contradict the findings and conclusion of other workers reported in ref 7-10.

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Communications to the Editor

Hemitactic Polypropylene: An Example of a Novel Kind of Polymer Tacticity

Polypropylene, almost 30 years after its discovery, is still a central point in macromolecular stereochemistry. Many studies have been carried out recently by means of ^{13}C NMR spectroscopy to determine the configuration sequences in samples obtained by direct polymerization or after equilibration in the presence of epimerizing catalysts.[1-3] Methyl resonance has been found to be particularly sensitive to the stereochemical environment, and the microstructure of the polymer has been determined in terms of pentads and in some cases of heptads.

In this paper we wish to illustrate a new stereoisomer of polypropylene having a particular type of order and characterized by a ^{13}C NMR spectrum markedly different from those reported in the literature. The high-field region of the ^{13}C NMR spectrum of our sample, recorded at 137 °C in 1,2,4-trichlorobenzene at 50.3 MHz (Varian XL 200), is shown in Figure 1 and compared with that predicted for a purely atactic sample. The spectrum shows only the signals of seven of the ten pentads—pentads mrmr, mrmm, and rrmr are missing. Furthermore, the intensity of the signals centered on the mm triad is practically identical with that of the signals centered on the rr triad. The arrangement of the intensity of the signals can be expressed as follows, starting from the low-field signals: 3:2:1:4:0:0:3:2:1 as compared with the sequence 1:2:1:2:4:2:1:2:1 of a Bernoullian sample with m = 0.5. Peaks are very sharp and in some cases we find evidence of resolution at the heptad level, especially when the spectrum is run at room temperature. In the region of the spectrum between 45 and 47 ppm from Me$_4$Si, typical of methylene groups, the distribution of the signals is far narrower than in conventional atactic polymers: in particular, the low-field and high-field signals, due, respectively, to the hexads mrmrm, rrmrm, and rrmrr and rmrmr, rmrmm, and mmrmm, are not detectable. As a general rule, all the successions containing closed odd sequences of m or r dyads are missing.

An explanation of all these facts is forthcoming if we take into consideration the method of preparation of our polypropylene sample. This was obtained by reduction of poly(2-methylpentadiene), which, in turn, had been obtained by inclusion polymerization of the monomer in perhydrotriphenylene.[4] The structure of this high-melting, scarcely soluble product was found to be head-to-tail 1,4-trans-isotactic on the basis of IR, X-ray, and ^{1}H NMR spectra. In the polymer no defects of the 1,2- or 1,4-cis type was found; the degree of isotacticity has not yet been determined accurately because of the low solubility, but, as can be seen from the experiments described here, it can reasonably be expected to be very high. Reduction of the polymer with diimide produced in situ starting from tosylhydrazide[5,6] takes place slowly because of the heterogeneity of the system and of the degree of substitution on and around the double bond. By repeated treatments a polymer is obtained with a degree of unsaturation below 3-5% and free from aromatic impurities.

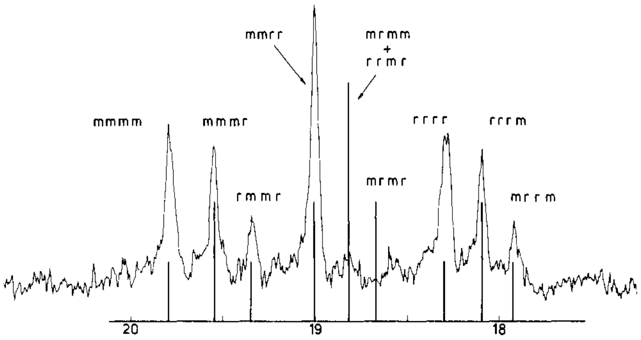
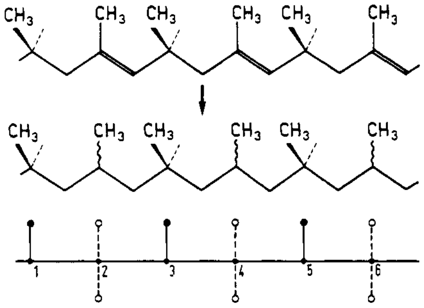


Figure 1. ^{13}C NMR spectrum of the methyl region of "hemitactic" polypropylene.

Scheme I



The structures of the unsaturated and of the saturated polymer are given in Scheme I. From a constitutional point of view the hydrogenated polymer must be considered as a head-to-tail polypropylene. As concerns the stereochemical point of view, it is necessary to make a distinction between the tertiary atoms of the odd series and those of the even series. If we assume the polymer to contain initially 100% isotactic dyads, atoms 1, 3, 5, etc. all have the same relative configuration because they reflect the regularity of the unsaturated polymer. The configuration of atoms 2, 4, 6, etc. is, on the other hand, determined at the moment of hydrogenation, which is largely nonspecific.

