As reported in the literature[1–3], isotactic polypropylene (PP) obtained with a *rac*-ethylenebis(1-indenyl)-zirconium dichloride plus methylaluminoxane catalyst system includes a small amount of regioirregular structural units formed by 2,1-insertion of propylene monomer in addition to the ordinary 1,2-inserted monomeric units[4]. There are two modes of stereochemical configurations in the polymer chain containing the regioirregular unit, i.e. *meso* and racemic placements.

With regard to the racemic stereochemical configuration, two different types of structures concerning the regioirregular units have been reported as follows[1–3]:



racemo-1



racemo-2

The above stereostructures are of great interest from the viewpoint of catalyst performance on stereospecificity; namely the presence of the *racemo*-1 structure means that the 2,1-insertion of propylene unit takes place stereospecifically, while the *racemo*-2 means quite the opposite.

In our previous paper[2], the stereochemical structure of regioirregular units has been investigated by the chemical shift calculation devised by Cheng and Bennett[5], distortionless enhancement by polarization transfer (d.e.p.t.) measurement and the $^{13}C-^{1}H$ shift correlation two-dimensional n.m.r. method. Among these three determination techniques, the most decisive data on the stereostructure were obtained by two-dimensional n.m.r. spectroscopy. From these analyses, we have drawn the conclusion that the *racemo*-1 as well as the *meso* structures are present as a regioirregular structure. However, no detailed descriptions concerning the determination of the racemic stereochemical configuration were given in the previous paper[2].

In this paper, the details of two-dimensional n.m.r. analysis are reported. The stereostructure of the polymer chain containing the regioirregular unit of PP obtained with the above-mentioned catalyst system will be fully discussed through the chemical shift calculation and $^{13}C-^{1}H$ shift correlation two-dimensional n.m.r. Moreover, the stereochemical configuration of the racemic structure will be investigated through analysis of regioirregular units contained in a copolymer of propylene with a small amount of ethylene.

EXPERIMENTAL

Polymerization

Polymerization of propylene and copolymerization of propylene with a small amount of ethylene were described in the previous paper[2]. The homopolymer of run no. 2 and the copolymer (ethylene unit content = 4.7 mol%) of run no. 9 in the previous paper[2] were re-examined in this work.

N.m.r. analysis

^{13}C (^{1}H) n.m.r. analyses for PP homopolymer and copolymer were described in the previous paper[2]. For

