Proton Magnetic Resonance Spectra of Polypropylene in Solution

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During recent years, high resolution nuclear magnetic resonance spectroscopy has been applied to the study of polymers. In some cases, however, the polymer is not fully soluble to the required concentration, so that a well-resolved spectrum can not be obtained. When we use this method, there are a few restrictions on both the polymer and the solvent. First of all, a polymer solution of an appropriate concentration, say at least five per cent or so, is necessary for a detailed analysis of the NMR spectrum. On the other hand, the resonance peaks due to the solvent itself should not disturb those of the polymer.

In the case of ordinary polypropylene, the molecular weight is so high that we can scarcely obtain a well-resolved spectrum even at elevated temperatures. We have applied, therefore, a " weak " controlled thermal degradation to polypropylene in order to reduce the molecular weight and increase the solubility. The thermal degradation employed was so weak that it did not give rise to any significant change in the infrared absorption spectrum of the sample. By making use of this technique, an attempt is made in this paper to measure the degree of stereoregularity of polypropylene. A further object of the work is to study a saturated polymer with small difference in chemical shift.

So far as we know, few investigations[1-3] using high resolution NMR spectrometers have been made of polypropylene. This probably arises from the complexity of the spectrum because of the small difference in chemical shift. Very recently, a spin decoupling technique has been successfully employed to observe the stereochemical configurations of the molecular chains of some polymers.[4,5] This technique, as well as the use of partially-deuterated polymers, will be an effective means to overcome the complexity of the spectrum.

Experimental

Several kinds of commercial polypropylene were used in this work. The limiting viscosity numbers of the original samples, [η], are shown in Table I.

TABLE I. LIMITING VISCOSITY NUMBER AND DENSITY OF ORIGINAL SAMPLE

Original sample	[η]*	Density
A	1.28	0.9126
B	1.71	0.9095
C-1	1.35	0.9080
C-2	1.52	

* Obtained at 135°C in tetraline.

For the sample, C-2 NMR measurements were carried out without any preliminary treatment. The other samples were first extracted with boiling *n*-heptane. The solvent had been renewed every three hours until no precipitate could be seen when it was poured into methanol. Then, the residue was separated by filtration and dried at 60°C in a vacuum. This was used as the sample termed " *n*-heptane-insoluble " in Table II. On the other hand, the extracted polymers were precipitated in a large amount of methanol; after filtration, they were dried in vacuo at 40°C. Then they were extracted with ether to give the *n*-heptane-extracted and the ether-soluble samples in the table. The acetone-extracted sample (sample 10) was obtained from an atactic polypropylene (C-3) by extraction with boiling acetone; again the residue was extracted with ether to prepare the ether-extracted sample (sample 2). The thermal degradation of the samples was carried out in vacuo. The conditions are shown in Table II. For samples 3, 5, 7 and 9 the processes of extraction were omitted and the thermal degradation technique immediately employed, while for samples 1, 2 and 10 only the former processes were employed. Finally, the other samples were obtained by thermal degradation of the residues remaining after the extraction with *n*-heptane.

All spectra were obtained with a Varian DP-60 spectrometer at about 140°C, except for the spectrum of the polypropene-1,1-d_2 sample. For this sample a nuclear magnetic resonance spectrometer, Mullard SL44 Mk. II, operating at 40 Mc/s was employed. Each 10% sample in *o*-dichlorobenzene was sealed in a glass tube together with a 0.2% antioxidant and 0.4% tetramethylsilane as internal standards. The peak positions were determined by using the sideband technique and were expressed by " the τ-scale."[6]

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[1] S. Sato, R. Chûjô, T. Ozeki and E. Nagai, *J. Polymer Sci.*, **62**, S 101 (1962).

[2] F. C. Stehling, paper presented at the Washington Meeting of the American Chemical Society, Washington, March, 1962.

[3] K. Nukada and S. Ônishi, paper presented at the Symposium on High Polymers, Nagoya, October, 1963.

[4] S. Satoh, R. Chûjô and E. Nagai, paper presented at the Meeting of the Physical Society of Japan, Fukuoka, October, 1963.

[5] F. A. Bovey, E. W. Anderson and D. C. Douglass, *J. Chem. Phys.*, **39**, 1199 (1963).

[6] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958); *J. Chem. Phys.*, **29**, 963 (1958).

TABLE II. PREPARATION AND PROPERTY OF EACH SAMPLE

Sample No.	Original sample	Preliminary treatment		Property	
		Extraction	Thermal degradation	[η]	Density
1	C-1	*n*-Heptane-extracted	—	0.85	0.9102
2	C-3*	Ether-extracted	—	0.82	0.9114
3	C-1	—	290°C, 3hr.	0.85	0.9102
4	C-1	*n*-Heptane-insoluble	280°C, 5hr.	0.82	0.9114
5	A	—	270°C, 0.5hr.	0.82	0.9125
6	A	*n*-Heptane-insoluble	290°C, 3hr.	0.87	0.9126
7	B	—	270°C, 3hr.	0.85	0.9132
8	B	*n*-Heptane-insoluble	300°C, 5hr.	0.81	0.9122
9	C-2	—	—	(1.52)	
10	C-3*	Acetone-extracted			

* An atactic polypropylene.

