Communications to the Editor

Carbon-13 Observations of the Stereochemical Configuration of Polypropylene[1]

Polypropylene has been intensively studied by both proton[2] and ^{13}C nmr.[3-9] The latter studies indicate great promise, but the spectral resolution so far achieved has not been sufficient to resolve still outstanding questions concerning configurational sequence assignments and steric purity in this polymer.[10-12] As these questions are of considerable potential significance both with respect to the conformational energies of paraffinic chains and to the mechanism of action of Ziegler–Natta catalysts, a more searching study appears to be needed. We report here in a preliminary fashion the results of such a study, reserving a more detailed description of the experimental measurements and their interpretation for a later publication.

Experimental Section

Materials. Sample a was prepared by polymerization of propylene (120 g) in *n*-heptane (300 ml) at −78° in the presence of a catalyst system consisting of 0.003 mol of VCl_4, 0.003 mol of anisole, and 0.015 mol of $Al(i\text{-}C_4H_9)_2Cl$.

Sample b was prepared by polymerization of propylene (40 g) in *n*-heptane (100 ml) at −78° in the presence of a catalyst system consisting of 0.003 mol of VCl_4 and 0.005 mol of $Al(C_3H_5)_2Cl$.

Sample c was prepared by polymerization of propylene (30 g) in 150 ml of *n*-heptane at −78° in the presence of a catalyst system consisting of 0.00025 mol of VCl_4 and 0.0035 mol of $Al(C_2H_5)_2Cl$.

Samples d, e, and f were prepared by polymerization of propylene at 5 atm of pressure at 70° in the presence of a catalyst system consisting of 0.5 g of $TiCl_3$ HRA (Stauffer) and 1 ml of $Al(C_2H_5)_2I$ in 200 ml of toluene. The crude polymer, after washing to remove catalyst and drying, was exhaustively extracted with boiling *n*-heptane.

Sample d is the fraction soluble in boiling *n*-heptane (6% of the total polymer). Sample e is the fraction insoluble in boiling *n*-heptane (94%). Sample e was subsequently extracted for 60 hr with boiling *n*-octane; the residue after extraction is sample f (90% of the original crude polymer).

More detailed descriptions of the catalyst system employed are reported in the literature.[13-15]

Methods. Spectra were observed using a Varian XL-100 spectrometer modified for pulse Fourier transform spectroscopy and interfaced with a Nicolet Model 1080 computer.[16] The protons were decoupled from the carbon nuclei using a random noise modulated decoupling field. The free induction decay was stored in 8K locations using a dwell time of 250 μsec, *i.e.*, a spectral window of 2000 Hz. This corresponds to a resolution of 0.5 Hz. The optimum observed methyl resonance line width for a single species (*i.e.*, for a highly stereoregular polymer such as that corresponding to Figure 2e or -f) was *ca.* 1 Hz. The pulse was located at the "low-field" (high-frequency) end of the spectrum (commonly 25.16210 MHz). Pulse intervals were 4 to 5 sec. The number of transients accumulated varied from 2500 to 12,300, depending on the concentration of the polymer. Solutions were made up in 1,2,4-trichlorobenzene to 3.5-7.0% (w/v). The lower concentrations were used for the highly isotactic samples and represented approximately the limit of solubility. Observations were made at 135–140°. The use of elevated temperatures is very important; the 25-MHz spectra reported here are better resolved than the 55-MHz spectrum run at 55°.[9]

Peak intensities were measured by tracing the resonances on tracing paper and then cutting them out and weighing them; this is believed to be more reliable than the use of a planimeter or the Nicolet program at present accessible to us.

Experimental Results

Figure 1 shows the complete spectrum of a predominantly isotactic polypropylene. As described in previous work,[3-9] the peaks correspond to β-CH_2, α-CH, and methyl carbons in order of increasing shielding. The methyl resonance clearly exhibits a greater range of chemical shifts for configurational sequences than do the other resonances and this region of the spectrum is therefore principally employed in our studies.