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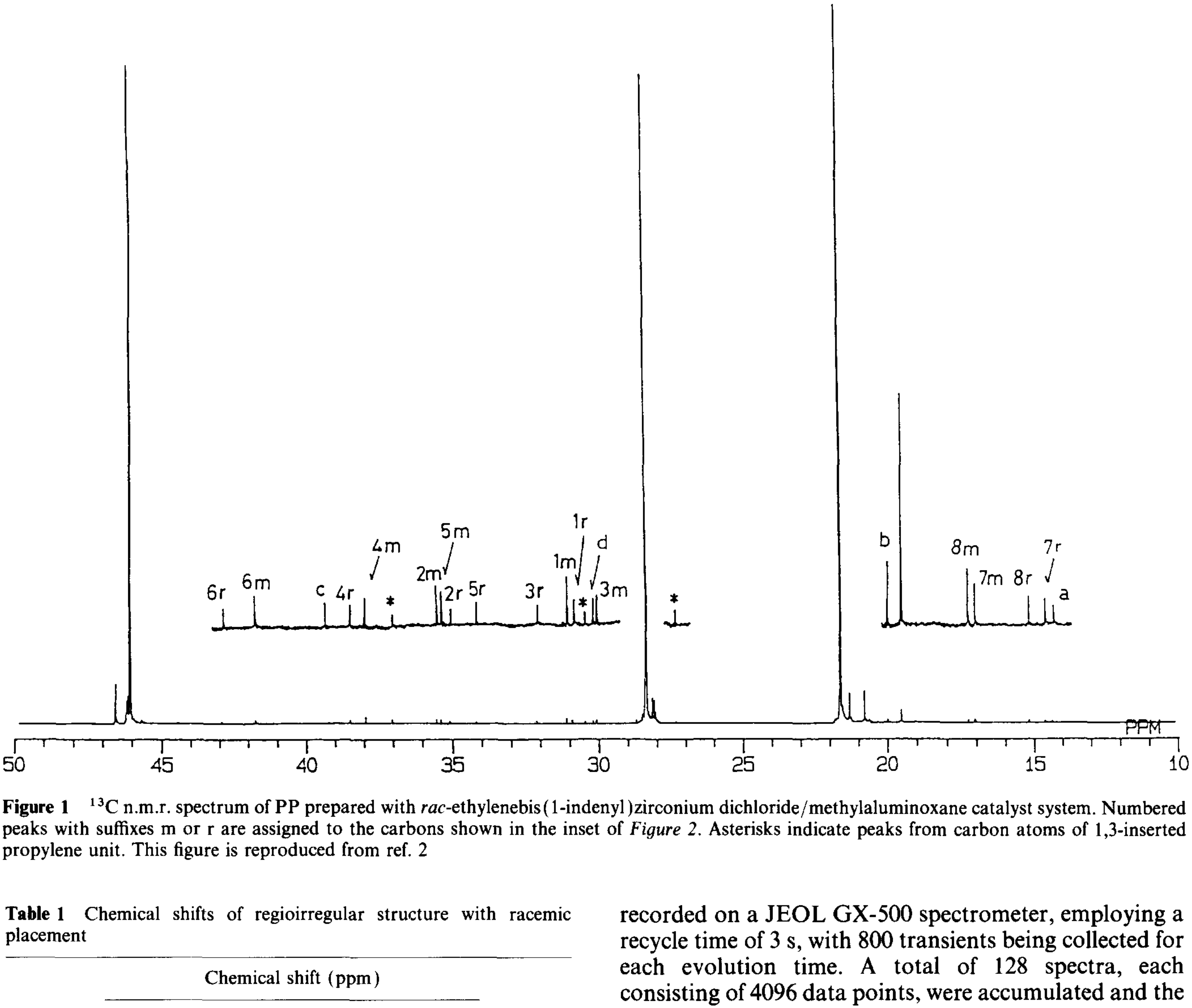
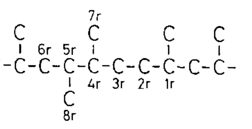


Figure 1 ^{13}C n.m.r. spectrum of PP prepared with *rac*-ethylenebis(1-indenyl)zirconium dichloride/methylaluminoxane catalyst system. Numbered peaks with suffixes m or r are assigned to the carbons shown in the inset of *Figure 2*. Asterisks indicate peaks from carbon atoms of 1,3-inserted propylene unit. This figure is reproduced from ref. 2

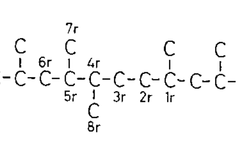
Table 1 Chemical shifts of regioirregular structure with racemic placement

Peak no.[a]	Chemical shift (ppm)			Carbon species
	Obs.	Calc. (*racemo*-1)	Calc. (*racemo*-2)	
1r	30.92	31.32	31.27	CH
2r	35.11	35.09	35.01	CH_2
3r	32.12	32.13	32.28	CH_2
4r	38.52	38.08	37.60	CH
5r	34.25	34.92	35.20	CH
6r	42.92	43.19	43.63	CH_2
7r	15.15	15.34	16.05	CH_2
8r	14.63	15.12	14.76	CH_3

[a] Numbering of carbon atoms is as follows:


$-C-\overset{C}{C}-\overset{6r}{C}-\underset{\underset{8r}{C}}{\overset{5r}{C}}-\underset{4r}{\overset{\overset{7r}{C}}{C}}-\underset{3r}{C}-\underset{2r}{C}-\underset{1r}{\overset{C}{C}}-C-\overset{C}{C}-$

racemo-1


$-C-\overset{C}{C}-\overset{6r}{C}-\underset{5r}{\overset{\overset{7r}{C}}{C}}-\underset{\underset{8r}{C}}{\overset{4r}{C}}-\underset{3r}{C}-\underset{2r}{C}-\underset{1r}{\overset{C}{C}}-C-\overset{C}{C}-$

racemo-2

the measurement of the $^{13}C-^{1}H$ shift correlation two-dimensional n.m.r. spectrum, the polymer solution was prepared by dissolving ~200 mg of PP homopolymer at 125°C in a mixture of 0.5 ml hexachlorobutadiene and 0.05 ml perdeuteriobenzene. The spectrum was recorded on a JEOL GX-500 spectrometer, employing a recycle time of 3 s, with 800 transients being collected for each evolution time. A total of 128 spectra, each consisting of 4096 data points, were accumulated and the data matrix was zero-filled to 256 x 4096 points with a frequency range of 1200 Hz in ^{1}H and 7500 Hz in ^{13}C dimension.