Results and Discussion

The Study of Each Spectrum.—Typical spectra are shown in Fig. 1, except for that of sample 1, from which we could not obtain well-resolved spectrum by any means.

Several points of interest have come to light during the course of the measurements. First, the spectrum of sample 10 is somewhat different from those of the others, and it doesn't change in the temperature range 23∼140°C. Contrary to our result, the corresponding spectrum given by Satoh et al.[1] (their sample 2) exhibits a prominent peak at 8.75 τ. This is probably due to the fact that their sample was polymerized by a Ziegler-type catalyst, while ours were not. That is, the peak at 8.75 τ may be ascribed to some *n*-paraffins or polyethylenes. This fact may be of interest, but it will not be gone into further here. Secondly, the difference between the spectrum of sample 2 and that of sample 8 has attracted our great interest. Especially, the remarkable change in the middle region of the spectra seems to suggest the possibility of the stereoregularity measurement of the polymer chains. According to Natta, the ether soluble sample consists of molecular chains with an atactic configuration. Therefore, the spectrum of sample 2 shown in Fig. 1 may be decomposed into two parts, one isotactic and one syndiotactic. On the other hand, the *n*-heptane-insoluble fraction contains mainly isotactic molecular chains. Therefore, the spectrum of sample 8 must be very similar to that of a purely isotactic polymer. This point will be discussed in detail later.

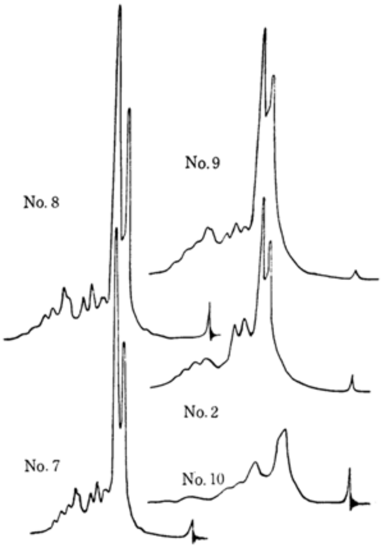

Fig. 1. NMR spectra of the samples shown in Table II.

The physical properties of each sample after the preliminary treatments are also given in Table II. A comparison of the spectra in Fig. 1 leads to the conclusion that the solubility of polypropylene roughly depends on the value of [η]. However, in the case of sample 9, a rather well-resolved spectrum was obtained regardless of the large value of [η]. This result is probably due to the fact that the sample consists of molecular chains with less isotactic configurations. As was mentioned in the previous section, the extraction procedure always preceded the thermal degradation when both were needed. In contrast, when the thermal degradation was carried out before the extraction, all the *n*-heptane-insoluble samples gave poorly-resolved spectra, though their final values of [η] were much the same as those of the samples shown in Table II. This implies that the extraction procedure depends on both the stereoregularity of the polymer chains and the molecular weight distribution. At the present stage, it seems difficult to foretell which thermal degradation

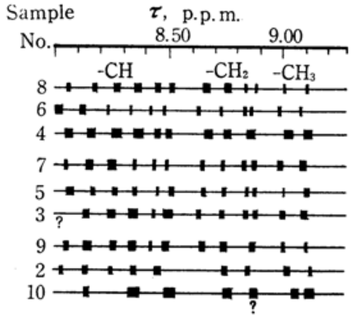

Fig. 2. Values of chemical shift for the samples given in Table II.

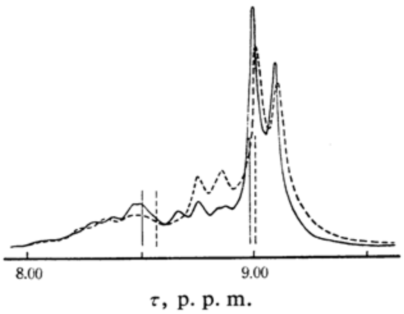

Fig. 3. Normalized spectra of isotactic and atactic polypropylenes. Vertical lines devide the whole area into three parts in the ratio of 1 : 2 : 3 from left to right.

—— Isotactic P. Pr.
- - - Atactic P. Pr.

condition is adequate to a certain polypropylene. In any case, however, the thermal degradation must be carried out as mildly as possible.

