# $^{13}C$ n.m.r. determination of the isotacticity of the propylene homopolymer part in ethylene–propylene block copolymers

**Takashi Kanezaki*, Kazuo Kume and Kazuo Sato**
*Polymer Research Laboratory, Idemitsu Petrochemical Co. Ltd, 1-1 Anesaki-Kaigan, Ichihara, Chiba 299-01, Japan*

**and Tetsuo Asakura**
*Department of Biotechnology, Tokyo University of Agriculture and Technology, Nakacho 2-chome, Koganei, Tokyo 184, Japan*
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Ethylene–propylene block copolymer (B-PP) consists of two parts: propylene homopolymer and copolymer of ethylene and propylene. A method for determining the isotacticity, *mmmm*, of the propylene homopolymer part in B-PP is proposed here, using only the $^{13}C$ n.m.r. spectrum of B-PP. This is a conventional method to determine the isotacticity with high precision.

**(Keywords: $^{13}C$ n.m.r.; ethylene–propylene block copolymer; isotacticity)**

## INTRODUCTION

Ethylene–propylene block copolymer (B-PP) is one of the most important industrial polymers. A small amount of ethylene unit is usually introduced to isotactic polypropylene (I-PP) in order to improve the mechanical properties such as impact strength. Therefore, it is difficult to determine the isotacticity of the I-PP part in B-PP because of the presence of ethylene units. To date, two methods have been used for determining the isotacticity.

The first method is a 'sampling method'. During B-PP preparation, the isotactic polymerization of propylene is first performed, followed by copolymerization with ethylene in the presence of the isospecific catalyst. Just before the second polymerization with ethylene, I-PP alone is collected and the isotacticity of I-PP is determined by $^{13}C$ n.m.r. spectroscopy. At present, $^{13}C$ n.m.r. is the most powerful analytical method for determining the tacticity of polypropylene, and pentad- or heptad-level assignments have been reported for the methyl carbon[1–8]. Since this sampling method gives the isotacticity directly, the tacticity determined for the I-PP in B-PP is reliable. However, the sampling itself is complicated and is not applicable to commercial B-PP samples.

The second method is the fractionation of B-PP samples. B-PP sample is dissolved at 135°C in *p*-xylene (5 g/700 ml), then the solution is cooled gradually to room temperature. The precipitated fraction is considered to be I-PP whose isotacticity is determined by $^{13}C$ n.m.r. This method is relatively simple and avoids sampling during B-PP polymerization. However, there is a possibility that small amounts of the ethylene–propylene (E-P) part still remain in the precipitated fraction; peaks from the E-P part are sometimes observed in the fraction. In addition, the fractionation requires at least 10 h.

Thus, it is necessary to develop an analytical method, other than these two methods, to determine in detail the isotacticity of the I-PP part of the B-PP sample. In this paper, we propose a conventional method to determine directly and with high precision the isotacticity of the I-PP part in B-PP from the $^{13}C$ n.m.r. spectrum of B-PP. The validity of this method is supported by a comparison with the isotacticity of I-PP obtained by the sampling method.

## EXPERIMENTAL

### *Materials*

Isospecific homopolymerization of propylene was carried out in the presence of Ziegler–Natta catalysts and a part of the sample was obtained as I-PP. After this sampling, a small amount of ethylene was added and the polymerization, i.e. copolymerization of propylene and ethylene, was continued. Thus, sets of B-PP and I-PP samples were obtained. Ten kinds of B-PP and I-PP sets were prepared by changing the ethylene content from 2.3 to 8.2 wt%.

To gain further information from analysing the $^{13}C$ n.m.r. spectrum of B-PP, E-P copolymers (EPR) and I-PP samples were prepared independently. EPR samples were prepared by the following procedure. B-PP samples were dissolved at 135°C in *p*-xylene, then the solution was cooled gradually to room temperature. After the precipitated fraction (mainly I-PP) was removed by filtration, the solution of EPR was obtained. This was precipitated by pouring into large amounts of methanol. Seventy-five EPR samples were obtained. Thirty-four kinds of I-PP ($mmmm \geq 93$ mol%) were prepared with the same catalyst as that used in the B-PP polymerization.

### *$^{13}C$ n.m.r. measurements*

$^{13}C$ n.m.r. spectra were measured at 130°C using a JEOL-EX400 n.m.r. spectrometer operating at 100.1 MHz.