RESULTS AND DISCUSSION

^{13}C n.m.r. analysis of regioirregular unit in homopolymer

The ^{13}C n.m.r. spectrum of the homopolymer observed at 125.8 MHz, although essentially the same as that shown in the previous paper[2], is presented in *Figure 1* in order to show the full-scale spectral features. All the small peaks are due to the regioirregular structures with both *meso* and racemic placements present in a 6:4 ratio, 1,3-inserted monomer unit (that of $-(CH_2)_4-$ unit) and the polymer chain end-group[2].

To elucidate the stereochemical configuration of the regioirregular unit with racemic placement, the ^{13}C n.m.r. chemical shift calculations were first made for the two possible racemic structures, *racemo*-1 and *racemo*-2, by using the additive rules accounting for substituent effects as well as configurational sequences devised by Cheng and Bennett[5]. The results are summarized in *Table 1* together with the observed chemical shifts and the carbon species determined by d.e.p.t. measurement. The calculated values for the *racemo*-1 structure have already been reported in the previous paper[2], but some of them are revised here.

From these results, however, it is difficult to say

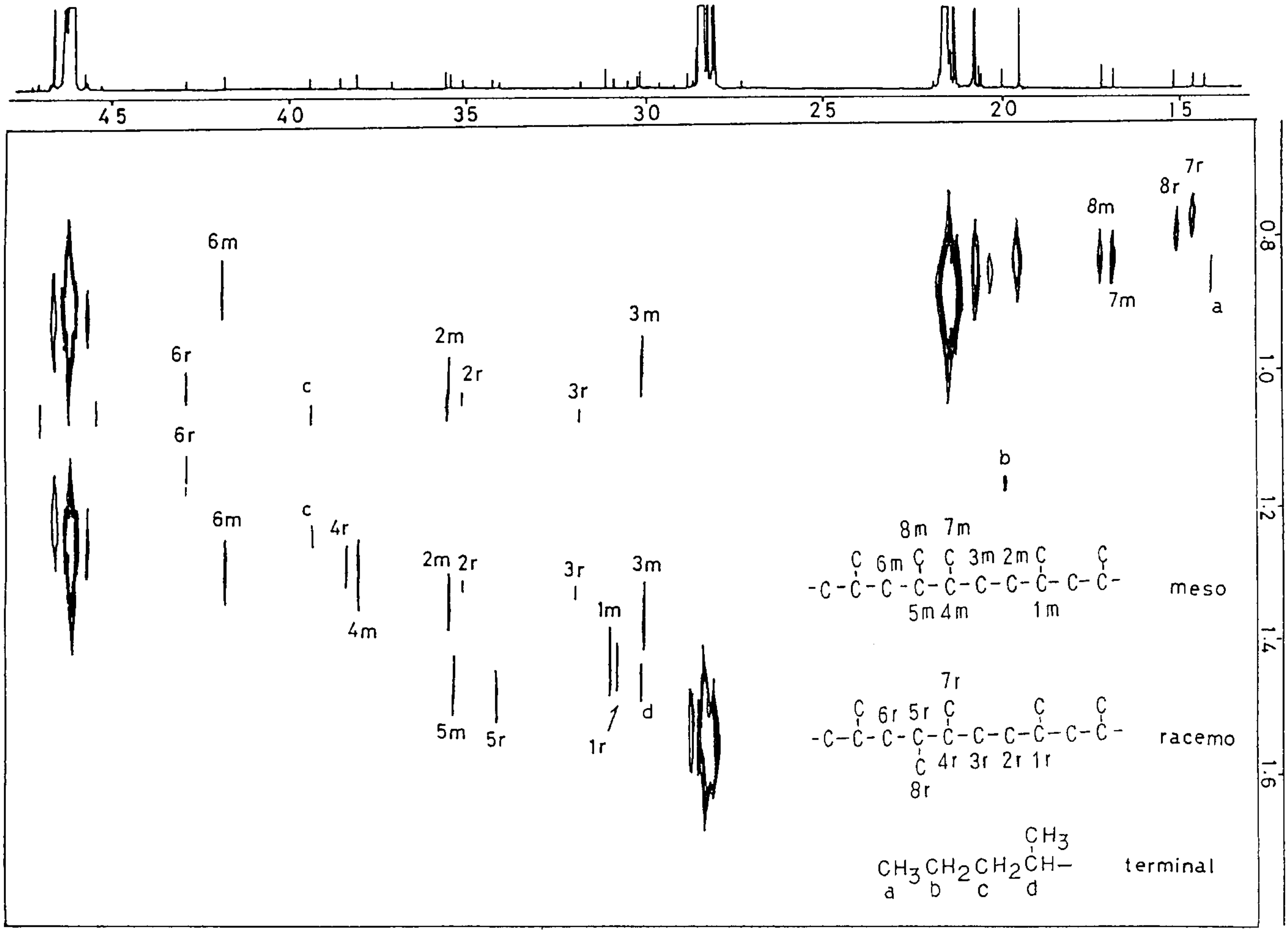


Figure 2 $^{13}C-^{1}H$ shift correlation two-dimensional n.m.r. spectrum of PP prepared with *rac*-ethylenebis(1-indenyl)zirconium dichloride/methylaluminoxane catalyst system

definitely that only one of the two racemic model structures reproduces exclusively well the observed ^{13}C chemical shifts because there are no significant differences in the chemical shift values calculated for the two structures. Therefore, the stereochemical configuration concerning the racemic placement was analysed with the aid of the $^{13}C-^{1}H$ shift correlation two-dimensional n.m.r. method as described in the following section.

Two-dimensional n.m.r. analysis of regioirregular unit in homopolymer

The observed $^{13}C-^{1}H$ shift correlation two-dimensional spectrum is shown in *Figure 2*. Attention is focused on the C–H correlation peaks associated with the carbons designated as 6r and 6m (see the inset of *Figure 2*), showing that the chemical shift difference (0.12 ppm) of the two protons bonding to the 6r carbon atom is much smaller than that (0.43 ppm) of the two protons to the 6m carbon. The result means that the two 6r protons are in a magnetically similar environment.