Figure 2 shows the values of the chemical shift for each sample. We can not find out any difference among the samples separated from various brands of polypropylene except for that between samples 2 and 10. The resonance peaks between 8.95 τ and 9.15 τ are ascribed to the methyl groups. It is found that the methyl resonance of atactic polypropylene shows a slight shift towards a higher magnetic field than that of isotactic polypropylene. Unfortunately, however, the shift is not large enough to be employed for the stereoregularity measurements. Very recently, this small shift has been independently confirmed more accurately by Nukada et al.³⁾

Normalized spectra of atactic and isotactic polypropylenes, i. e., samples 2 and 8, are shown in Fig. 3. Vertical solid and broken lines separate the whole area of each spectrum into three parts in the ratio of 1 : 2 : 3 from left to right. These three parts roughly correspond to the α-proton, methylene and methyl resonances respectively. As we have already pointed out, the central parts corresponding to the methylene resonance are markedly different from each other. Especially, the resonance region of the methylene groups in the isotactic part of the polymer chains seems to be much broader than that in the syndiotactic part. We can not observe any noticeable change in any α-proton resonance region.

Now, let us assume that the ideal spectrum of either isotactic or syndiotactic polypropylene is available, and that the stereochemical configuration of the polymer chain is homogeneous; all the observed spectra can then be separated straightforwardly into isotactic and syndiotactic components, so that the degree of stereoregularity of each sample may be determined. The homogeneity of the configuration will be realized to a considerable extent by the extraction of the sample with a suitable solvent. Thus, not only the preparation of an absolutely isotactic polymer but also a theoretical approach to the ideal spectrum is a matter of importance for the measurement of stereoregularity. It is known that isotactic polypropylene can be easily obtained as the residue of extraction with *n*-heptane from the commercial sample, whereas it is rather difficult to obtain syndiotactic polypropylene. However, even the former will not give the ideal spectrum in the strict sense. We believe that the analysis of spectra is the shortest way at present to obtain the ideal spectrum.

For the sake of convenience, we have introduced the following value, X, as a measure of the stereoregularity of the polymer chain :⁷⁾

$$X=\frac{\begin{pmatrix}\text{Relative intensity of}\\ \text{the peak at } 8.87\,\tau\end{pmatrix}}{\begin{pmatrix}\text{Average relative intensity of}\\ \text{the peaks at } 9.0\,\tau \text{ and } 9.1\,\tau\end{pmatrix}}$$

At first, we used apparent peak heights instead of the peak areas to evaluate the X-value; we found that the X-value varies from 0.15 to 0.50 in accordance with the stereochemical configuration of the polymer chain. On such occasions, however, not the peak height but the peak area should be used if possible. Therefore, our next problem was to separate each peak in order to measure the relative area. In case the spectrum is not so well resolved, it is very important to have some knowledge concerning the relative intensities of the peaks as well as the peak positions of the ideal spectrum. Therefore, we shall try to calculate the theoretical spectra due to the methylene groups of polypropylene.

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7) Y. Kato and A. Nishioka, paper presented at the 3rd Symposium on Nuclear Magnetic Resonance Spectroscopy, Osaka, November, 1963.

ABC_2 and A_2B_2 Spectra. — In some vinyl polymers, the "backbone" methylene protons will approximately give rise to the NMR spectra of the ABC_2 (or A_2B_2) system in the notation of Bernstein et al.[8] Let us assume that the electron-coupled spin-spin nuclear magnetic interaction between any two hydrogen nuclei can be disregared if more than two carbon-carbon bonds separate the nuclei. For the sake of simplicity, we will consider first a molecular chain with a planar zigzag conformation. Then, together with the neighboring α-protons, the metylene protons in the isotactic part can be regarded as an ABC_2 spin system, where the α-protons refer to C_2, while in the syndiotactic part they all together constitute a A_2B_2 spin system, where the methylene protons refer to A_2. This is the case with polypropylene if the spin-spin coupling constants between the methylene and the methyl protons are very small. For isotactic polypropylene the individual polymer molecules assume "gauche" rather than "trans" configurations and are, therefore, frozen in helical conformations, that is, the three-monomers one-turn helix. If the helical conformation is preserved even in the solution, the methylene resonance would be expected to give an A_2B_2 spectrum, contrary to the case of a planar zigzag conformation.

The basic functions and the complete matrix for the A_2B_2 spin system have been given by Pople et al.[9] In this system there are two electronic screening constants, σ_A and σ_B, together with four different spin coupling constants, J_{AA}, J_{AB}, J'_{AB}, J_{BB}. The chemical shift difference, δ_{AB}, is given by $\sigma_A - \sigma_B$.

By evaluation of the matrix elements one finds that the secular determinant factors into one 4×4, five 2×2, and two 1×1 submatrices. A total of twenty-eight transitions have to be considered in this case.

