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# High-Resolution Proton Magnetic Resonance Analysis of Polypropylenes

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# High-Resolution Proton Magnetic Resonance Analysis of Polypropylenes

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## ABSTRACT

The dyad and triad tacticities of polypropylenes were determined quantitatively with the aid of a computer from the 100-MHz proton magnetic resonance spectra in o-dichlorobenzene solution at 165°C. The contents of tactic dyad and triad evaluated from the 100-MHz PMR spectra are in fair agreement with the values determined from the 220-MHz PMR and $^{13}C$–($^{1}H$) spectra, respectively. The fraction soluble in boiling ethyl ether of polymer prepared with the $Ti(O\text{-}n\text{-}Bu)Cl_3$–$AlEt_2Cl$ catalyst shows a character of stereorandomness, and the ethyl ether-soluble portion of polymer polymerized with the $TiCl_3$–$AlEt_2Cl$ catalyst has a character of stereoblock sequence. Furthermore, by IR analysis, it has become apparent that the former has a $-(CH_2)_2-$ group formed by two propylene units in a tail-to-tail arrangement.

## INTRODUCTION

Many studies of the tacticity of polypropylene have been made using proton magnetic resonance (PMR) at 60 and 100 MHz [1-14]. The PMR spectra of polypropylenes, however, are difficultly resolvable because of small chemical shift differences and complex spin-spin coupling patterns. A few authors were able to make a partial interpretation and to obtain semiquantitative tacticity data [1, 3, 10, 15]. The use of a 220-MHz PMR spectrometer has greatly facilitated the observation of low-intensity peaks [16]. The interpretation of the isotactic polypropylene spectrum has also been aided by recent studies of the proton spectra of selectively deuterated polymers in which tetrad resonances have been clearly observed and tentatively assigned to the six possible tetrad structures [17, 18]. But, in the case of nondeuterated polymers, especially less stereoregular samples, detection and quantitative evaluation of tactic triad sequences are not easy using the 220-MHz spectra.

It is very important in regulating the physical properties of polypropylene products and in analyzing commercial polymers to evaluate the tactic dyad and triad placements. The 100-MHz methylene and methyl proton resonances of atactic polymer are marginally useful for the characterization of steric isomerism in terms of the quantitative determinations of tactic dyad and triad contents, respectively.

In this paper we report on the quantitative evaluation of tactic dyad and triad placements of polypropylene by comparison computer simulations with the observed 100-MHz spectrum which has good resolution and a high signal-to-noise ratio.

## EXPERIMENTAL

### Polymer Used

A high molecular weight, very highly isotactic polypropylene (IPP) was obtained by boiling the n-octane extraction of a polymer prepared in the presence of the $TiCl_3$-$AlEt_2Cl$ catalyst. The ratio of absorbances at 997 and 974 $cm^{-1}$ in the IR spectrum was 0.995 [19].

A highly syndiotactic polypropylene (SPP) was prepared using a catalytic system of $VCl_4$-anisole-$AlEt_2Cl$, which has been described by Natta et al [20]. The ratio of optical density at 867 and 977 $cm^{-1}$ was 0.414 [21].

Two kinds of atactic polymers were prepared with two different Ziegler-Natta catalysts. Sample APP1 is the boiling ethyl ether-soluble fraction of a polymer obtained by the $TiCl_3$-$AlEt_2Cl$ catalyst. Sample APP2 was obtained by ethyl ether extraction at the boiling point of a polymer prepared with the catalytic system Ti(O-n-Bu)$Cl_3$–$AlEt_2Cl$. Sample APP2-ES and sample APP2-C7S are the boiling ethyl ether-soluble and the boiling n-heptane-soluble fractions of sample APP2, respectively.

### Spectra Measurements

The 100-MHz PMR spectra were obtained with a JOEL 4H-100 spectrometer. All spectra were obtained from 7 to 20% (wt/vol) solution in o-dichlorobenzene at 165°C. The samples were degassed, and hexamethyldisiloxane (HMDS) was added as internal standard.

The 220-MHz spectra were obtained using a Varian HR-220 spectrometer. Approximately 5 to 15% solutions in o-dichrobenzene were employed with tetramethylsilane (TMS) as internal reference.

The $^{13}C$–($^1H$) spectra were observed by external lock field sweep in absorption mode at 25.14 MHz. in the trans-decalin solution at 150°C using a JNM PS-100 spectrometer. Total spin decoupling were done using JNM IS-100 and JNM SD-HC equipments. The drift of the field was automatically corrected by signal trigger technique using a JEC-5 spectrum computer. The effective signal-to-noise ratio was improved by means of the multiple scan average technique (2000 times) using a JEC-5 spectrum computer.

