Carbon-13 Magnetic Resonance Spectra of Some Polypropylenes and Ethylene–Propylene Copolymers[1]

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ABSTRACT: The natural-abundance ^{13}C magnetic resonance spectra of isotactic, syndiotactic, and atactic polypropylenes and ethylene–propylene copolymers have been determined at 15.08 MHz. The chemical shifts of the carbons of the polymers have been compared with calculated values. The microtacticity of the polymers is discussed in terms of their ^{13}C spectra.

Proton magnetic resonance (pmr) spectroscopy has become increasingly important in structural studies of synthetic polymers in recent years.[2] Frequently, however, lack of resolution or overlap of resonance peaks makes the proton resonance spectra less useful than might be hoped. The information available from carbon-13 magnetic resonance (cmr) spectra is therefore expected to be an extremely useful adjunct to the proton spectra. Indeed, because the normal range of ^{13}C chemical shifts is so large (200 ppm compared to 10 ppm for protons), cmr spectroscopy is, in fact, uniquely well suited for the study of polymers. Johnson, Heatley, and Bovey[3] have reported cmr spectra for several important synthetic polymers, including isotactic and atactic polypropylene, and their results confirm the potential of cmr spectroscopy as a means of examining polymer structures.

We report here chemical shifts for the carbons of a number of relatively low-molecular-weight polypropylenes and propylene copolymers. The stereochemistry of these particular polymers has been previously determined by pmr and infrared spectroscopy.[4]

Polypropylene molecules may be defined as isotactic, syndiotactic, or atactic, depending upon whether the stereochemistry of the methine carbons is repeating (*mmmmmm*),[5] alternating (*rrrrrr*),[5] or random or nearly random (*mmrmrr*),[5] respectively. Polypropylenes, as well as copolymers of propylene with 10–20% ethylene, of each of these types have been studied in the present investigation.

Experimental Section

The samples of isotactic polypropylene were obtained by successive extractions with boiling *n*-pentane (less stereoregular sample **1a**) and with boiling *n*-hexane (more stereoregular sample) of the same crude polymer prepared in the presence of the catalyst system $TiCl_3HRA–Al(C_2H_5)_2I$ in *n*-heptane at 15° in the presence of H_2 to decrease the molecular weight.[6] The sample of syndiotactic polypropylene (**1b**) was prepared in the presence of the catalyst system $VCl_4–Al(C_2H_5)_2Cl$–anisole in *n*-heptane at −78°.[7] The amorphous sample (**1c**) was prepared in the presence of the catalyst system $VCl_4–Al(C_2H_5)_3$ in *n*-heptane at −78°.[8] Hydrogen was added to reduce the molecular weight.

The copolymers were prepared in an analogous way with the catalyst systems $TiCl_3HRA–Al(C_2H_5)_2I$ in *n*-heptane at 15° (sample **2a**), $VCl_4–Al(C_2H_5)_2Cl$–anisole in *n*-heptane at −78° (sample **2b**), and $VCl_4–Al(C_2H_5)_3$ in *n*-heptane (sample **2c**).[8] In all cases hydrogen was added to reduce the molecular weights.

The spectra were taken with the DFS spectrometer previously described[9] at 15.08 MHz with complete proton decoupling.[10] Benzene and chloroform were used as solvents as well as internal references for measuring chemical shifts. Samples used to obtain the spectra were saturated or nearly saturated solutions of the polymers in these solvents near their boiling points. At the probe temperature (~35–40°), some of the samples were quite viscous. Despite this, relatively sharp resonance lines (~2–5 Hz at half-height) were obtained for all spectra. From 30 to 100 scans were required for the polypropylenes and 100–500 scans for the copolymers.

Results and Discussion

Polypropylenes. Chemical shifts for polypropylene (without regard to stereoregularity) may be calculated using the empirical formula for hydrocarbon ^{13}C chemical shifts given by Grant and Paul.[3,11] This calculation ignores the steric interactions unique to each of the three types of polypropylenes which are imposed by restriction of rotation. However, as shown in Table I and Figure 1, the calculated values are in quite good agreement with the relative positions of the resonance peaks in the experimental spectra.

The line shapes for the methylene and methyl carbon resonance peaks are independent of the exact decoupler frequency (with noise decoupling) over a considerable range of frequencies. Therefore, the broadened appearance of these peaks is not the result of incomplete decoupling. Two samples of isotactic polypropylene **1a** were studied, one with high stereoregularity and low solubility and another (shown in Figure 1) with lower stereoregularity and higher solubility. In agreement with the earlier studies,[3] only the three major peaks were observed for the former, confirming its high degree of stereoregularity. The additional peaks seen in Figure 1

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(1) Supported by the National Science Foundation.