This finding indicates that the *racemo*-1 is a more plausible structure, because the two protons attached to the 6r carbon atom have quite similar chemical environments. The small chemical shift difference observed for the two 6r protons may be explained by the long-range effect from the methyl group designated as 7r.

The same long-range effect is also reflected in the chemical shifts of the 6m protons, resulting in a larger separation of their peaks in comparison with the shifts of methylene protons in the ordinary isotactic polypropylene sequence.

^{13}C n.m.r. analysis of regioirregular unit in copolymer

The ^{13}C n.m.r. spectrum of propylene copolymer containing 4.7 mol% of ethylene unit is shown in *Figure 3*. The spectral features are essentially the same as those of the copolymer with ethylene content of 1.3 mol% reported in the previous paper[2], where all the peaks on the spectrum were assigned as shown in *Figure 3*.

Although the stereochemical configuration of the regioirregular unit was given in our previous paper, a detailed discussion was not described there. Similarly to the analysis of the homopolymer, the chemical shift calculation is not conclusive as to the stereostructure (*meso* or racemic) of the regioirregular unit in the copolymer as shown in *Table 2*.

From the n.m.r. data shown in *Figure 3*, however, it is noticeable that only one type of regioirregular structure, which was formed by the preferential ethylene insertion at the chain ends of 2,1-inserted propylene unit, was observed in the copolymer. In order to explain this n.m.r. result, the polymerization mechanism concerning the formation of the regioirregular structure was reinvestigated. The reaction scheme that generates regioirregular structures can be drawn as shown in *Figure 4*. As evident from *Figure 4*, the n.m.r. data which show that only one type of regioirregular structure is formed in the copolymerization, is difficult to interpret unless