IR spectra were obtained on molded blocks of polymer samples using a Hitachi EPI-G3 spectrometer.

## RESULT AND DISCUSSION

The major interest in the numerous earlier PMR studies of polypropylenes has been the determination of tacticity. The PMR spectra of polypropylenes, however, are resolvable only with difficulty because of the small difference in chemical shift. In addition, quantitative analysis requires further improved resolution and signal-to-noise ratio. Lack of resolution or overlap of resonance peaks frequently makes the proton resonance spectra less useful than what might be hoped. The chemical shifts in the 100-MHz PMR spectra of propylene polymer are detectably affected by the structural arrangements of two and three monomer sequences: the dyads may be easily distinguished because the methylene hydrogens of alternances have the same chemical shift, whereas those of the permanances have different chemical shifts depending on whether the hydrogens are syn or anti. The part of the spectrum relative to the methyls allows one to detect the presence of isotactic, heterotactic, and syndiotactic triads.

Woodbrey and co-workers have reported an analysis of tactic placements of polypropylenes using PMR at 60 MHz [15]. The tacticity calculation proposed by them is based on the fractionated five area of proton resonance appearing in the methyl region, and on the assumption that the overlap contributions are equal. It is, however, difficult to keep resolution constant each time measurements of PMR spectra are repeated. Furthermore, as the chemical shifts of the methyl resonances vary by changes in the tactic sequence of polymers, it is impossible to extimate the content of heterotactic triad quantitatively using the method proposed by Woodbrey et al.

We tried to determine the contents of tactic dyad and triad quantitatively from well-resolved spectra of polypropylenes at 100 MHz with the aid of an electronic computer.

First, it is necessary to estimate the relative area in each peak of the 100-MHz spectra of IPP and SPP. For this purpose, it was decided to examine polymers that have the highest possible sterical purity; these were obtained in the presence of highly stereospecific catalyst systems, isotactic and syndiotactic, respectively. Figure 1 shows the complete 100 MHz spectra of the IPP and SPP samples. As is well known, the more intense doublet for polymers of high tactic purity (with lines centered at $\delta$ = 87.25 Hz for IPP and at $\delta$ = 83.25 Hz for SPP) are due to the central methyl protons of tactic triads. The methylene proton resonances of IPP are complicated by spin-spin coupling between isotactic placements, and by further coupling between each methylene proton and the flanking methine proton. As Fig. 1(A) shows, the peaks of the anti-proton consisted of quinted signals overlapped partially with the methine proton resonances (see Fig. 2). However, the well-resolved peaks of the methyl and the syn proton are observed in o-dichlorobenzene at 165°C. On the contrary, as Fig. 1(B) shows, the spectrum of SPP consists of relatively simple broader peaks compared to IPP.

Second, we developed the computer program "NMR-RSV" to calculate the area in each peak of an overlapped PMR spectrum on the assumption of suitable Lorentzian curves. This program consists of two parts: (1) from an arbitrary chosen set of frequencies, intensities, and half-widths of twenty-five lines, the computer can generate a table of frequencies and intensities of the lines expected in the PMR spectrum. (2) If a spectrum thus calculated bears a recognizable resemblance to an observed spectrum, the program causes the computer to perform an iterative calculation by means of which the calculated intensities of assigned lines are brought as close as possible (by