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*To whom correspondence should be addressed

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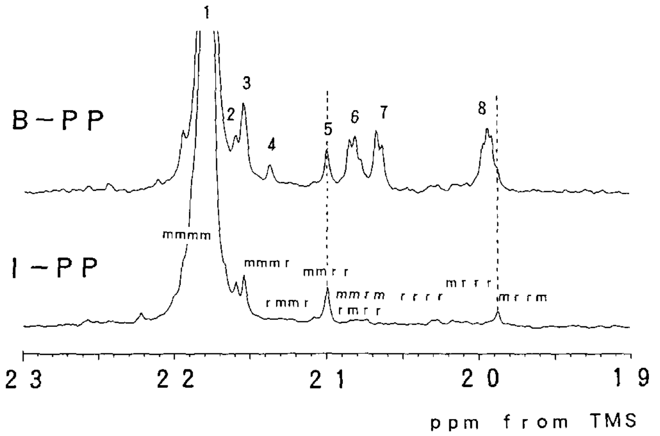

**Figure 1** The methyl region of $^{13}C$ n.m.r. spectra of ethylene–propylene block copolymer (B-PP) and isotactic polypropylene (I-PP) samples. The I-PP was obtained by sampling during the B-PP polymerization process (see text)

The polymer samples were dissolved in the mixed solvent of 1,2,4-trichlorobenzene and benzene-$d_6$ (9:1 volume ratio). The polymer concentration was 7 wt%. In all measurements, broad-band noise decoupling was used to remove $^{13}C-^{1}H$ coupling. The pulse repetition time was 4 s (45° pulse) and 1000–2000 scans were performed. Tetramethylsilane (TMS) was used as internal chemical shift reference.

## RESULTS AND DISCUSSION

*Figure 1* shows the methyl region of $^{13}C$ n.m.r. spectra of B-PP and I-PP samples. The latter was obtained by sampling during the B-PP polymerization process.

The assignment of the methyl region of highly isotactic PP has been reported[1–3]. Except for the main peak, *mmmm*, the peaks *mmmr*, *mmrr* and *mrrm* are clearly observed. The relative intensities are 2(*mmmr*):2(*mmrr*): 1(*mrrm*), indicating catalytic control in I-PP polymerization[9]. The peaks *rmmr*, *mmrm*, *rmrr*, *rrrr* and *mrrr* are also detected, although the peak intensities are quite low.

In the B-PP spectrum, the peaks 1, 2, 3, 5 and the shoulder peak of 8 are assigned to *mmmm* (1+2), *mmmr* (3), *mmrr* (5) and *mrrm* (shoulder peak of 8), respectively, in the I-PP part. The peaks 4, 6, 7 and 8 are therefore assigned to the EPR part in the B-PP sample. This is confirmed by the $^{13}C$ n.m.r. spectra (methyl region) of a series of soluble fractions of the EPR part only in seven B-PP samples (*Figure 2*). The assignment of EPR has been reported[10] as shown in *Figure 2*. It is noted that peaks 1 and 3 in the spectrum of B-PP come from both EPR and I-PP parts. Thus, it is not easy to determine directly the isotacticity of the I-PP part from the $^{13}C$ n.m.r. spectra of B-PP.

From the $^{13}C$ n.m.r. spectra of the EPR part in *Figure 2*, it is noted that the intensities of both peaks, *I* (PPPPP) and *I* (PPPEP+PPPEE) decrease relatively with increasing ethylene content in a series of EPR samples. It is therefore possible to estimate the relative intensities of *I* (PPPPP) from those of *I* (PPPEP+PPPEE) in the spectra of B-PP because the peak PPPEP+PPPEE does not overlap with the I-PP peaks except for the very small peak of *mmrm*+*rmrr*. *Figure 3* shows the plots of the ratio of the peak intensities, *I* (PPPPP)/*I* (EPPEP+EPPEE) against the ratio of the peak intensities *I* (PPPEP+PPPEE)/*I* (EPPEP+EPPEE) obtained from the $^{13}C$ n.m.r. spectra of 75 EPR samples. The correlation coefficient is 0.85. If the ratio of the peak intensities, *I* (PPPEP+PPPEE)/*I* (EPPEP+EPPEE), is obtained in the spectrum of B-PP, the peak intensity of PPPPP can be estimated. By subtracting the peak intensities, *I* (PPPPP), of the EPR part from the intensities of peaks 1 and 2, the fraction of *mmmm* in the I-PP part will be obtained.

The fraction of *mrrm* in the I-PP part can be obtained from the separation of peak 8, assuming a Lorentzian in the expanded spectra of B-PP because the position of the *mrrm* peak is slightly up-field of peak 8, PEPEP+PEPEE+EEPEE, in the EPR part.

It is difficult to determine the fraction of *mmmr* from the B-PP spectra directly because peak 3 is assigned to both *mmmr* of the I-PP part and PPPPE of the EPR part.

The fraction of *mmmr* is assumed to be the same as that of *mmrr* because the polymerization process of the I-PP part is under catalytic control (*Figure 1*)[9].

The fractions of *rmmr*, *mmrm*+*rmrr*, *rrrr* and *mrrr* of I-PP are very small, but not negligible, in the determination of the fraction of *mmmm* in the B-PP sample. Therefore, we will try to obtain the information independently. The $^{13}C$ n.m.r. spectra of 34 I-PP samples with *mmmm* fractions from 93.9 to 97.7 mol% were used to determine the fractions of *rmmr*, *mmrm*+*rmrr*, *rrrr* and *mrrr* relative to the fraction of