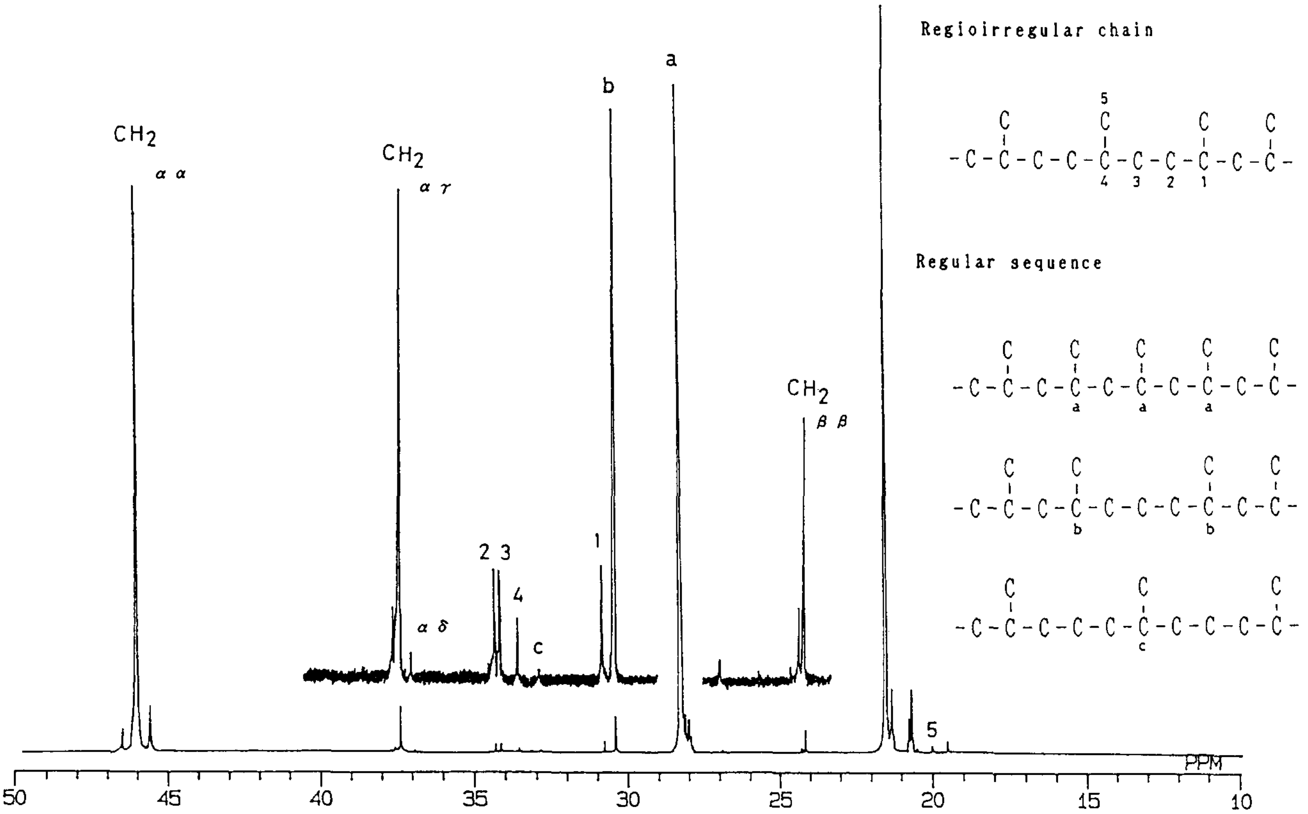
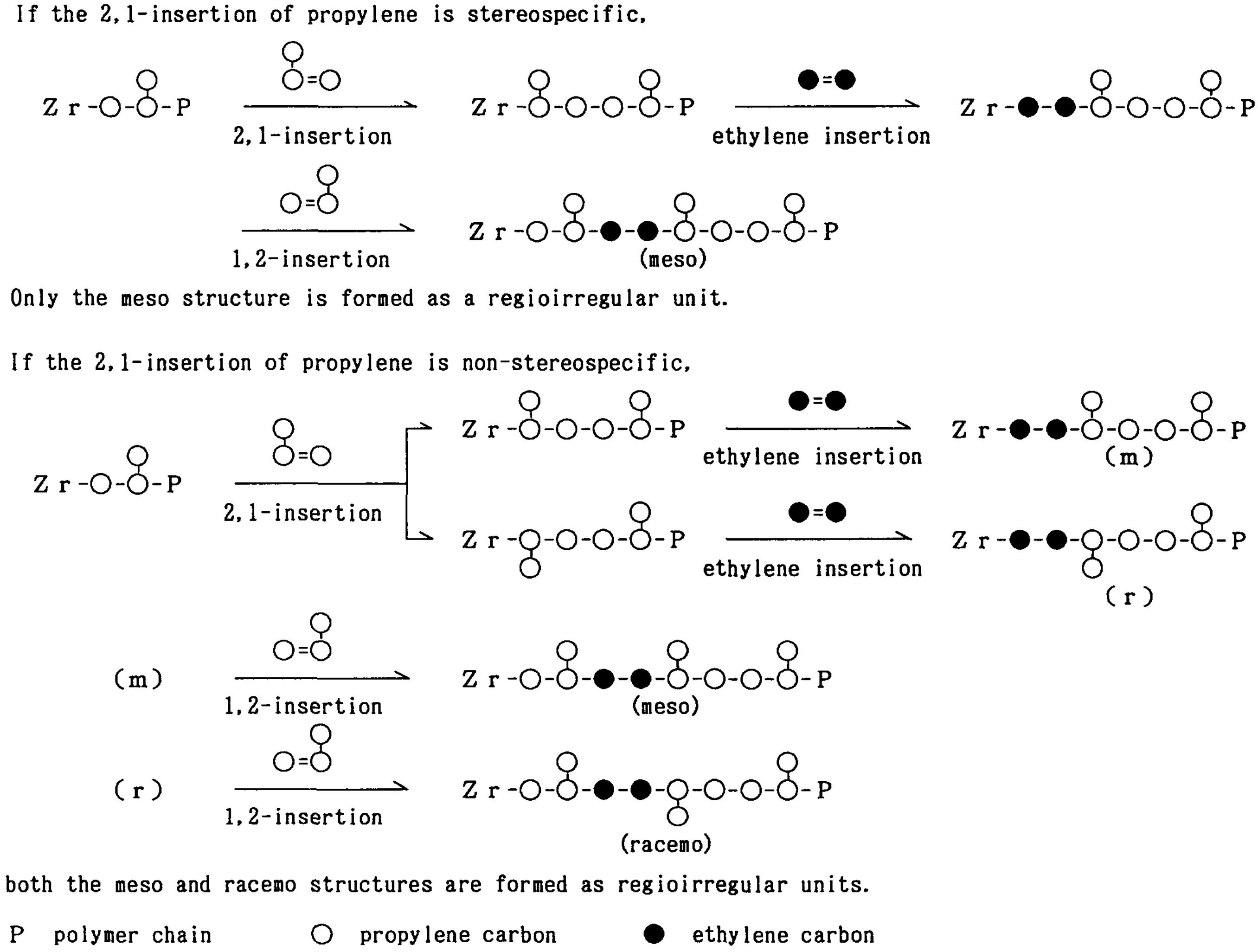