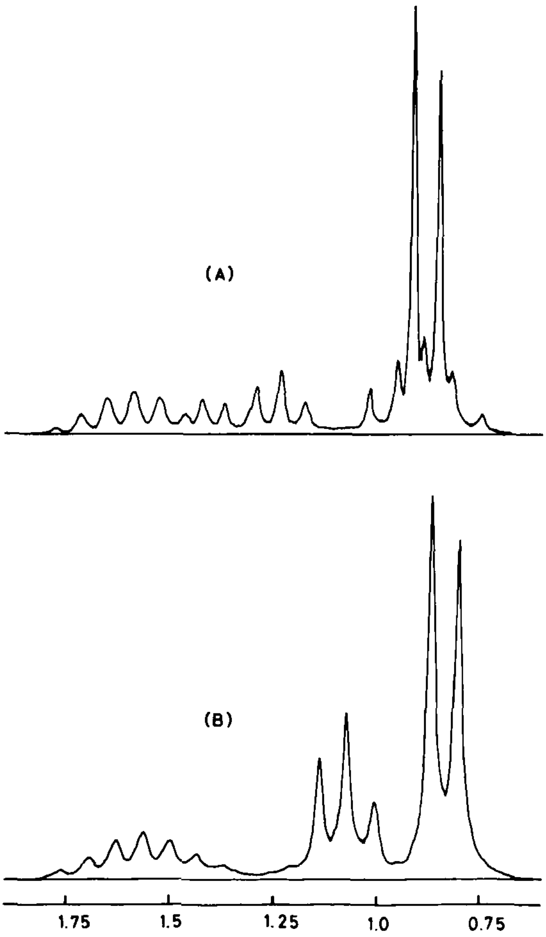


FIG. 1. The 100-MHz PMR spectra of two polypropylenes: (A) IPP, (B) SPP.

the least squares criterion) to the corresponding observed lines within some validity limit on intensities. The table of the relative area, frequencies, intensities, and half-widths of lines which yield this best fit are then printed out, together with information about the expected errors of intensities. Though analysis of more complex spectra has

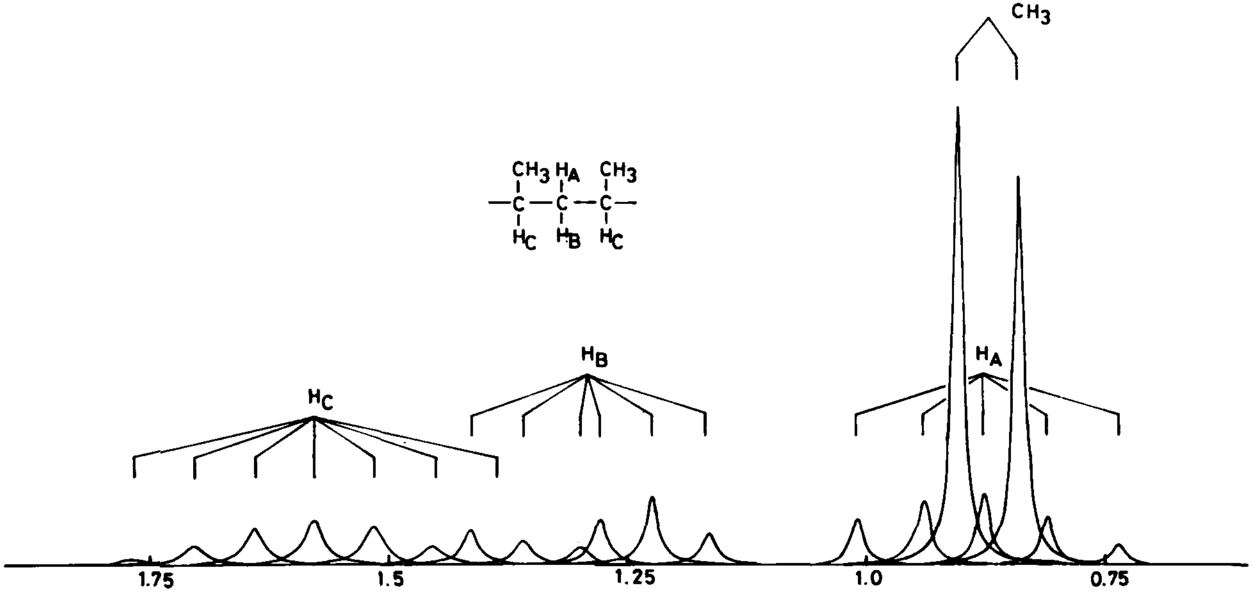


FIG. 2. The decomposed spectrum of isotactic polypropylene (100 MHz).

most often been performed using iterative techniques, trial and error fitting has been extensively used but suffers from the disadvantages of tediousness, slow convergence, lack of clear-cut criteria for halting computational work, and uncertainty in the errors of derived parameters. The major limitation of this technique is the resolution of the experimental spectrum. If two lines are unresolved in an observed spectrum, then any assignment based on this pair considered as a single line is doomed to failure.

Figure 2 shows the decomposed spectrum of IPP. The relative area of lines of the syn($H_A$) and anti($H_B$) protons is in good agreement with that of the calculated spectrum using the NMR parameters presented by Heatley et al. [17] with ±0.5% (see Fig. 3).

## Analysis of Mixture of IPP and SPP

As shown in Fig. 4, a quantitative evaluation of an IPP-SPP ratio is easy by the 220-MHz spectra from the relative area of the peaks due to the meso and racemic methylene protons. However, the five lines of the syn proton are not detectable. On the other hand, as shown in Fig. 5, the 100-MHz spectra of the same samples as in Fig. 4 show the well-resolved five lines of the syn proton which overlapped partially with the racemic proton signals.