Next, the complete set of wave functions and all the elements of the matrix of the spin Hamiltonian for the ABC_2 system have been written by Cohen et al.[10] However, their analysis has been applied only to the ABX_2 case, where the resonance of the nucleus C is well removed from those of the A and B nuclei. In general, the ABC_2 spin system involves seven different constants, σ_A, σ_B and σ_C, and J_1, J_2, J_3 and J_4. However, because of disregarding all the spin-spin coupling constants between any two α-protons, the parameter J_4 vanishes in the present case, as is shown in Fig. 4.

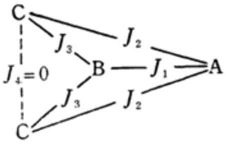

Fig. 4. Spin-spin coupling constants for the ABC_2 case, where $J_4=0$.

For this case the Hamiltonian operator is:

$$\mathscr{H} = \mathscr{H}^{(0)} + \mathscr{H}^{(1)} \tag{1}$$

Where:

$$\mathscr{H}^{(0)} = -\nu_A I_Z(A) - \nu_B I_Z(B) - \nu_C\{I_Z(C_1) + I_Z(C_2)\} \tag{2}$$

$$\mathscr{H}^{(1)} = J_1\boldsymbol{I}(A)\cdot\boldsymbol{I}(B) + J_2\boldsymbol{I}(A)\cdot\boldsymbol{I}(C_1) + J_2\boldsymbol{I}(A)\cdot\boldsymbol{I}(C_2) + J_3\boldsymbol{I}(B)\cdot\boldsymbol{I}(C_1) + J_3\boldsymbol{I}(B)\cdot\boldsymbol{I}(C_2) \tag{3}$$

where:

$\nu_i = \eta H_0(1-\sigma_i)$

H_0 is the external magnetic field,

η is a constant which converts magnetic units to energy units in cycles per second (c/s),

$\boldsymbol{I}$ is the nuclear spin vector, and

I_z is the Z component of the vector $\boldsymbol{I}$.

Adopting the notation of Pople et al.,[9] the complete set of basic functions and the matrix elements of the spin Hamiltonian is given in Table III. The diagonalization of the Hamiltonian involves the solution of one 4×4 matrix and two 3×3 matrices. In such a case, the numerical method must be used. In addition, the trial-and-error fitting procedure is so tedious that all the calculations were carried out with a digital computer, Musashino-1-β. Therefore, Tables III, IV and V are arranged so as to draw up a program for the electronic digital computer immediately. Table V lists both the resonance frequencies and the relative peak intensities; transitions are allowed only between the eigenfunctions of the same symmetry and with total spins differing by 1 from each other. Accordingly, thirty-four transitions in all are allowed in the ABC_2 case. Following Bernstein et al.,[8] each transition may be labeled as an A, B or C transition according to the change in spin, giving rise to the resonance line when the chemical shifts are much greater than the spin-spin coupling constants. When all the species of nuclei change their spin simultaneously, the line is labeled as a combination line.

Calculated Spectra.—The spectrum of syndiotactic polypropylene has been calculated by

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[8] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, 35, 65 (1957).

[9] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y. (1959), p. 138.

[10] A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.*, A252, 488 (1959).

TABLE III. BASIC FUNCTIONS AND COMPLETE MATRIX ELEMENTS OF THE HAMILTONIAN FOR ABC_2 SPIN SYSTEM*

i	Function Ψ_i	Diagonal element						Off-diagonal element	
		$\nu_1/2$	$\nu_2/2$	ν_3	$J_1/4$	$J_2/2$	$J_3/2$		
0	$\alpha\alpha\alpha\alpha$	+	+	+	+	+	+	$H_{1,2}$	$=J_2/\sqrt{2}$
1	$(1/\sqrt{2})\alpha\alpha(\alpha\beta+\beta\alpha)$	+	+		+			$H_{4,6}$	
2	$\beta\alpha\alpha\alpha$	−	+	+	−	−	+	$H_{5,7}$	
3	$\alpha\beta\alpha\alpha$	+	−	+	−	+	−	$H_{8,10}$	
4	$\alpha\alpha\beta\beta$	+	+	−	+	−	−	$H_{1,3}$	$=J_3/\sqrt{2}$
5	$(1/\sqrt{2})\alpha\beta(\alpha\beta+\beta\alpha)$	+	−		−			$H_{4,5}$	
6	$(1/\sqrt{2})\beta\alpha(\alpha\beta+\beta\alpha)$	−	+		−			$H_{6,7}$	
7	$\beta\beta\alpha\alpha$	−	−	+	+	−	−	$H_{9,10}$	
8	$\alpha\beta\beta\beta$	+	−	−	−	−	+		
9	$\beta\alpha\beta\beta$	−	+	−	−	+	−	$H_{2,3}$	$=J_1/2$
10	$(1/\sqrt{2})\beta\beta(\alpha\beta+\beta\alpha)$	−	−		+			$H_{5,6}$	
11	$\beta\beta\beta\beta$	−	−	−	+	+	+	$H_{13,14}$	
12	$(1/\sqrt{2})\alpha\alpha(\alpha\beta-\beta\alpha)$	+	+		+			$H_{8,9}$	
13	$(1/\sqrt{2})\alpha\beta(\alpha\beta-\beta\alpha)$	+	−		−				
14	$(1/\sqrt{2})\beta\alpha(\alpha\beta-\beta\alpha)$	−	+		−			$H_{4,7}=0$,	
15	$(1/\sqrt{2})\beta\beta(\alpha\beta-\beta\alpha)$	−	−		+			$(\Psi_m\|H\|\Psi_n)\equiv H_{m,n}$.	