(2) For an excellent review of the literature in this area through 1968, see J. C. Woodbrey in "The Stereochemistry of Macromolecules," Vol. 3, A. D. Ketley, Ed., Marcel Dekker, New York, N. Y., 1968, Chapter 2.

(3) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).

(4) (a) E. Lombardi, A. L. Segre, A. Zambelli, A. Marinangeli, and G. Natta, *J. Polym. Sci., Part C*, **No. 16**, 2539 (1967); (b) A. Zambelli, G. Natta, and I. Pasquon, *ibid., Part C*, **No. 4**, 411 (1963).

(5) The stereochemical notation used here is that proposed by H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).

(6) (a) G. Natta, I. Pasquon, A. Zambelli, and G. Natti, *Makromol. Chem.*, **70**, 191 (1964); (b) G. Natta, H. Mazzanti, P. Longi, and F. Bernardini, *Chim. Ind. (Milan)*, **41**, 419 (1959).

(7) A. Zambelli, I. Pasquon, R. Signorini, and G. Natta, *Makromol. Chem.*, **112**, 160 (1968).

(8) A. Zambelli, G. Natta, I. Pasquon, and R. Signorini, *J. Polym. Sci., Part C*, **No. 16**, 2485 (1967).

(9) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967).

(10) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **60**, 1152 (1968).

(11) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

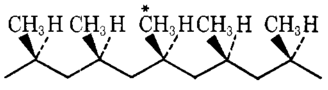
TABLE I
CHEMICAL SHIFTS OF THE POLYPROPYLENES[a]

Carbon	Calcd	Exptl[b] 1a	1b	1c
CH_2–	148.9	146.6 147.5[c]	146.5[c] 147.3	145.5–148.8
CH–	166.5	165.2[c] 165.5	165.5[c]	165.5
CH_3	172.9	171.7[c] 172.0 172.7 173.2	172.7 173.2[c]	171.6 172.0 172.5 172.7 173.2 173.4

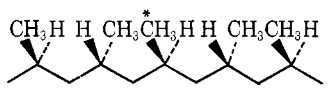
[a] All chemical shifts are in parts per million upfield from CS_2 (calculated assuming δ_{CS_2} for benzene equal to 65.0 ppm). [b] These values are in agreement with those obtained by Johnson, Heatley, and Bovey (ref 3) for similar polypropylenes. [c] Major peak.

for the second sample clearly indicate that the stereoregularity of the polymer is less than 100%. The stereoregularity of the syndiotactic polypropylene **1b** shown in Figure 1B is also less than 100%, but apparently is quite high.

In the spectrum of atactic polymer, it is of significance that *at least* six different methyl peaks may be distinguished. This means that the resonance position of a methyl carbon in polypropylene is influenced by next-nearest as well as nearest neighbor methyls.[12] If this is the case, ten different methyl carbon resonances are possible. The fact that only six are observable may be the result of a lack of resolution or coincidentally similar chemical shifts of some of the methyl carbons. Thus, it appears that cmr provides the first real ability for distinguishing polypropylene pentads[13] by nmr methods.[3,14] Unfortunately, it is not possible on the basis of the present data to make specific assignments for individual pentads except for those exhibited in the spectra of the syndiotactic and isotactic polymers. In the spectrum of **1a** at least three additional methyl carbon peaks corresponding to three different pentads are observed. Deviations from stereoregularity in isotactic polypropylene may be of the type . . .*mmmrrmmm*. . . (yielding a total of four different pentads), or of the type . . .*mmmrmmm*. . . (yielding only three different pentads). The present evidence indicates, then, that the deviations from steric regularity in isotactic polypropylene **1a** are either of the first type or of both types with some overlap of peaks. It seems to rule out the second type as the sole deviation.