The evaluation of the IPP-SPP ratio was done as follows: (1) on the assumption that the area of the lines appearing at the highest and lowest field in the methine proton resonance is equal, the area of the anti-proton resonance was evaluated by subtracting the area of the methine proton resonance from the total area of the anti- and methine proton resonances. (2) Although the half-widths of the peaks due to the racemic proton resonances change with the length of tactic sequence of polymer, it was assumed that the area ratio of each component of a triplet is constant; the area ratio of the three peaks is 19.39, 46.94, and 33.67% from the high field (the probable error was within ±1.0%). From the two resolved peaks of a triplet due to the racemic protons, the area of the racemic proton resonances is calculated. Thus, from the above considerations, the IPP-SPP ratio may be calculated.

The IPP-SPP ratio of three samples is listed in Table 1, together with the data obtained by the 220-MHz spectra. In the 220-MHz spectra the IPP-SPP ratio was evaluated with the area, which was determined by the ordinary weighting method of recording paper, under the $\beta$ proton resonance. The IPP-SPP ratio obtained by the 100-MHz spectra were in good agreement with the results of the 220-MHz spectra.

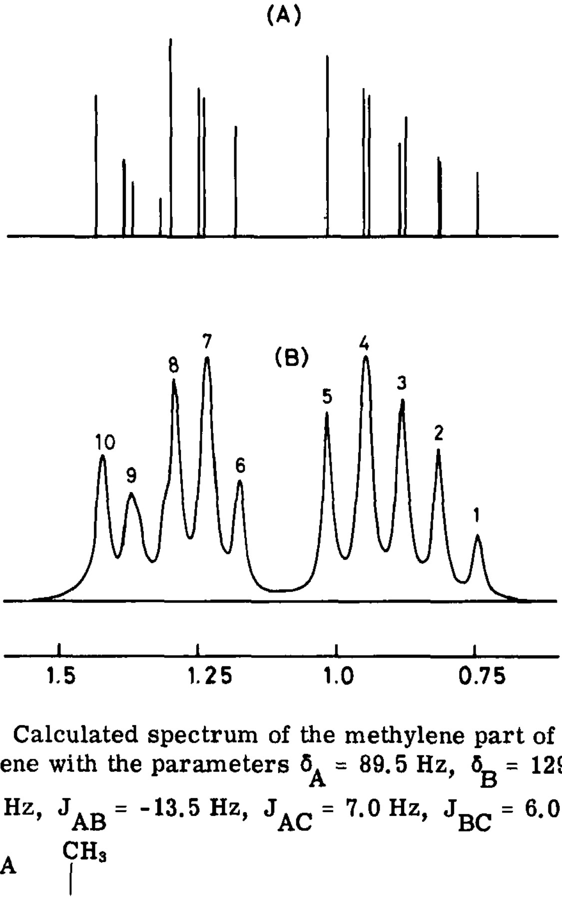
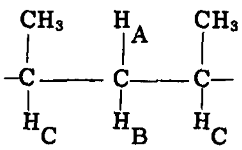


FIG. 3. Calculated spectrum of the methylene part of isotactic polypropylene with the parameters $\delta_A$ = 89.5 Hz, $\delta_B$ = 129.3 Hz, $\delta_C$ = 158.6 Hz, $J_{AB}$ = -13.5 Hz, $J_{AC}$ = 7.0 Hz, $J_{BC}$ = 6.0 Hz [17].


$$\begin{array}{ccc} CH_3 & H_A & CH_3 \\ | & | & | \\ -C- & C & -C- \\ | & | & | \\ H_C & H_B & H_C \end{array}$$

$ABC_2$ spin system.

The above results, therefore, suggest that the dyad placements of polypropylenes can be determined from the 100-MHz PMR spectra.