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Table I
Pentad Composition

sequence	probability	rel intens calcd	rel intens exptl
mmmm	$(\alpha^2 + \alpha^3)/2$	3	2.72
mmmr	$\alpha^2(1 - \alpha)$	2	2.07
rmmr	$\alpha(1 - \alpha)^2/2$	1	0.96
mmrr	$\alpha(1 - \alpha)$	4	3.90
mmrm rmrr		0	<0.4
rmrm		0	0
rrrr	$[(1 - \alpha)^2 + (1 - \alpha)^3]/2$	3	2.87
rrrm	$\alpha(1 - \alpha)^2$	2	2.13
mrrm	$\alpha^2(1 - \alpha)/2$	1	1.06

If we examine a triad centered on an even atom, taking α as the probability that the substituent will form an m dyad with each of the two adjacent methyls, the probability of an mm triad is still α. On the other hand, if we examine a triad centered on an odd atom, the probability of an mm triad is α^2. If we consider all the triads of the polymer, the frequency of mm triads is $(\alpha + \alpha^2)/2$, that of mr (rm) triads is $\alpha(1 - \alpha)$, and that of rr triads is $(1 - \alpha + (1 - \alpha)^2)/2$. Fractions of longer sequences are obtained analogously. Table I gives the expressions for pentads and expected values with $\alpha = 0.5$. These are in excellent agreement with the experimental values. A more complete approach, taking into account a variable degree of tacticity for poly(2-methylpentadiene), will be discussed in a forthcoming publication. However, we may here anticipate the information that experimental findings are in agreement with a content of more than 95% of isotactic dyads.

Three main conclusions can be drawn from this work. We have obtained a chemical demonstration of the structural assignments of the ^{13}C NMR spectrum of polypropylene. Perfect agreement has been observed at the pentad level, though we believe that the method will yield its best result in the examination of longer sequences (as a matter of fact 22 of the 36 heptads are forbidden or scarcely probable).

At the same time we have obtained a demonstration of the high degree of isotacticity of poly(2-methylpentadiene) prepared by inclusion polymerization in perhydrotriphenylene.

Finally, we have obtained a new type of polypropylene in which one tertiary atom out of every two is highly stereoregular. This represents the first example of a new class of polymer stereoisomers, for which we suggest the term *hemitactic polymers*.

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Raman Spectroscopic Study of Highly Deformed Polyethylene

A number of flexible polymers have been solid-state extruded or drawn to form ultraoriented, high-modulus fibers.[1] Because of the high anisotropic mechanical properties achievable, these materials, especially polyethylene, have created a great deal of scientific interest. Information obtained from X-ray scattering, electron microscopy, vibrational spectroscopy, and calorimetric measurements has been used to form a number of structural models, each differing in the description of the crystallite size and connectivity.[2-8] From all indications, the molecular orientation in these highly deformed materials is extremely high. However, their tensile moduli are generally an order of magnitude below those derived from force constant calculations.[1] This difference is usually taken as evidence for a significant number of structural defects in the samples. Therefore, the length distribution of straight-chain segments is of great interest. Without elaborating on possible structures, in this paper we will use "straight-chain segments" or L to denote the fully planar-zigzag segment between conformational defects. The long periodicity measured by small-angle X-ray scattering (SAXS) is often used as a measure of the straight chain segment distribution. This method is not entirely satisfactory because the SAXS long period is really only an average value including both the amorphous and crystalline regions.

The longitudinal acoustic mode (LAM) in the very low frequency region of Raman spectra provides a direct measurement of the distribution of the straight chain segment length in these highly deformed materials. The frequency of the LAM vibrational mode is inversely proportional to L. A number of reports have used this LAM to study the distribution of the straight chain segment length in drawn or extruded ultraoriented, high-modulus polyethylene.[9-14] These studies have shown microstructural features at the 50–600-Å level can be inferred from the frequency, bandwidth, and intensity of LAM. The most comprehensive studies have been carried out by Capaccio and co-workers.[11] They used the Raman technique in conjunction with other physical techniques such as X-ray and GPC in order to derive the crystalline component.

Recently, Snyder and co-workers pointed out that temperature and frequency factors must be considered when transforming LAM shape to chain length distribution (12). Because of these spectroscopic effects, the true number distribution of extended chain segments is sensitive to the observed LAM half-width, $\Delta L_{1/2}$. This is especially true when the LAM-1 width is extremely broad, as seen in most highly deformed polyethylenes. We found in a series of solid-state extruded samples that the observed LAM half-width increased substantially with increasing draw ratio, affecting the position of the peak in the chain length distribution.[13] Considerable difference was observed between the most probable chain length, $L_{\max}$, measured by the Raman technique and the SAXS long periodicity.[13,15] We have carried out a new study to follow structural changes for a series of solid-state extruded polyethylene samples. Our low-frequency Raman spectroscopic results are reported here.

Experimental Section. Methods and Samples. High-density polyethylene with a weight-average molecular weight of 59 000 and a number-average molecular weight of 20 000 was used in this study. We have used the split-billet method developed here at The University of Massachusetts to deform quenched polyethylene sheets

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