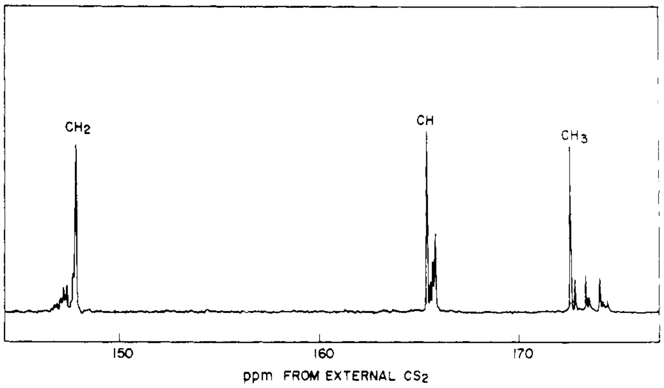

Figure 1. Complete 25-MHz ^{13}C spectrum of a predominantly isotactic polypropylene (sample d; see Experimental Section), observed in *ca.* 3.5% (w/v) 1,2,4-trichlorobenzene solution at 135°.

In Figure 2 are shown methyl spectra of six representative polypropylene samples ranging from moderately highly syndiotactic (a and b) through atactic (c) to highly isotactic (e and f). Spectrum d represents the same polymer as Figure 1. The triad assignments are the same as those made previously[3,4] and are unequivocal. The fine structure in each triad region, in most cases resolved to the base line or nearly so, is assigned to pentad sequences in the following manner

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(1) (a) Istituto di Chimica delle Macromolecole del CNR; (b) Bell Laboratories.

(2) Proton nmr studies through 1970 are summarized by F. A. Bovey in "High Resolution NMR of Macromolecules," Academic Press, New York, N. Y., 1972, pp 132-143, 169-173, and 199-203. Relevant later work is referenced below.

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

(4) F. A. Bovey in "NMR Basic Principles and Progress," P. Diehl, E. Fluck, and R. Kosfeld, Ed., Springer-Verlag, Berlin, 1971, pp 16-19.

(5) See A. Zambelli in ref 4, pp 107-108.

(6) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, 4, 330 (1971).

(7) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, 4, 475 (1971).

(8) Y. Inoue, A. Nishioka, and R. Chûjo, *Makromol. Chem.*, 152, 15 (1972).

(9) L. F. Johnson, *Anal. Chem.*, 43, 28A (1971).

(10) P. J. Flory and Y. Fujiwara, *Macromolecules*, 2, 327 (1969).

(11) P. J. Flory, *Macromolecules*, 3, 613 (1970).

(12) P. J. Flory, *J. Polym. Sci., Part A*, 11, 621 (1973).

(13) A. Zambelli, G. Natta, I. Pasquon, and R. Signorini, *J. Polym. Sci., Part C*, 16, 2485 (1967).

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

(15) G. Natta, I. Pasquon, A. Zambelli, and G. Gatti, *J. Polym. Sci.*, 57, 387 (1961).

(16) H. Sternlicht and D. M. Zuckerman, *Rev. Sci. Instrum.*, 43, 525 (1972).

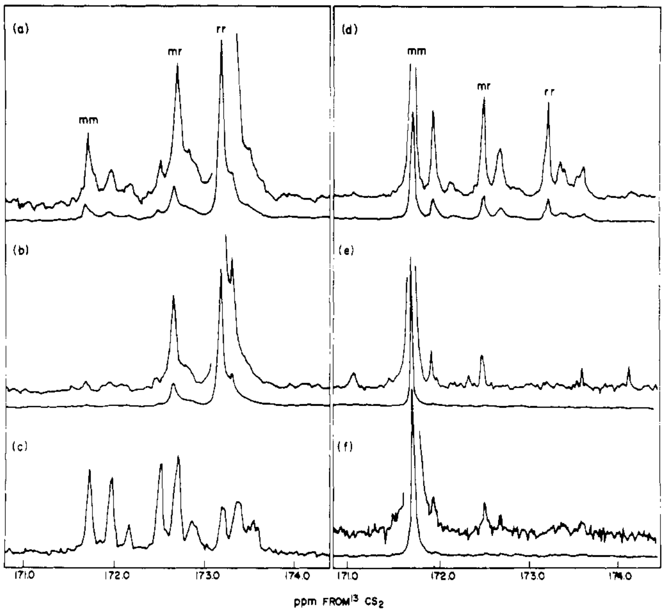

Figure 2. Methyl ^{13}C resonances of polypropylene samples of varying stereoregularity, observed under similar conditions to those for Figure 1. The samples vary from predominantly syndiotactic (a and b) through atactic (c) to highly isotactic (e and f). The lettering of the spectra is the same as that for the sample preparations in the Experimental Section. Sample d is the same as shown in Figure 1.