## The Quantitative Evaluation of Tactic Dyad and Triad Placements

Figure 6 shows the 100-MHz spectrum of Sample APP1 together with the calculated spectrum. In spite of high resolution, sample APP1 gives a spectrum of broad envelopes of many lines which

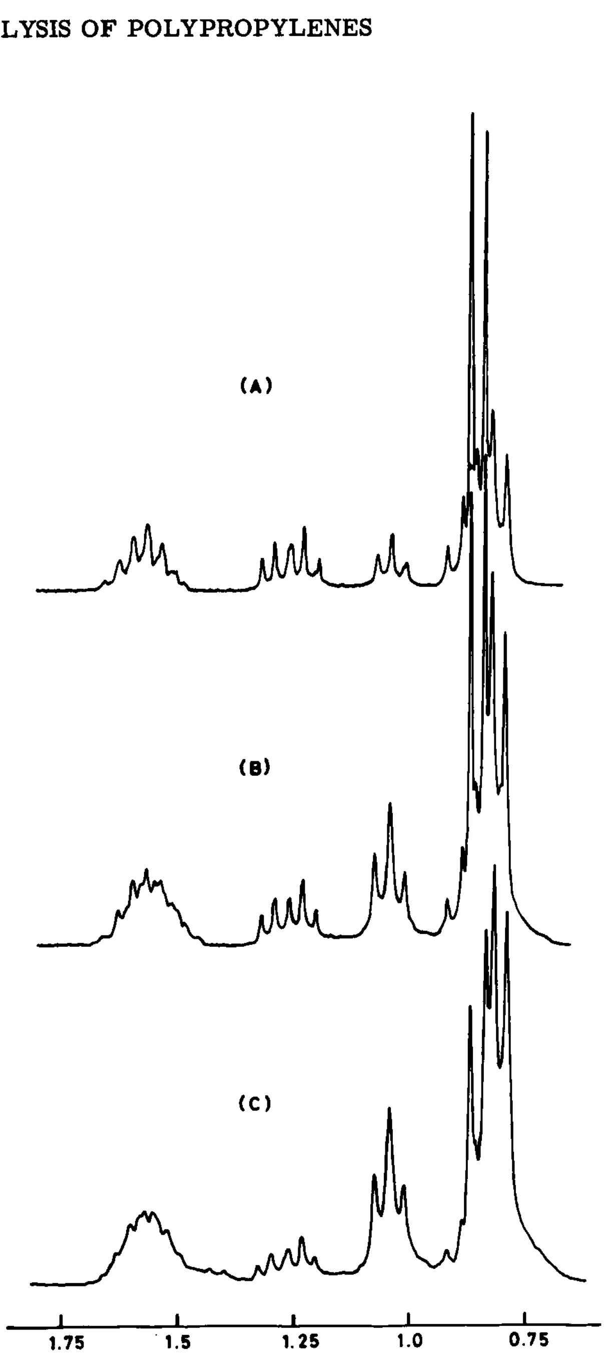


FIG. 4. The 220-MHz spectra of mixtures of IPP and SPP: (A) sample Mix 1, (B) sample Mix 2, (C) sample Mix 3.

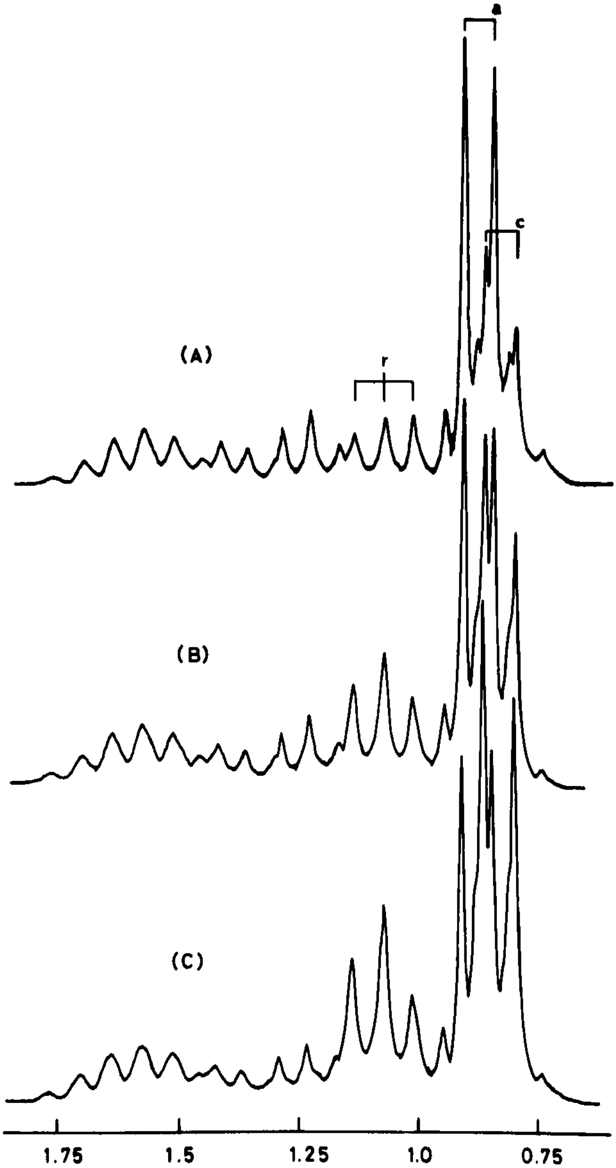


FIG. 5. The 100-MHz spectra of the same samples as in Fig. 4.