* Spin-spin coupling constant J_4 has been omitted (see text).

TABLE IV. EIGENVALUES AND EIGENFUNCTIONS FOR THE ABC_2 SPIN SYSTEM

Eigenvalue	Symmetry of wave function and total spin	Eigenfunction
E_0	S_2	$a_{0,0}\Psi_0$
E_1	S_1	$a_{1,1}\Psi_1+a_{1,2}\Psi_2+a_{1,3}\Psi_3$
E_2		$a_{2,1}\Psi_1+a_{2,2}\Psi_2+a_{2,3}\Psi_3$
E_3		$a_{3,1}\Psi_1+a_{3,2}\Psi_2+a_{3,3}\Psi_3$
E_4	S_0	$a_{4,4}\Psi_4+a_{4,5}\Psi_5+a_{4,6}\Psi_6+a_{4,7}\Psi_7$
E_5		$a_{5,4}\Psi_4+a_{5,5}\Psi_5+a_{5,6}\Psi_6+a_{5,7}\Psi_7$
E_6		$a_{6,4}\Psi_4+a_{6,5}\Psi_5+a_{6,6}\Psi_6+a_{6,7}\Psi_7$
E_7		$a_{7,4}\Psi_4+a_{7,5}\Psi_5+a_{7,6}\Psi_6+a_{7,7}\Psi_7$
E_8	S_{-1}	$a_{8,8}\Psi_8+a_{8,9}\Psi_9+a_{8,10}\Psi_{10}$
E_9		$a_{9,8}\Psi_8+a_{9,9}\Psi_9+a_{9,10}\Psi_{10}$
E_{10}		$a_{10,8}\Psi_8+a_{10,9}\Psi_9+a_{10,10}\Psi_{10}$
E_{11}	S_{-2}	$a_{11,11}\Psi_{11}$
E_{12}	a_1	$a_{12,12}\Psi_{12}$
E_{13}	a_0	$a_{13,13}\Psi_{13}+a_{13,14}\Psi_{14}$
E_{14}		$a_{14,13}\Psi_{13}+a_{14,14}\Psi_{14}$
E_{15}	a_{-1}	$a_{15,15}\Psi_{15}$

Satoh et al.[1] In this work we will calculate the spectrum due to methylene protons present mainly in the isotactic part of the polymer chains. However, it is assumed that the spectra can be analyzed in terms of the ABC_2 spin system.

Fortunately, while this calculation was being carried out, it was kindly pointed out to the authors by Mr. Yoshihito Komatsu that the NMR spectra of polypropene-2-d_1 and polypropene-2, 3, 3, 3,-d_4 had been examined by Stehling.[2] According to the results, the spectra of polypropene-2-d_1 samples are quite analogous to those of polypropene-2, 3, 3, 3-d_4 samples, except that an additional peak due to the methyl protons can be observed. Though the methyl groups in the isotactic part of the polymer chains are not equivalent to those in the syndiotactic part, both of them give rise to the same unresolved resonance peak. This probably proves that the spin-spin coupling constant between methylene and methyl protons of polypropylene is fairly small. Therefore, we can neglect it as an approximation to reduce the complicated spectrum due to the methylene protons to the ABC_2 or A_2B_2 case.

By means of an electronic computer, attempts were made to find some sets of the chemical shifts and the spin-spin coupling constants which fit the frequencies of the observed lines. In practice, three resonance peaks at 8.65 τ, 8.75 τ and 8.87 τ were used in order to judge whether or not the set of δ and J parameters fits the resonance frequencies of the observed

