Polymer Nuclear Magnetic Resonance Spectroscopy.
XVII. Tetrad Resonances in Polypropylene

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ABSTRACT: Assignments have been made of the resonances of tetrad configurational sequences observed in the 220-MHz proton spectra of poly(propylene-*cis*- and -*trans*-1,2,3,3,3-d_5).

Many studies of the tacticity of propylene polymers have been made[2-13] using proton nuclear magnetic resonance at 60 and 100 MHz. Ferguson[13] has reported the 220-MHz spectra of isotactic and syndiotactic polypropylene. Although the spectra depend a great deal on the polymer tacticity, indicating that the chemical shifts are sensitive to the relative configurations of the neighboring sites of steric isomerism in the chains, for some time only triad[14] sequences were clearly resolved.[3,5] However, recently Zambelli and Segre[11] have observed and partially assigned clearly resolved tetrad peaks in the 100-MHz deuterium decoupled spectra of atactic poly(propylene-*cis*- and -*trans*-1,2,3,3,3-d_5). We wish to report here a complete tetrad assignment.

Figure 1 shows the 220-MHz spectra of these polymers run as 10% (w/v) solutions in *o*-dichlorobenzene at 140° on a Varian Associates HR-220 spectrometer, using hexamethyldisiloxane as internal reference. The polymers are the same as those used by Zambelli and Segre.[11] Since all proton–proton spin coupling has been effectively removed by deuteration, the proton resonances appear as singlets at the chemical shifts of the various tetrads. Of the six possible tetrads, four have central methylene groups in each of which the protons are magnetically nonequivalent (the *mmm*,[15] *mmr*, *rmr* and *mrr* tetrads) while two have central methylene groups in each of which the protons are equivalent (the *mrm* and *rrr* tetrads). Hence a total of ten possible chemical shifts is expected of which nine are observed for the two polymers combined. Since the polymerization is stereospecifically *cis*,[8,12,16] and the monomers were essentially stereochemically pure *cis* or *trans*, then only the *anti* and *syn meso*-methylene protons appear for the *cis* and *trans* monomers, respectively.[8] The terms *syn* and *anti* refer to the methylene protons on the same and opposite sides of the backbone plane, respectively, as the methyl groups when a *meso* dyad takes up the planar zigzag configuration. In contrast to the *m*-centered tetrads, both chemical shifts of the *mrr* tetrad must be observed in equal abundance in both polymers because of the symmetry of racemic units. One of the *mrr* peaks corresponds to tetrads formed in the direction $\overrightarrow{mrr}$ while the other corresponds to those formed in the direction $\overrightarrow{rrm}$.

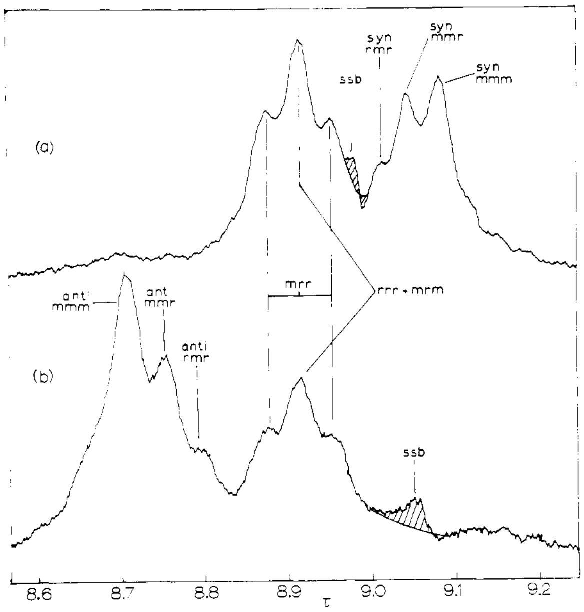

Figure 1. (a) 220-MHz proton nmr spectrum of atactic polypropylene-*trans*-1,2,3,3,3-d_5; 10% (w/v) in *o*-dichlorobenzene at 145°; (b) similar spectrum of polypropylene-*cis*-1,2,3,3,3-d_5.

The *mmm* and *rrr* assignments were made by comparison with the chemical shifts of similarly deuterated, very highly isotactic and syndiotactic polymers, as suggested by Zambelli and Segre.[11] The *mmr* and *rmr* peaks were assigned on the basis of an expected

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regular progression in chemical shift of the central *m* dyad as the flanking *m* dyads are replaced by *r* dyads. Such regularity is observed for the *mmm*, *mmr*, and *rmr* chemical shifts in poly(methyl methacrylate)[17] and poly(vinyl chloride).[18] The *mrr* tetrad is assigned by us on the basis of an examination of the spectrum of atactic poly(propylene-2-d_1) in which geminal coupling is introduced into the spectra of those tetrads with magnetically nonequivalent methylene groups. In this spectrum, no peaks were present at the chemical shift of either of the two peaks labeled *mrr* in Figure 1, indicating that both were split by geminal coupling and therefore belonged to the *mrr* tetrad. The *mrm* tetrad is assigned by us to the same chemical shift as the *rrr* tetrad since approximate measurements of the *mmr*, *rmr*, and *mrr* intensities, when substituted into the relationship[14]

$$(mmr) + 2(rmr) = (mrr) + 2(mrm)$$

gave a substantial proportion of the *mrm* tetrad which could be accommodated only within the central peak. Thus measurement of peak heights in Figure 1b gives the values 0.194, 0.113, and 0.250 for (*mmr*), (*rmr*), and (*mrr*), respectively, giving the value 0.085 for (*mrm*), which is comparable to the intensity of the (*rmr*) tetrad and can be placed reasonably only as suggested.

Several small peaks other than those assigned to tetrads are evident in Figure 1. These may be attributed variously to hexads, impurities in the monomers, or possibly head-to-head units.

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Polymer Nuclear Magnetic Resonance Spectroscopy. XVIII. The Nuclear Magnetic Resonance Spectrum, Dimensions, and Steric Interactions of Isotactic Polypropylene

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ABSTRACT: The 220-MHz proton nmr spectrum of a highly isotactic sample of polypropylene has been examined and interpreted in detail. The polymer was shown to contain 2% racemic dyads occurring randomly at junctions of isotactic sequences of opposite configurations. The mean-square end-to-end distance of this polymer was measured under Θ conditions, and comparison of the value obtained with theoretical predictions of Flory, Mark, and Abe[11] permitted an approximate measurement of the strength of steric interactions within the polypropylene chain. Additional information on the steric interactions was obtained from a comparison of the chemical shifts of racemic dyads in isotactic and syndiotactic chains.

Nuclear magnetic resonance has been well established as the most useful method of studying polymer configurational and conformational properties. The subject has been reviewed several times.[1-7] The advent of nmr instruments with superconducting magnets has greatly improved the sensitivity and resolution of this technique, as shown by recent studies of the 220-MHz proton spectra of poly(methyl methacrylate),[8] poly(vinyl chloride),[9] and isotactic polystyrene.[10] In this paper we wish to report a similar study of a highly isotactic polypropylene sample, having as its objective the accurate determination of its stereochemical structure. Calculations by Flory, Mark, and Abe[11] have shown that the end-to-end distance of an isotactic polymer chain and its temperature coefficient are sensitive to both intramolecular steric overlaps between large groups and to the incorporation of a small amount of syndiotactic dyad "impurity" within the chain. However, the latter has not been specified sufficiently accurately for the isotactic polymers whose dimensions have been reported in the literature,[12-15] thus making comparisons between theory and experiment of doubtful value. This paper reports the first measurement of the dimensions of an isotactic polymer of accurately known tacticity.

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