The relative intensities are arbitrarily represented as those for a strictly atactic polymer, that is, with a Bernoullian probability of isotactic placement P_m = 0.5, although we shall see below that these polymers do not actually obey such statistics. These assignments agree with those of Inoue *et al.*,[8] except in the rr region, where their assignments of *rrrr* and *mrrm* are the reverse of ours. It is obvious from the examination of the spectra of the syndiotactic polymers (Figure 1a,b) that this cannot be correct. The assignments proposed above are the most probable and self-consistent that we can offer at the present time. It is well known to all workers in this field that it is extremely difficult to prove such assignments rigorously.

It is qualitatively evident from even a casual inspection of Figure 2 that at least some of these polymers depart markedly from Bernoullian stereochemical statistics. Note that in the predominantly syndiotactic polymer (a) the *mmmm* pentad is the most probable isotactic sequence (on the other hand, the similar polymer (b) does not show this characteristic). Again, in the predominantly isotactic polymer (d) the *rrrr* pentad is the most probable syndiotactic sequence. We shall deal with these matters quantitatively in a subsequent publication.

The spectra of the highly isotactic polymers 2e and 2f are of particular interest in comparison to previous proton observations and the conclusions which have been drawn from them.[17,18] It was previously concluded that the predominant configurational defect in a highly isotactic polypropylene specimen is the single *r* sequence, most clearly evident in the 220-MHz proton spectra as a triplet resonance at τ 8.9 assigned to the tetrad sequence *mrm*.

The present results support this assignment. Spectra 2e and 2f are very similar to the C-13 spectrum (not shown) of the polypropylene sample overboard in ref 18 and reported to contain 2% of racemic dyads. In all three spectra, the most clearly observable resonances, aside from the principal *mmmm* resonance at 171.7_3, are sharp singlets of equal intensity at 171.9_5 and 172.5_0. According to the assignments proposed above, these correspond to *mmmr* and *mmrm*, respectively, appearing consistently at these positions (within ±1 Hz) in all the spectra in Figure 2 in which they can be detected. According to the necessary frequency relations,[19] modified for the absence of *rr* sequences

$$(r) = (1/2)(mmrm) = (1/2)(mmmr)$$

Results on spectrum 2f are not reported at this time because of significantly lower signal-to-noise ratio in this spectrum. For the other samples, we find (in mol %

Sample	*mmrm*	*mmmr*	*r*
Spectrum 2e	2.1	1.9	1.0
Reference 18	2.5	2.6	1.3

The *r* dyad frequency of the ref 18 sample is thus estimated to be somewhat lower than found by proton measurements, although it is reasonable to conclude that the measurements agree within their probable error.

In spectrum 2e (and to a lesser extent in the spectrum of the sample reported in ref 18) there are weak sharp resonances at *ca.* 173.6 and 174.1 ppm; these do not appear in spectrum 2f. At present, we cannot assign these resonances. Infrared estimates of possible head-to-head:tail-to-tail content in these polymers do not support an assignment to such structures.

(17) F. Heatley and A. Zambelli, *Macromolecules*, 2, 618 (1969).

(18) F. Heatley, R. Salovey, and F. A. Bovey, *Macromolecules*, 2, 619 (1969).

(19) H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, 45, 1565 (1966).

A. Zambelli,[1a] D. E. Dorman,[1b] A. I. Richard Brewster,[1b] and F. A. Bovey*[1b]

Istituto di Chimica delle Macromolecole del CNR, Milan, Italy and Bell Laboratories, Murray Hill, New Jersey 07974

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