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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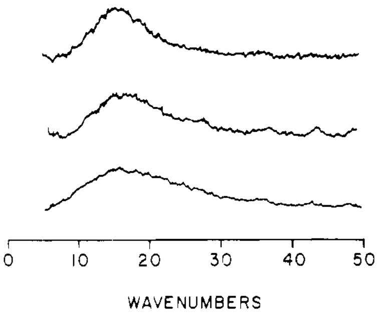

Figure 1. Low-frequency Raman spectra obtained for polyethylene extruded at 80 °C by the split-billet technique: top curve, initial sample; middle curve, draw ratio of 5; bottom curve, draw ratio of 7.

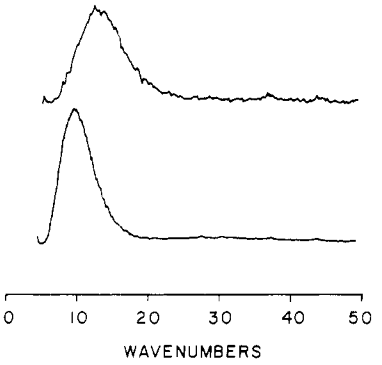

Figure 2. Low-frequency Raman spectra obtained for polyethylene extruded at 130 °C by the split-billet technique: top curve, draw ratio of 7; bottom curve, draw ratio of 24.

to high degrees of extension.[1] Details of sample preparation are given elsewhere.[14]

We are particularly interested in the effect of temperature and draw ratio on the chain orientation and straight chain segment length distribution during extrusion. These changes cannot be examined during extrusion but were determined by removing partly extruded billets and examining the material at positions inside and outside the die hole which were at various stages of deformation. The draw ratio, λ, was measured directly from the displacement of ink marks originally separated by 0.125 in. An alternative method is to measure the ratio of the cross-sectional area of the deformed and initial sample.

Raman Spectroscopy. Raman spectra were obtained with a microprocessor-controlled Jobin-Yvon HG.2S laser Raman spectrometer. The availability of digitized Raman data provides us with a number of powerful data analysis algorithms. The Raman-active bands in the high-frequency region exhibit polarization characteristics consistent with uniaxial symmetry. The low-frequency LAM observed are shown in Figures 1 and 2. We have removed the Rayleigh scattering by a technique developed in our laboratory.[14] The LAM peak is corrected for Boltzmann temperature effects and then converted to the straight chain segment distribution as done by Snyder and coworkers.[12] As we observed previously, the breadth of the LAM-1 bands for the 80 °C sample increased significantly as a function of draw ratio. This is plotted in Figure 3.

Results and Discussion. As stated previously, the models developed for ultraoriented, high-modulus fibers all emphasize high molecular orientation. However, the amount, size, and perfection of the crystalline components and their connectivity differ from model to model. There is no question, however, that structural defects exist even in the most highly drawn or extruded samples. As can be seen in Figures 1–3, the L_{max} and $\Delta L_{1/2}$ vary as a function of increasing draw ratio and processing temperature. For polyethylene extruded at low temperatures (the effective melting temperature is raised by pressure) both the peak frequency and half-width increase as a function of draw ratio. This suggests highly deformed samples contain a large number of short straight-chain segments. Similar data have been obtained for polyethylene drawn at 60 °C.[15] However, the occurrence of shorter segments does not necessarily imply the existence of thin lamellae. Experimental[16] and theoretical studies[17,18] suggest that the structural defects can disrupt the straight-chain segments and redistribute the LAM-1 intensity. For highly drawn polyethylene, Peterlin postulated that the number of defects may be as high as one for every five chain stems of the crystalline block.[18] Furthermore, both spectroscopic and X-ray evidence have shown the existence of a different crystalline phase with monoclinic unit cells.[19,20] Paraffin and polyethylene samples subjected to various thermal, chemical, and mechanical treatments showed this monoclinic phase.[21] In our previous studies, a combination of vibrational spectroscopic and thermal analyses suggested that a relationship exists between these conformational defects and the amount of the monoclinic phase.[16,19] However, if only occasional, isolated chains or small groups adopted monoclinic packing, this might not be observed in X-ray diffraction.

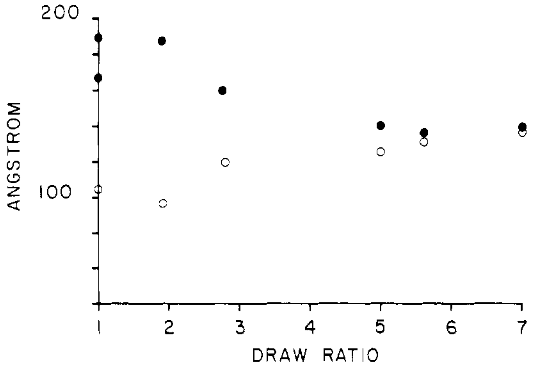

Figure 3. Change of L_{max} (●) and $\Delta L_{1/2}$ (○) for the 80 °C sample as a function of draw ratio.