TABLE V. ALLOWED TRANSITIONS FOR THE ABC_2 SPIN SYSTEM

Transition	Frequency $\nu=\Delta E/h$.	Relative intensity	Nucleus
1	E_1-E_0	$[(\sqrt{2}a_{1,1}+a_{2,1}+a_{3,1})a_{0,0}]^2$	A
2	E_2	etc.	B
3	E_3		C
4	E_4-E_1	$[a_{1,1}(\sqrt{2}a_{4,4}+a_{5,4}+a_{6,4})$ $+a_{2,1}(\sqrt{2}a_{6,4}+a_{7,4})$ $+a_{3,1}(\sqrt{2}a_{5,4}+a_{7,4})]_2$	C
5	E_5	etc.	B
6	E_6		A
7	E_7		comb.
8	E_4-E_2		comb.
9	E_5		comb.
10	E_6		C
11	E_7		B
12	E_4-E_3		comb.
13	E_5		C
14	E_6		comb.
15	E_7		A
16	E_8-E_4	$[a_{4,4}(a_{8,8}+a_{9,8})$ $+a_{5,4}(\sqrt{2}a_{8,8}+a_{10,8})$ $+a_{6,4}(\sqrt{2}a_{9,8}+a_{10,8})$ $+\sqrt{2}a_{7,4}\cdot a_{10,8}]^2$	B
17	E_9	etc.	A
18	E_{10}		comb.
19	E_8-E_5		C
20	E_9		comb.
21	E_{10}		A
22	E_8-E_6		comb.
23	E_9		C
24	E_{10}		B
25	E_8-E_7		comb.
26	E_9		comb.
27	E_{10}		C
28	$E_{11}-E_8$	$[a_{11,11}(a_{8,8}+a_{9,8}+\sqrt{2}a_{10,8})]^2$	A
29	$E_{11}-E_9$	etc.	B
30	$E_{11}-E_{10}$		C
31	$E_{13}-E_{12}$	$[a_{12,12}(a_{13,13}+a_{14,13})]^2$	B
32	E_{14}	etc.	A
33	$E_{15}-E_{13}$	$[a_{15,15}(a_{13,13}+a_{14,13})]^2$	A
34	$E_{15}-E_{14}$	etc.	B

peaks. In the judgment a tolerence of ±2 c/s was taken into account. We assumed in the first place that $\nu_A-\nu_C=40.5$ c/s, and that $\nu_B-\nu_C=13.5$ c/s, and we tried to obtain some sets of the other parameters which approximately fit the resonance positions. From the study of a series of acetylated sugars, it has been established by Lemieux et al.[11] that the spin-spin coupling constant for a pair of axial hydrogens on adjacent carbon atoms is in the 5~8 c/s range, that that for pairs of equatorial hydrogens is 3~4 c/s, and that that for axial and equatorial hydrogens is 2~3 c/s. Therefore, the parameters J_2 and J_3 were chosen within the range from −10 to +10 c/s. Since the simultaneous change of all signs of the spin-spin coupling constants does not affect the spectrum, the sign of J_1 was arbitrarily chosen as positive in each case. The absolute value of J_1 was varied progressively by 0.5 c/s within the 12~14 c/s.

The parameter J_1 was taken to be +13.5 c/s. The applicability of this value has also been confirmed by the spectra of polypropene-

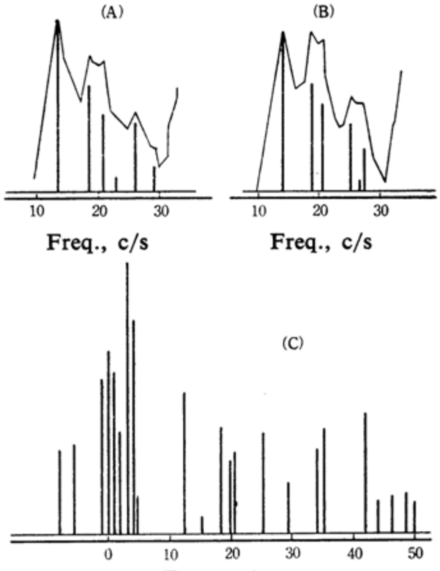

Fig. 5. ABC_2 spectra calculated with the sets of parameters; $\nu_A-\nu_C=40.5$ c/s, $\nu_B-\nu_C=13.5$ c/s, $J_1=13.5$ c/s and (A) $J_2=2.0$ c/s, $J_3=-7.0$ c/s; (B) $J_2=-3.0$ c/s, $J_3=-6.0$ c/s and (C) $J_2=-7.0$ c/s, $J_3=8.0$ c/s.

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[11] R. V. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 2237 (1958).