Figure 3 ^{13}C n.m.r. spectrum of a 95.3 mol% propylene–4.7 mol% ethylene copolymer



If the 2,1-insertion of propylene is stereospecific,

Only the meso structure is formed as a regioirregular unit.

If the 2,1-insertion of propylene is non-stereospecific,

both the meso and racemo structures are formed as regioirregular units.

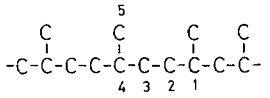
P polymer chain ○ propylene carbon ● ethylene carbon

Figure 4 The proposed reaction scheme for generation of regioirregular structures

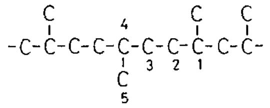
Table 2 Chemical shifts of regioirregular structure in copolymer

Peak no.[a]	Chemical shift (ppm) Obs.	Calc. (*meso*)	Calc. (*racemo*)	Carbon species
1	30.82	31.32	31.23	CH
2	34.33	34.79	34.81	CH_2
3	34.17	34.49	34.72	CH_2
4	33.62	33.98	33.80	CH
5	20.05	20.31	20.11	CH_3

[a] Numberingof carbon atoms is as follows:



meso



racemo

the 2,1-insertion of propylene is stereospecific. This finding strongly supports that the racemic structure found in the homo-PP is the *racemo*-1 type.

CONCLUSIONS

From the n.m.r. data, it is concluded that the 2,1-insertion of propylene monomer is also stereospecifically controlled by the catalyst.

In the homopolymerization, 1,2-propylene insertion at the chain end of 2,1-inserted propylene unit is less stereospecific probably due to the steric hindrance of two neighbouring methyl groups, giving the *meso* and racemic placements in a 6:4 ratio.

On the other hand, in copolymerization with a small amount of ethylene, only one regioirregular stereochemical configuration is observed because the monomer insertion at the chain end of 2,1-inserted propylene unit is preferentially made by ethylene.

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