TABLE 1. Analysis of Mixtures of IPP and SPP

| Sample | IPP[a] (%) | SPP[a] (%) | IPP[b] (%) | SPP[b] (%) | IPP[c] (%) | SPP[c] (%) |
|---|---|---|---|---|---|---|
| Mixture 1 | 73.9 | 26.1 | 73.5 | 26.5 | 74.5 | 25.5 |
| Mixture 2 | 55.0 | 45.0 | 54.6 | 45.4 | 53.4 | 46.6 |
| Mixture 3 | 39.5 | 60.5 | 38.7 | 61.3 | 39.1 | 60.9 |

[a] Obtained from the methylene proton resonances at 100 MHz.
[b] Obtained from the methyl proton resonances at 100 MHz.
[c] Obtained from the methlene proton resonances at 220 MHz.

consists of relatively short tactic sequences of propylene units as contrasted with those of IPP-SPP mixtures. However, this enveloped spectrum has no important influence upon the determination of tactic placements. The more intense doublet components correspond to the line positions of central methyl proton resonances of isotactic triads. In addition, the relatively weak and shouldered two doublet components (designated b and c) are assigned, on the basis of early established results, to the lines of the methyl proton resonances of heterotactic and syndiotactic triads, respectively. The methyl doublet peaks of heterotactic triad are overlapped with the lines of the syn proton (designated 2 and 3 in Fig. 3). In the racemic proton resonance region, the line at the highest field position of a triplet due to the racemic proton resonances overlapped with that of the syn proton (designated 5 in Fig. 3), and the other lines may be resolved from the peaks of the syn- and anti-protons.

The evaluation of the tactic dyads was done by the same method as that of the IPP-SPP ratio. The contents of tactic triads were evaluated as follows: from the total area of the syn- and methyl-proton resonances, equations were established:

$$S_A = S_a + S_b + S_c + S_{syn}$$

$$S_{syn} = S_{anti}$$

$$S_b = S_A - (S_a + S_c + S_{anti})$$

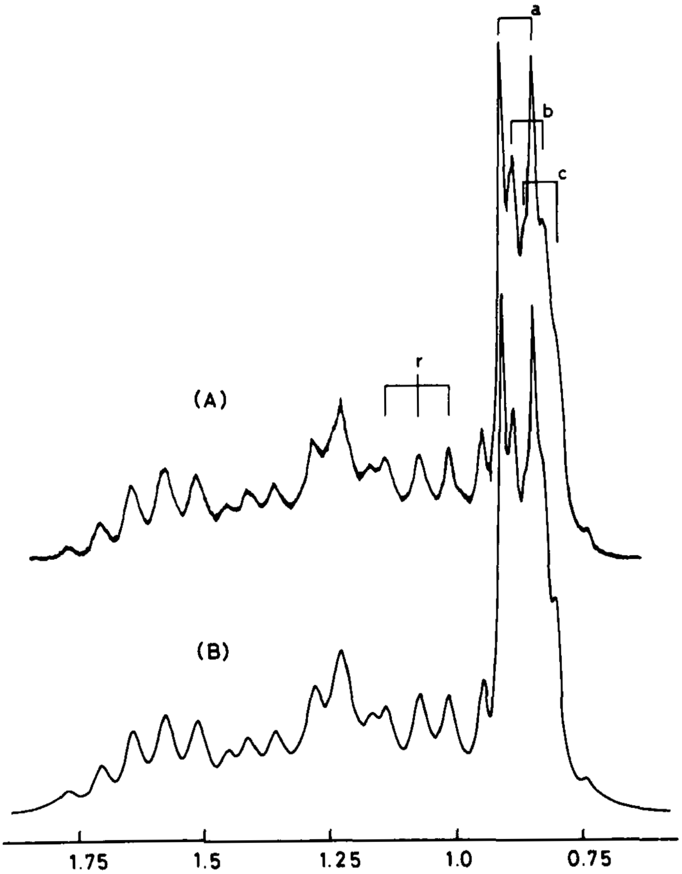


FIG. 6. Comparison of the observed (A) and the calculated (B) spectra of sample APP1.

where $S_a$, $S_b$, and $S_c$ are the peak areas of doublets due to the isotactic, heterotactic, and syndiotactic methyl proton resonances, respectively. $S_{syn}$ and $S_{anti}$ are the peak area of the syn- and anti-proton resonances, respectively.