2, 3, 3, 3-d_4 obtained by Stehling. The two non-equivalent methylene protons give a typical spectrum of the AB system, and the value of J observed from the spectrum has been reported to be about 13.2 c/s.[2]

For all the sets of parameters which fit the observed line positions, we calculated the peak intensities in order to compare them with the observed resonance peaks. It was found that only three sets fit the observed peaks moderately well. They are shown in Fig. 5. From the appearance of the above-mentioned three resonance peaks, especially that of the central one, we may conclude that the best fit at this stage is this set of parameters:

$$\nu_A - \nu_C = 40.5 \text{ c/s}$$
$$\nu_B - \nu_C = 13.5 \text{ c/s}$$
$$J_1 = 13.5 \text{ c/s}$$
$$J_2 = -7.0 \text{ c/s}$$
$$J_3 = 8.0 \text{ c/s}$$

Furthermore, the electronic computer was used to revise the set of parameters so as to find a best fit. The revised parameters were:

$$\nu_A - \nu_C = 39.0 \text{ c/s}$$
$$\nu_B - \nu_C = 14.0 \text{ c/s}$$
$$J_1 = 13.5 \text{ c/s}$$
$$J_2 = -6.0 \text{ c/s}$$
$$J_3 = 7.5 \text{ c/s}$$

From these values it may be concluded that the conformation of isotactic polypropylene in solution is somewhat different from that of the solid, that is, the helical conformation.

Further revision seems to be of little avail so long as we consider only the above-mentioned three peaks, because they are rather poorly resolved. Therefore, the information concerning the positions and intensities involves a slight ambiguity. The calculated spectrum for this set of parameters is illustrated in Fig. 6, where each resonance line in the central part has been replaced by an isosceles triangle with the same height as the line and a 4 c/s half-height peak width. By synthesizing the triangles, the theoretical spectrum for the methylene protons can be obtained. It should be noticed that resonance region of the methylene protons contained in isotactic polypropylene is very wide. Accordingly, great care must be taken in the analysis of the spectrum.

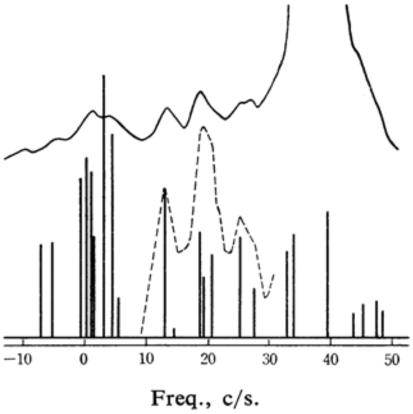

Fig. 6. Comparison between the experimental and the theoretical spectra of polypropylene. The parameters of the calculated spectrum are $\nu_A - \nu_C = 39.0$ c/s, $\nu_B - \nu_C = 14.0$ c/s, $J_1 = 13.5$ c/s, $J_2 = -6.0$ c/s and $J_3 = 7.5$ c/s.

The Analysis of Observed Spectra. — In the preceding section, the theoretical spectrum of methylene protons in isotactic polypropylene was obtained. When the total intensity (or area) of the spectrum is normalized to unity, the relative intensities of the three resonance peaks at 8.65 τ, 8.75 τ and 8.87 τ are 0.0426, 0.0733 and 0.0437 respectively. For the sake of convenience, let us denote these three resonance peaks as A-, B- and C-peaks respectively. Both the B- and C-peaks contain more than two calculated resonance lines, whereas the A-peak has only one effective peak. Each one of the resonance lines contained in B- and C-peaks can be assigned as a combination line. This information is very important for decomposing each peak in the observed spectra as a means of measuring the degree of stereoregularity of the polymer chain.

As has already been explained, syndiotactic polypropylene gives rise to the resonance peaks due to the methylene groups, which can be interpreted in terms of a A_2B_2 spin system. Therefore, with the following constants:

$$\delta_{AB} = 27.0 \text{ c/s}$$
$$J_{AA} = 13.5 \text{ c/s}$$
$$J_{AB} = 8.0 \text{ c/s}$$
$$J'_{AB} = 6.0 \text{ c/s}$$
$$J_{BB} = 0 \text{ c/s}$$

the spectrum of the methylene protons has been calculated. The result is shown in Fig. 7. In this case, however, the observed spectrum is very simple, as one can easily imagine from the spectrum of atactic polypropylene (sample 2). Hence, only two very similar resonance peaks due to the methylene protons will be available for revising the set of parameters. Therefore, there remain some ambiguities in the theoretical spectrum of syndiotactic polypropylene. However, it is a striking feature of the spectrum that no resonance peak can be observed in the vicinity of 8.65 τ. On this basis the degree

TABLE VI. ANALYSIS OF OBSERVED SPECTRA[a)]

Sample No.	Obsered peak intensity		Isotactic component			Estimated syndiotactic fraction at B and C peaks
	A	B+C	x[b)]	x'[c)]	x''[d)]	
2	0.020_9	0.22_0	0.49	0.46	0.38	0.31
5	0.036_4	0.13_4	0.85	0.91	0.90	0.21
7	0.038_0	0.12_6	0.89	0.96	0.95	0.18
8	0.040_2	0.12_4	0.94	0.97	0.96	0.19

a) The whole area is normalized.
b) Calculated from the fraction of A-peak.
c) Based on the assumption that the (B+C) fraction of the ideal spectrum of syndiotactic polypropylene equals 0.30_7.
d) Based on the spectrum shown in Fig. 7.