1a, $\delta_{CS_2}{}^{*} = 171.7$



1b, $\delta_{CS_2}{}^{*} = 173.2$

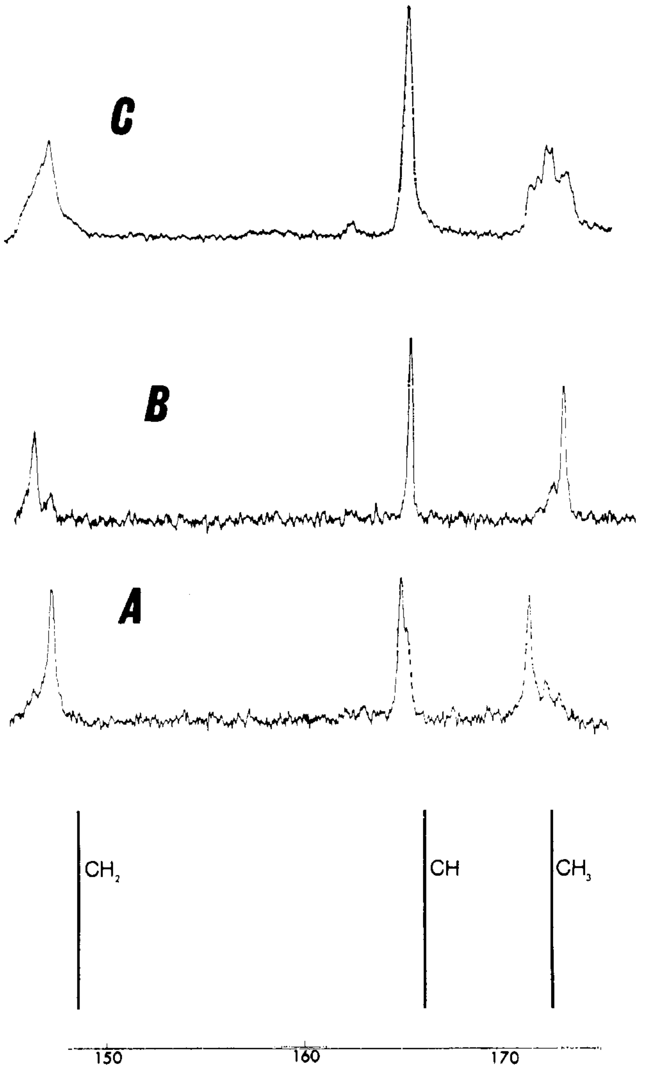
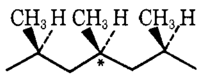
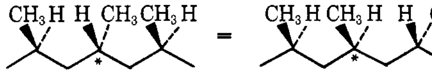


Figure 1. Experimental and calculated ^{13}C spectra of polypropylenes in parts per million upfield from CS_2: (A) isotactic, 100 scans; (B) syndiotactic, 40 scans; (C) atactic, 534 scans.

Regarding the methine regions in these spectra, it is clear that only triads are distinguishable, and these rather poorly. The assignments shown seem reasonable. This region of the spectrum of **1a** also illustrates the rather low steric regularity for the sample shown.



$\delta_{CS_2}{}^{*} = 165.2$



$\delta_{CS_2}{}^{*} = 165.5$

Rather broad and indistinct bands are observed for the methylene carbons, and it does not seem practical to make specific assignments in these cases.

Copolymers. The three copolymers presented should be similar to the three polypropylenes discussed in the preceding section, except that 10–20% of ethylene units have been

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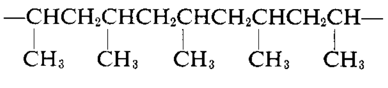
(12) If only nearest neighbor methyls had an effect, then only three methyl peaks should be observable.

(13) This nomenclature refers to the number of substituted carbons in a given sequence of the polymer chain. For example, a pentad of polypropylene consists of the structural unit



$$-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-$$

For reasons of symmetry it is common practice to speak of methyl and methine resonances in polypropylenes in terms of odd-numbered units (triads, pentads, . . .), while the methylene resonances are referred to in terms of even-numbered units (dyads, tetrads, . . .).

(14) A. Zambelli and A. Segre, *J. Polym. Sci., Part B*, **6**, 473 (1968).