The tactic dyad placements evaluated from the 100-MHz spectra are in good agreement with those obtained from the 220-MHz spectra, except for Samples APP2-ES and APP2-C7S. The tactic triads also agreed very closely with those obtained by the $^{13}C-(^1H)$ spectra (Table 2).

TABLE 2. The Tactic Dyad and Triad Placements of Polypropylene Samples

| | Dyad | | | Triad | | | Triad[c] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | i | s | i | I | H | S | I | H | S | 4(I)(S)/(H)$^2$ | $\left(CH_2\right)_2$ (mole %) |
| APP2 | 0.65 | 0.35 | 0.64 | 0.49 | 0.28 | 0.23 | 0.51 | 0.27 | 0.22 | 6.0 | 7.5 |
| APP2-ES | 0.56 | 0.44 | 0.52 | 0.33 | 0.37 | 0.30 | 0.34 | 0.38 | 0.28 | 2.6 | 12.8 |
| APP2-C7S | 0.89 | 0.11 | 0.86 | 0.81 | 0.11 | 0.08 | 0.79 | 0.13 | 0.08 | 15.5 | 10.1 |
| APP2-C7IS[a] | 0.97 | 0.03 | 0.97 | 0.95 | 0.04 | 0.01 | 0.95 | 0.04 | 0.01 | 23.8 | 2.8 |
| APP1 | 0.54 | 0.46 | 0.55 | 0.39 | 0.27 | 0.34 | 0.38 | 0.29 | 0.33 | 6.0 | 0 |

[a] A portion was insoluble in boiling n-heptane of Sample APP2.
[b] Obtained from the 220-MHz spectra.
[c] Obtained from the $^{13}C$–($^1H$) spectra.

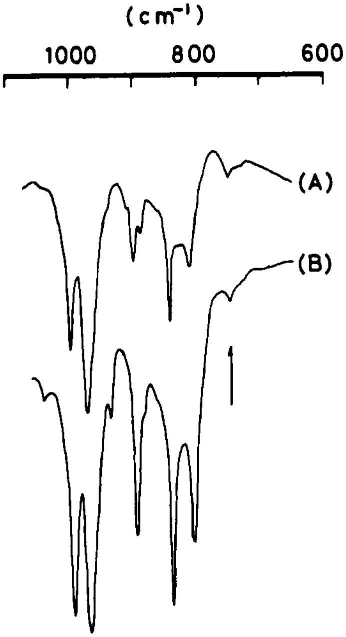


FIG. 7. The IR spectra of two polypropylenes: (A) sample APP2, (B) sample APP2-C7S.

In the case of Samples APP2-ES and APP2-C7S, the isotactic dyad placements are overestimated compared with the data obtained from the 220-MHz spectra. These disagreements were examined from the viewpoint of structural isomers. Figure 7 shows the IR spectra in the region of 700 to 1200 cm$^{-1}$ of polymer samples prepared with the Ti(O-n-Bu)$Cl_3$–$AlEt_2$ Cl catalyst system. The IR spectra of these samples show a band characteristic of absorption of $-(CH_2)_2-$ rocking vibration at 752 cm$^{-1}$. This means the presence of a tail-to-tail linkage of two propylene units. The amount of $-(CH_2)_2-$ group, determined by the method proposed by Bucci et al. [29], is the largest in Sample APP2-ES. The presence of the $-(CH_2)_2-$ group in all fractions seems to show that polymer prepared with this catalyst can generally contain this structurally irregular linkage of a tail-to-tail arrangement of two propylene units in the main chain. A few workers have reported that such a sequence occurs in the polymerization of propylene with vanadium catalyst systems [22-25]. The insertion processes of $\alpha$-olefine into vanadium-alkyl bond is considered to be:

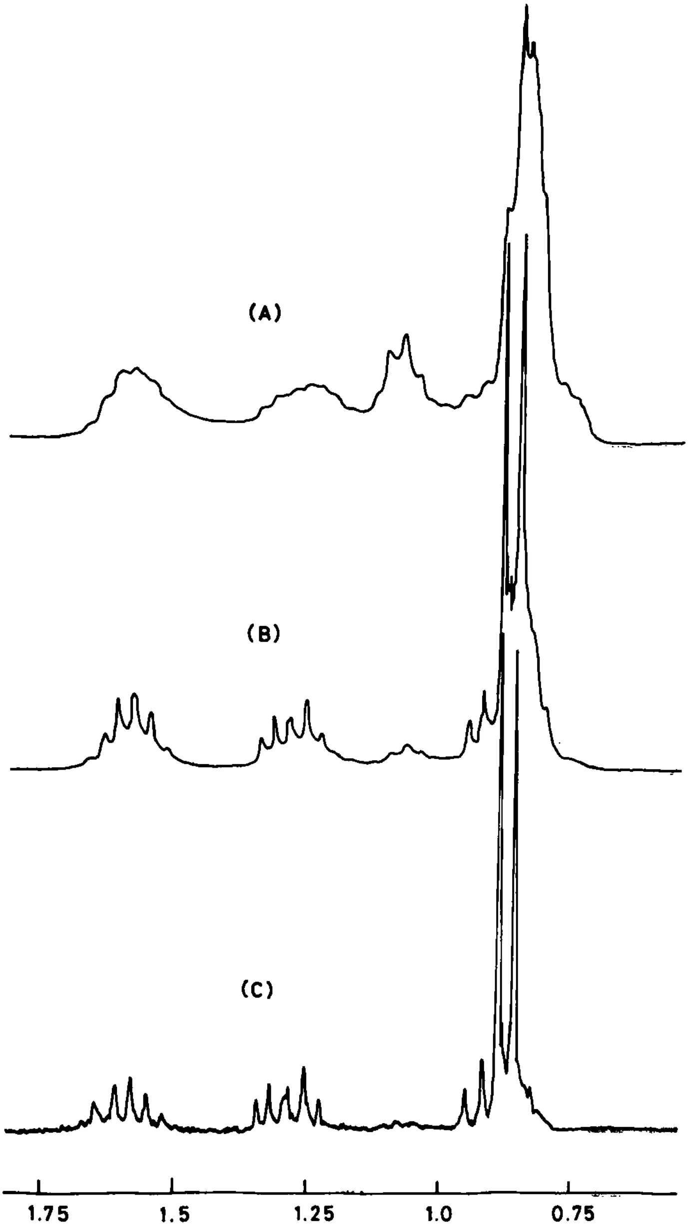
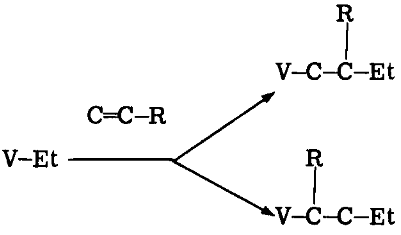


FIG. 8. The 220-MHz spectra of three polypropylenes; (A) sample APP2-ES, (B) sample APP2-C7S, (C) sample APP2-C7IS.



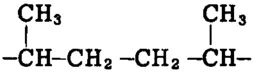
(I)

(II)

The vanadium ethyl bond prepared with $VCl_4$ and $AlEt_2Cl$ at -78°C is mainly metal alkyl (II), but with increasing polymerization temperature it is metal alkyl (I). It has also been suggested that the insertion process to give metal alkyl (I) breaks the syndiotactic sequences, resulting in the $-(CH_2)_2$ sequence [26, 27].

The above result suggests that the insertion of propylene into the Ti–C bond prepared with $Ti(O\text{-}n\text{-}Bu)Cl_3$–$AlEt_2Cl$ catalyst is similar to the vanadium catalytic systems.

The chemical shift of the methylene proton resonances in the


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

sequence is situated at a higher field than that of the methine proton resonance [26-28]. In the 220-MHz spectra the methine proton resonance gives high field tailing (Fig. 8). On the other hand, in the 100-MHz spectra the methylene proton resonances in the $-(CH_2)_2$ group are overlooked because the peaks due to the anti-proton overlap with the peaks of the anti-proton resonance. Therefore, from the above considerations, we overestimated the peak area of the anti-proton resonance. By analysis of the triads, it has become apparent that ether extract of polymer prepared with $TiCl_3$-$AlEt_2Cl$ catalyst has a stereoblock sequence character, while the stereoregularity of ether extract of polymer obtained by $Ti(O\text{-}n\text{-}Bu)Cl_3$–$AlEt_2Cl$ catalyst is completely random and the tactic sequence is very short. In addition, the triad data show clearly the inadequacy of Bernoullian statistics in describing the mechanism for stereochemical propagation; i.e., $4(I)(S)/(H)^2 > 1$.

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