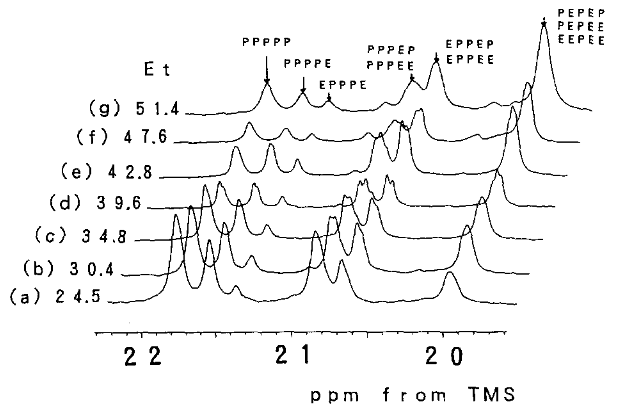

**Figure 2** The methyl region of $^{13}C$ n.m.r. spectra of EPR samples (see text). The pentad sequence assignments are shown. Et, E and P represent the ethylene content (wt%), ethylene and propylene, respectively

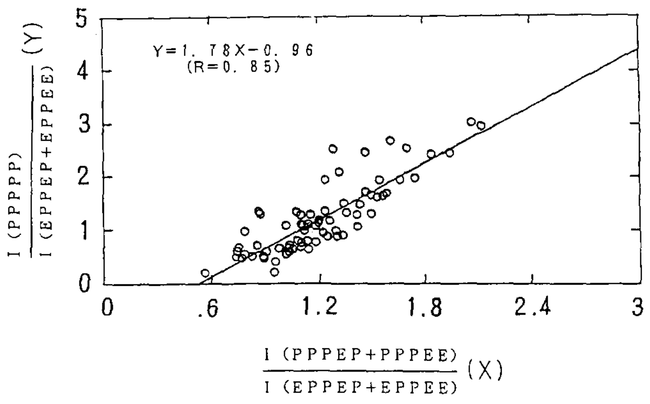

**Figure 3** Relationship between the ratio of the peak intensities, *I* (PPPPP)/*I* (EPPEP+EPPEE) and the ratio of the peak intensities, *I* (PPPEP+PPPEE)/*I* (EPPEP+EPPEE). R = correlation coefficient

**Table 1** Isotacticity of the I-PP part in B-PP determined by the sampling method and the method proposed here

| B-PP sample | Ethylene content (wt%) | Isotacticity (*mmmm*, mol%) Sampling method (1) | Present method (2) | Difference (2)−(1) |
|---|---|---|---|---|
| A | 2.8 | 96.6 | 96.2 | −0.4 |
| B | 2.3 | 96.6 | 96.7 | +0.1 |
| C | 3.4 | 95.3 | 95.6 | +0.3 |
| D | 7.0 | 96.0 | 96.3 | +0.3 |
| E | 8.2 | 96.6 | 96.2 | −0.4 |
| F | 5.0 | 97.3 | 97.4 | +0.1 |
| G | 4.4 | 97.0 | 96.7 | −0.3 |
| H | 2.9 | 96.6 | 97.1 | +0.5 |
| I | 3.1 | 98.6 | 98.4 | −0.2 |
| J | 5.1 | 97.7 | 98.2 | +0.5 |

*mmrr*. The average fractions are $0.18 \pm 0.12$ (*rmmr*), $0.37 \pm 0.13$ (*mmrm*+*rrmr*), $0.31 \pm 0.10$ (*rrrr*), $0.18 \pm 0.08$ (*mrrr*), when *mmrr* is assumed to be 1.

Thus, the fraction of *mmmm* of I-PP samples is calculated directly from the $^{13}C$ n.m.r. spectra according to the method described above. The I-PP parts are also obtained from corresponding B-PP samples by the sampling method during sample preparation. The $^{13}C$ n.m.r. spectra are also observed for the determination of isotacticity. The data are obtained from 10 sets of I-PP and B-PP samples (*Table 1* and *Figure 4*). The correlation coefficient is 0.92.

Thus, it is concluded that the present method for the determination of isotacticity of the I-PP part of B-PP has high precision.

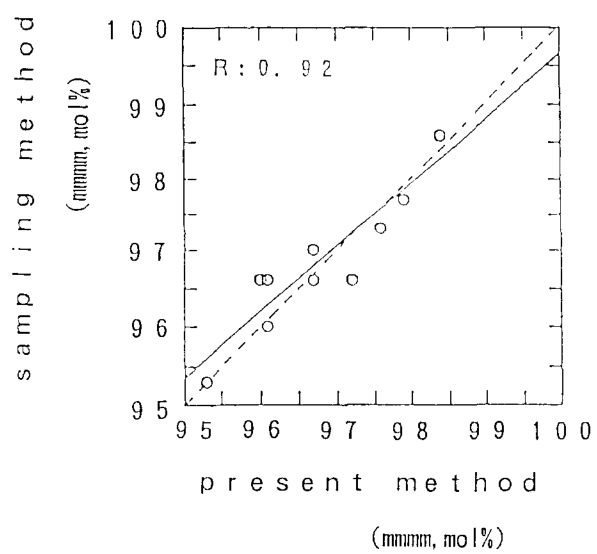

**Figure 4** Relation between the isotacticity of the I-PP part in B-PP obtained by the sampling method and the method proposed here. R = correlation coefficient

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