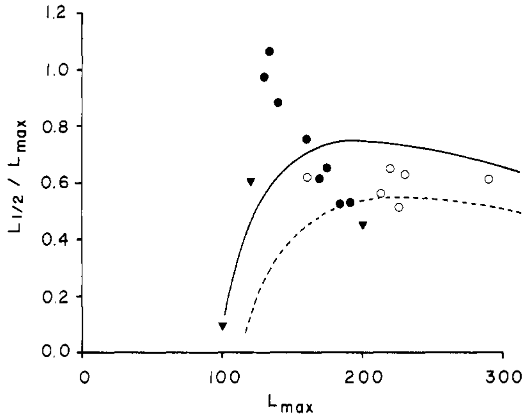

Figure 4. Relationship for $\Delta L_{1/2}$ and L_{max} in variously prepared polyethylene; (●) 80 °C sample; (○) 130 °C sample; (▼) annealed single crystals (ref 23). The solid line refers to the annealed polyethylene single crystals (ref 23) with d_0 = 292 Å and d_1 = −2.83 × 10^4 Å^2; the dashed line is calculated with d_0 = 247 Å and d_1 = −2.77 × 10^4 Å^2.

In a series of thermally annealed polyethylene essentially equilibrium structure single crystals, Snyder and coworkers found an empirical relationship to exist between the LAM $\Delta L_{1/2}$ and L_{max} in the chain-length distribution.[15]

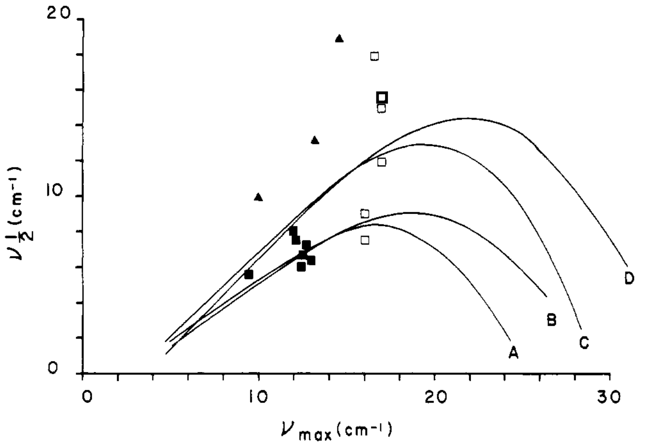

Figure 5. Relationship found for $\Delta\nu_{1/2}$ and $\nu_{\max}$ in variously prepared polyethylene. Line A was calculated by using Young's modulus, E, equal to 290 GPa, d_0 = 247 Å, and d_1 = −2.77 × 10^4 Å^2; line B was calculated with E = 360 GPa, d_0 = 247 Å^2, and d_1 = −2.77 × 10^4 Å^2; line C was calculated with E = 290 GPa, d_0 = 292 Å^2, and d_1 = −2.83 × 10^4 Å^2; line D was calculated with E = 360 GPa, d_0 = 292 Å, and d_1 = −2.83 × 10^4 Å^2. (□) 80 °C sample; (■) 130 °C; (△) our previous data (ref 13).

They defined a reduced half-width parameter, $\mu_L = \Delta L_{1/2}/L_{\max}$, to describe the degree of order for the crystalline component.[22] It was observed that $\Delta L_{1/2}$ and $L_{\max}$ are related by

$$\Delta L_{1/2} \simeq d_0 + d_1/L_{\max} \qquad (1)$$

where d_0 and d_1 are constants. Their data suggest that d_0 and d_1 are in the range 247–292 Å and −2.77 × 10^4 to −2.83 × 10^4 Å^2, respectively. This relationship is plotted in Figure 4. Since L and ν are inversely related ($L\nu = a$), eq 1 can be restated in terms of $\Delta\nu_{1/2}$ and $\nu_{\max}$. This equation, which may be written as

$$\Delta\nu_{1/2} = (ad_0 + d_1\nu_{\max})\nu_{\max}{}^2/a^2 \qquad (2)$$

can account for the LAM-1 band characteristics measured for their annealed polyethylene single crystals. This relationship is easier to apply since no conversion of the LAM-1 band to a distribution of length from the frequency space is involved in this case. Two values for Young's modulus of polyethylene are generally used in the literature,[12,23] leading to a = 2838 or 3162 Å cm^{-1}. Therefore, depending on the constants used in the relationship, one can obtain two ranges of relationships between the half-width and the peak position. This is shown in Figure 5. The reduced half-width, μ_L, for annealed polyethylene single crystals increases initially and then decreases to smaller values as the average value of the straight-chain length increases. Decreases of half-width, $\Delta L_{1/2}$, after exposure to sustained annealing is consistent with the general expectation that such treatment should lead to increased order.

One of the most interesting observations from the LAM measured for these highly deformed materials is that the LAM bands exhibit considerable departure from the relationship found for annealed single crystals of polyethylene. This was first seen in a highly drawn sample.[22] The low-frequency Raman data for our samples are also shown in Figures 4 and 5. It should be noted, however, that the departure only occurs for samples extruded at low temperatures (temperature must be corrected for the pressure used during extrusion). The samples extruded at 130 °C follow the same trend as annealed single crystals. Even though no fundamental reason exists to relate $\Delta L_{1/2}$ to $L_{\max}$, they seem to have particular relationships that occur for particular processing methods or history. The reduced half-width μ_L is a useful quantity, showing obvious differences in various polyethylene structures. The degree of chain mobility is an important factor in removing structural defects introduced during the mechanical deformation process. For samples extruded at low temperature, limited chain mobility exists. For samples extruded at high temperatures, more of the defects disappear, forming highly ordered structures which are dimensionally stable.[1] The annealed polyethylene single crystals approach more closely to equilibrium and therefore contain fewer structural defects, resulting in smaller μ_L values. Low-frequency Raman data obtained from variously prepared polyethylene samples differ significantly not only in the straight-chain length but in the reduced half-width for the distribution of length. Further detailed analysis is expected to yield information about the kind, number, and mobility of defects that various processing conditions introduced into the straight chain segment distribution.

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