of stereoregularity of any given sample can be estimated if an well-resolved NMR spectrum is available. From the fraction of the A-peak in each spectrum, we calculated the proportion of the isotactic component, x, for the several samples given in Table II. Then, by using the sum of the fractions of the B- and C-peaks, the proportion of the syndiotactic component at the peak positions was estimated. The results are given in Table VI. The resolution of the spectrum of sample 9 was so poor that the estimation was not made. The values of x calculated above probably include some errors because it is difficult to separate a small A-peak. Therefore, we assumed that the fraction of the syndiotactic component at the B- and C-peak positions equals 0.30_7, which can be obtained from the results concerning sample 2 in Table VI. Then we calculated again the proportion of the isotactic component, x'. The results are listed in the next column of x in Table VI.

Finally, the spectrum of polypropene-1, 1-d$_2$ was obtained at 40 Mc/s. The results shown in Fig. 8 show a poorly-resolved spectrum because of the high molecular weight of the sample. However, a set of parameters:

$$\delta_{AB}=27.0\ \mathrm{c/s}$$
$$J_{AB}=6.0\ \mathrm{c/s}$$

for the AB$_3$ spin system fits the contour of the observed spectrum very well. Converting these parameters to the case of 60 Mc/s, it seems obvious that no overlap will be observed between the α-proton resonances of polypropylene and the methylene proton ones, except for the $8.40\sim8.55\ \tau$ region.

From Figs. 5, 6 and 7 the theoretical X-value for isotactic polypropylene has been found to be $X_I=0.13_7$, and that for syndiotactic polypropylene, $X_s=0.55$.

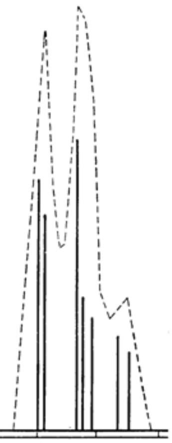

Fig. 7. The A$_2$ part of A$_2$B$_2$ type spectra with the parameters: $\delta_{AB}=27.0$ c/s, $J_{AB}=6.0$ c/s and $J'_{AB}=8.0$ c/s.

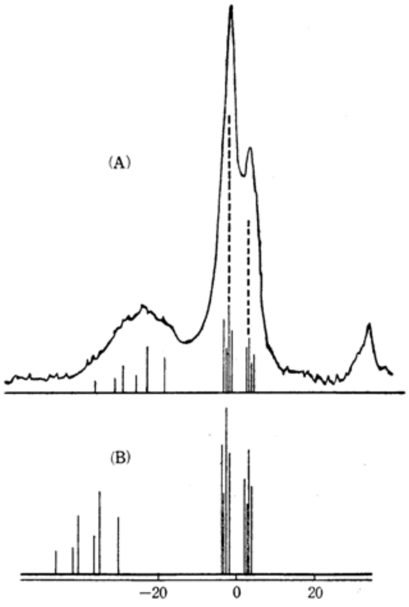

Fig. 8. NMR spectrum of polypropene-1, 1-d$_2$ obtained at 40 Mc/s (A), together with the theoretical analysis at 60 Mc/s (B). The dotted line means the sum of each group of resonance lines.

As a conclusion, if an well-resolved NMR spectrum of a given polypropylene sample is available, the proportion of the isotactic part (x') can be evaluated by measuring only the fraction of the area of the B- and C-peaks (F_1). The formula for the evaluation is:

$$x'=\frac{0.307-F_1}{0.190}$$

If the value of x' is close to unity, the following formula:

$$x'=\frac{F_0}{0.0426}$$

which is based entirely upon the theoretical spectrum of isotactic polypropylene, may be used, where F_0 means the fraction of the area of the A-peak.

In the near future the better resolution of individual resonance peaks will permit a more precise analysis of the stereoregularity of polypropylene.

Summary

The application of the NMR method to the study of commercial polypropylene seems to be restricted by some difficulties. A weak thermal degradation technique has therefore been employed to reduce the molecular weight of the polypropylene sample. However, the correspondence between the resultant molecular weight and the resolution of the spectrum is not always unique.

A remarkable difference between the NMR spectrum of isotactic polypropylene and that of atactic polypropylene can be found in the methylene resonance region. As an approximation, one may assume that the methylene groups of isotactic polypropylene give rise to the partial spectrum of an ABC_2 spin system, whereas those of syndiotactic polypropylene give rise to the partial spectrum of an A_2B_2 spin system. By means of an electronic computer, the best set of the δ and J parameters for the methylene resonance of isotactic polypropylene has been obtained. The results fit the observed spectrum fairly well. Using this information, the degree of stereoregularity (isotaxy) of a given polypropylene can be calculated. This method is applicable if an well-resolved NMR spectrum is available.

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