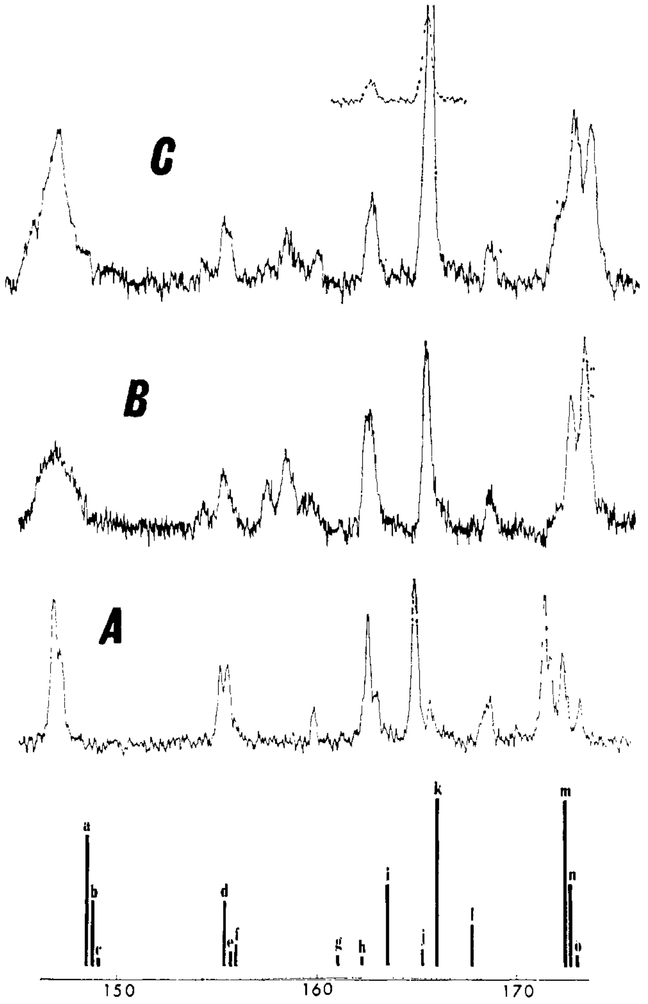


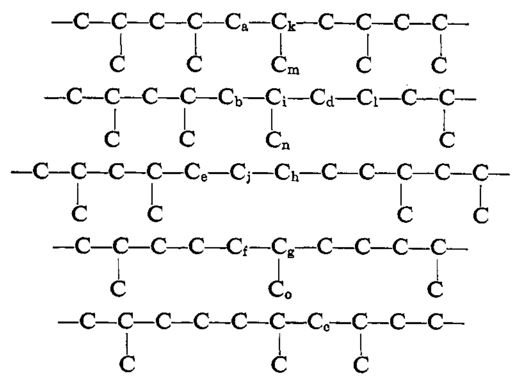
Figure 2. Experimental and calculated ^{13}C spectra of ethylene–propylene copolymers in parts per million upfield from CS_2: (A) isotactic, 250 scans; (B) syndiotactic, 382 scans; (C) atactic, 470 scans.

incorporated in the chains. The cmr spectra of these molecules are expected to consist of two parts, one representing the longer polypropylene segments of the molecular chains which would be similar to the spectra of the polypropylenes of corresponding tacticity, and a second part representing the ethylene and propylene carbons which are close enough together to modify one another's chemical shifts.

Once again, the formulas of Grant and Paul[11] were employed to calculate chemical shifts. Relative peak heights were estimated assuming a random distribution of the 20% of ethylene units. The calculated chemical shifts as well as the experimental ones are given in Table II. As can be seen in Figure 2, the calculated spectrum agrees fairly well with the spectrum of isotactic copolymer **2a** and less well with the other two. The ethylene portions of the spectra of atactic (**2c**) and syndiotactic (**2b**) copolymers appear to be generally similar.

TABLE II

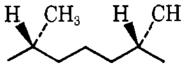
CHEMICAL SHIFTS OF THE ETHYLENE–PROPYLENE COPOLYMERS[a]



Carbon	Calcd	Exptl 2a	Exptl 2b	Exptl 2c
a	148.9	147.5	147.2	147.5
b	149.2	147.8	(145.6–148.0)	(145.1–148.8)
c	149.5			
d	155.8	155.6	154.7	154.6
e	156.1	156.0	155.9	155.9
f	156.4		167.9	157.8
			158.7	158.7
g	161.5	160.3	160.2	160.2
h	162.7	163.3		
i	164.0	162.9	162.7	162.8
j	165.8	166.0		
k	166.5	165.2	165.5	165.5
l	168.3	168.9	168.7	168.7
m	172.9	171.6	172.7	173.1
n	173.2	172.0	173.3	172.8
o	173.5	172.5		173.5
		173.2		

[a] All chemical shifts are in parts per million upfield from CS_2 (calculated assuming δ_{CS_2} for benzene equal to 65.0 ppm and for chloroform equal to 115.3 ppm).

On the basis of these spectra it is possible to speculate as to whether steric regularity is transmitted through an ethylene unit; that is, for example, with a catalyst normally producing isotactic polymer, does one observe formation of **3** or **4**, or a



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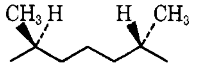

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mixture of these?

Only one peak is resolved in the region of carbon C_l, the central carbon in an isolated ethylene unit, for each copolymer. However, more peaks show up in the region of carbon C_d, the other carbon in the ethylene unit, for **2b** and **2c** than for **2a**. This may indicate that the former gives a mixture of **3** and **4** while the latter gives **3**. Additional experiments to clarify this point are in progress.[15]

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(15) A. Zambelli, paper presented at the Seventh NMR Colloquium, Haaken, 1970.